

# Report of the Literature Review Committee\*

## 21st Annual Review of the Literature on Fats, Oils, and Detergents. I.

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### Introduction

ECONOMICS OF THE INDUSTRY. The latest United States production data (*Fats & Oils Situation 170*, 24 pp.) available for fats and oils are as follows:

	For years beginning		
	Oct. 1 1952	Oct. 1 1953 preliminary	Oct. 1 1954 estimate
	mil. lbs.	mil. lbs.	mil. lbs.
Butter (actual weight).....	1,601	1,681	1,625
Lard and rendered pork fat.....	2,501	2,272	2,600
Edible beef fats.....	217	255	250
Edible vegetable oils (includes oil equivalent of seed exported).....	5,010	5,252	5,365
Soap fats (inedible animal fats, fish, whale and seal oil).....	2,754	2,765	2,820
Drying oils (linseed, tung and castor oils).....	557	815	718
Others (neats' foot, wool grease, fish-liver oil, etc.).....	37	31	25
<b>TOTALS.....</b>	<b>12,677</b>	<b>13,071</b>	<b>13,403</b>

It is interesting to note that in the discussion accompanying the above statistics it is pointed out that production of food fats in recent years has been greater than the total demand and stocks have increased rapidly. Most of these were cottonseed oil and butter acquired by the government under price support operations. However, recently there have been significant export sales of cottonseed oil, and prospects indicate a greater drop in carry over of vegetable oils by next October, mainly because of the continued heavy export of cottonseed oil. A more detailed account of recent government purchases for price support and future of the activity with regard to the 1954 crop, domestic and export sales, etc., are reported by Prichard (*Soap & Chem. Specialties 30*, No. 10, 50), who points out that our increasing production indicates that over production and price support will continue as problems in the industry.

Information on prices in the above suggests that domestic prices have remained fairly steady whereas world prices have risen. This has probably reflected an optimism with regard to exporting our over-production. In another discussion on prices of fats, oils and waxes the 1954 prices are rated at an index of 113.32 as compared to 101.39 for the previous year (anon.—*Oil Paint & Drug Repr.* 167, No. 5, 54). Other comments here show that total U. S. exports of all fats and oils, including oil equivalent of oil seed, for the marketing year ending the first of October were 50% higher than the previous record of 2,300 million lbs. in 1951-52. Cottonseed exports were the largest in 40 years, soybean exports broke the previous record by 18 percent, and linseed oil exports shattered all previous records. Production, shipment, need, use, etc., have been reviewed for Germany (Kolbrack—*Fette u. Seifen 55*, 911) and for the world (Kaufmann—*Ibid.* 56, 330).

During 1954 soap sales dropped about 11% as compared to 12% in 1953, while synthetic detergents sales for these years increased 11 and 22% respectively (Snell—*Chem. & Eng. News 33*, 22). The data are interpreted to indicate that an equilibrium between the two may soon be reached; but the trend may be altered by new uses for the synthetic detergents. In a lecture, Macon (*Ibid.* 560) said that the synthetic detergent share of the soap-synthetic market should rise to 75%: its present share is 58%. There also appeared several editorial comments on this subject which in general pointed out that the rising trend of synthetics is now at a slower pace. Three communications on detergents were on the world trends of the market (anon.—*Chem. Eng. News 32*, 3874; Sisley—*Rev. Française corps gras 1*, 16; Nebbia—*Olearia 7*, 188).

The active efforts in previous years to ease the situation brought about by oversupplies of animal fats were continued

by demonstrating the use of these in animal feeding (Magofin—*Soap, Sanit. Chemicals 30*, No. 3, 54; Kropf *et al.*—*J. Animal Sci.* 13, 630; Pearson & Tucker—*Ibid.* 970; Siedler & Schweigert—*J. Agr. & Food Chem.* 2, 193; anon.—*Ibid.* 112, 219, 1150, 1255) and poultry rations (Aitken *et al.*—*Poultry Sci.* 33, 1038; March & Biely—*Ibid.* 1069; Runnels—*Ibid.* 1090; Yacowitz & Chamberlin—*Ibid.* 1090). Other encouragements for using the fats were directed to the manufacture of emulsifiers and synthetic type detergents (McCauliff—*Soap Sanit. Chem.* 30, No. 3, 51) and extension of their usage in plastics, resins, plasticizers, detergents, lubricants, and waxes (Ault—*J. Am. Oil Chemists' Soc.* 31, No. 3, Suppl. 31).

General communications which contain information on economics, trade, production, etc., were written on the efficiencies of different types of cottonseed mills and their effects on oil supplies, prices, and returns to growers (Brewster—*J. Am. Oil Chemists' Soc.* 31, 618; U. S. Dept. Agr. Marketing Service Rept. No. 54), tall oils (Cannon—*Chem. Eng.* 61, No. 6, 142; Vilbrandt *et al.*—*Bull. Va. Polytech. Inst. Eng. Expt. Sta. Ser. No. 89*, 14 pp.), animal fatty acids (Pattison—*Soap,*

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*Chem. Specialties* 30, No. 12, 54; Christensen—*Ingenioren* 62, 866), fish oil production by the German fish meal industry (Dressen—*Fette u. Seifen* 56, 224), vegetable oils for the printing-ink industry (Desalme—*Bull. men. inform ITERG* 3, 126), and utilization of wastes and by-products of the vegetable oil industry (Khan—*J. Sci. Club*, India 6, 122).

Research activities on palm oil in West Africa (Thieme—*Fette u. Seifen* 56, 328) and of the American Meat Institute on animal fats (Lewis—*J. Am. Oil Chemists' Soc.* 31, No. 3, Suppl. 28), have been summarized. Basic devices for regulation in production and processing of fats and oils were also reviewed (Bönnff—*Fette u. Seifen* 399).

General information on economics and composition were found in papers on commercial oils and their sources (Kaufmann & Thieme—*Fette u. Seifen* 56, 513, 621, 715, 851, 938), wood oils of *Aleurites fordii* and *A. montana* (Bagot—*Oleagineux* 8, 581, 689, 761, 861), tung oils from the tea-garden areas in north Bengal (Choudhury & Chakrabarty—*Sci & Culture, India* 19, 260), utilization of rice oil of high acidity (Martinenghi—*Chim. e. ind., Milan*, 36, 264), varieties of cottonseed in India and their oil (Rao & Kuppaswamy—*Bull. Central Food Technol. Res. Inst., Mysore* 2, 303; Desikan & Murti—*Oils & Oilseeds J., India*, 5, No. 10/12, 24; 6, No. 9, 12; No. 10, 11; Harwalkar et al.—*J. Indian Chem. Soc. Ind. & News Ed.* 16, 87), olive oil (Schneider—*Fette u. Seifen* 56, 326), sperm oil in Japan (Kinjiro Iguchii Dai-ichi Kogyo Seiyaku Co.—*J. Oil Chemists' Soc., Japan* 2, 99) and palm oil as a source of vitamin A (Budowski—*Arch. venezolanos nutric.* 3, 309).

Several communications reflect a desire to find new sources of fats and oils or to increase usage of some little used sources. These pertained to: nine rare and uncatalogued sources of oil in Ecuador (Oilar—*J. Am. Oil Chemists' Soc.* 31, 142), gokhru seed (Shrivastava—*Oils & Oilseeds J., India*, 4, No. 9/10, 14), kamala seed and its oil (Gupta—*Ibid.*; Aggarwal—*Ibid.* 6, No. 3, 7), neem seed oil (Mitra—*Ibid.* 4, No. 9/10, 16), boliche, *Sapindus saponaria*, oil (Fernandez—*Anales fac. farm. y bioquim., Univ. nacl. mayor San Marcos, Lima*, 3, 122), moringa or ben oil of East Africa (Bennett et al.—*Colonial Plant & Animal Products* 3, 55), oil and livestock fodder from gourds (Kranjc—*Kem. Zbornik* 1951, 80), raisin seed oil (Menesson & Maricourt—*Inds. agr. et aliment, Paris*, 70, 769), jojoba oil (*J. Chem. Ed.* 31, 253), the first commercial sesame crop in the United States (anon.—*J. Agr. & Food Chem.* 2, 107), and cuttle-fish oil (Takei—*Bull. Japan, Soc. Sci. Fisheries* 18, 569). Similar publications in which new characteristics and compositions are recorded will be cited in the section of this review on characteristics and composition.

**COMPETING MATERIALS.** Much of the information on competing materials appears as editorials, news notes, etc., which will be summarized without reference to their origin. The principal competition with soaps is from petroleum. The materials being substituted for part of the fatty lubricant thickeners appears to be organic silicones, inorganic silica gels, pectic material and cellulose. This will be evident in the division on lubricants in the section on products. Drying oils are finding competition from latex coating products whose sales have multiplied 20 fold between 1945 and 1952, and in floor coverings from competing vinyl resins and other synthetics.

New communications on the subjects which follow also reflect continued activities in obtaining cheap substitutes for fat from petroleum: development and potential of synthetic fats (Seaman—*Chem. & Processing Eng.* 35, 165, 241), drying oils from kerosene hydroxy acids (Serb-Serbin—*Byull. Obmenu Opyt. v Lakokrasoch Prom.* 1953, No. 4, 18), protective coating resins from petroleum hydrocarbons (Geiser—*U. S. 2,654,732*), synthetic drying oils (Nelson & Gleason—*U. S. 2,650,209*), preparation of fatty alcohols from gas-oil fractions (Moore & Hess—*U. S. 2,653,959*), and fatty alcohols from paraffin oxidation (Hentrich & Kirstahler—*Ger. 358,395 Cl. 120*).

**MICROBIOLOGICAL FAT.** Shibazaki (*J. Japan Chem.* 6, 517) reviewed the literature on production of fat by synthesis with microorganisms.

In a survey of potential fat-producing molds by a group of investigators, 43 strains selected from 10 species were examined in different solutions of nutrient inorganic salts together with sucrose (Woodbine et al.—*J. Exptl. Botany, London*, 2, 204; Murray et al.—*Ibid.* 4, 251; Gregory & Woodbine—*Ibid.* 314; Gad & Walker—*J. Sci. Food Agric.* 5, 339). Yields as high as about 40% on the basis of sugar used were obtained. The best producers of fat were *Penicillium javanicum* and *Aspergillus nidulans*. The detailed account of this work shows

the effect of nitrogen, sodium phosphate and magnesium sulfate concentrations, and the substitution of glucose for part of the sugars on yield. Similar work on the production of fat using *Rhizotorula gracilis* by Steinberg & Ordal (*J. Agr. Food Chem.* 2, 873) showed that the rate of fat formation was increased linearly with media of pH from 3.0 to 8.5; that decreasing the temperature from 28 to 22° lowered the rate to less than half; that addition of calcium, sodium or iron to the media was unnecessary; and that ethanol or glycerol did not increase fat formation. Descriptions of fat production from sweet potato juice by microorganisms of the *Endomyces* or *Oidium* types have indicated that the presence of a small amount of alcohol either added or formed by slight fermentation of the media will induce fat yields as high as 47% on a dry basis (Nakahama & Ishida—*Japan 4992* [1952]; *J. Fermentation Technol., Japan* 30, 100, 260). The fat production of *Debaryomyces nicotianae* was compared to that of 13 other yeasts (Giovannozzi-Sermanni—*Il. Tabacco* 8, 174). The fungi, *Mucor nucedo* and *Styranus*, have been found to be particularly rich in fats (Blinc—*Kem. Zbornik* 1951, 13).

**NEW COMPREHENSIVE LITERATURE.** The previous review of this series was published in *J. Am. Oil Chemists' Soc.* 31, 176, 236. A review of the same scope by the Oils and Fats Group of the Society of Chemical Industry (*Repts. Prog. Applied Chem.* 38, 339) cites the outstanding developments of the previous year. Other reviews on the fat, oil and detergent industry were written by Schwitzer (*Chem. Eng. Rev.* 35, 204), Paquot (*Rev. fermentations et inds. aliment.* 8, 139), and Maekawa (*J. Oil Chemists' Soc. Japan* 2, 119). Another review contained economical and technical information as related to India's five-year plan (Takagi—*Ibid.* 3, 121). Reports written on discussions at the First Detergent Congress show that this field was well reviewed (Sisley—*Soap & Chem. Specialties* 30, No. 12, 50; anon.—*Fette u. Seifen* 56, Suppl. pages No. 8). Volume II of a series of books on "Progress in the Chemistry of Fats and Other Lipides" contains reviews on: polymorphism of glycerides, autoxidation of fats, nutritional significance of fats, surface properties of fatty acids and allied substances, urea adducts of fatty acids, infrared absorption spectroscopy in fats and oils, and countercurrent fractionation of lipides.

Other new books of the fat, oil, and detergent field are:

Vegetable Fats and Oils. By E. W. Eckey & L. P. Miller. Am. Chem. Soc. Monograph No. 123. Reinhold Publ. Co., New York. 836 pp.

Oils, Fats, and Waxes. By C. Griffiths. Science Pubs., London. 85 pp.

The Buttermakers Manual. By E. H. McDowall. New Zealand Univ. Press, Wellington, N. Z. 1600 pp.

Hydrogenation et isomerisation des corps gras par les catalyseurs au nickel sur support. By G. N. Catravas. M. Declume, Lons-le-Saunier, France. 156 pp.

Pharmaceutical Emulsions and Emulsifying Agents. 2nd Ed. By L. M. Spalton. Chemist & Druggist, London. 138 pp.

Physical Properties of Fatty Acids, Glycerides, and Derivatives. By W. S. Singleton. U. S. Bur. Agr. & Ind. Chem. Mimeographed Circ. Ser. AIC-361. 33 pp.

Fazovaya struktura triglits'eridov. By G. B. Ravich & G. G. Tsurinoy. Izdatel'stvo Akad. Nauk S.S.S.R., Moscow. 137 pp.

Methodes d'analyse et de controle industriel des matieres grasses. By Geo. & J. P. Wolff. H. Dunod, Paris. 262 pp.

Index des huiles sulfonees et detergents modernes. T. II. By J. P. Sisley. Ed. Teintex, Paris.

Synthetische Wasch- und Reinigungsmittel. By H. Stüpel. R. Kohlhammer, Stuttgart, Germany. 568 pp.

Myla i novye moyushchie sredstva. By S. A. Dmitriev. Izdatel'stvo Akad. Nauk S.S.S.R., Moscow. 149 pp.

Detergency Evaluation and Testing. By J. C. Harris. Interscience Pubs., New York. 210 pp.

Analisis quimico cuantitativo de los detergentes sinteticos anionicos. By J. Carlos. Color (Aitea), Buenos Aires. 8 pp.

Detergent Solutions. By K. G. A. Pankhurst. Royal Inst. Chem., London. 21 pp.

Wäscher-Jahrbuch. Bdg. II. 310 pp. Bdg. III. 321 pp. Edited by E. Glasgow. Wäschereitech. und Chemie. Marburg, Germany.

Manufacture and Application of Lubricant Greases. By C. J. Boner. Reinhold Publ. Co., New York. 977 pp.

A series of lectures presented as a short course on "Inedible Fats and Fatty Acids" appeared in a journal (*J. Am. Oil Chemists' Soc.* 31, 485) and is also available as a separate booklet (Am. Oil Chemists' Soc., Chicago, Ill. 115 pp.).

### Production Processes

**ANIMAL AND FISH FAT EXTRACTION.** The communications describing modern rendering processes were: a review of the newest techniques (Paquot—*Rev. Francaise corps gras* 1, 351), methods of continuous rendering (Lieberman—*Myasnaya Ind. S.S.S.R.* 24, No. 6, 14), the centrifuge rendering apparatus of Anufrieva (Vechkanov—*Ibid.* 25, No. 2, 11), flow sheets and description of Reliable Packing Co. Danish unit (Thompson—*Food Eng.* 26, No. 9, 72, 102), and impulse rendering (Chayen & Ashworth—*J. Appl. Chem. London*, 3, 529). Lapshin (*Myasnaya Ind. S.S.S.R.* 25, No. 2, 55) discussed and reviewed the heat penetration and temperature conduction aspects of rendering fat.

The Pavia rendering process, which involves comminuting fatty tissue, extruding in the form of sheets, heating to about 140° F. and separating the fat, has been patented in the United States (Pavia—*U. S.* 2,671,098). Kramer (*U. S.* 2,697,112) patented further extraction of the residue of this process by pulping in a high speed "blender" and separating the pulp on Fourdrinier screens. Other patented equipment for fat rendering involved transfer of fatty tissue trimmings from cutting tables by pumping through pipes to the renderer (Noble—*U. S.* 2,681,270) and a cooker for rendering in which the charge may be submitted to high pressure and subsequent vacuum cookings (Illsley—*U. S.* 2,673,790).

The quality of whale oil has been investigated with regard to season, species, on-board-ship rendering processes, and storage (Okura & Yamada—*Repts. Japan. Marine Products Co. Res. Lab. No. 5*, 83 pp.). Particular attention was given to the effect of these factors on the composition, color, acidity and peroxide value. Einarsson *et al.* (*J. Agr. Food Chem.* 2, 946) have developed empirical equations to predict the press efficiency of removing oil from dried fish. The factors involved in the equation were pressing time, pressure, age of the dried meal, original oil content, and final moisture content. A new process for production of fish liver oils comprised dehydration of the livers in oil medium and separation of the oil by filtration and centrifugation (Greenfield—*U. S.* 2,651,647). In this process, emulsions were avoided, because the emulsifiers such as phospholipides, sterols and free fatty acids, prefer the fatty liquid medium to the nonfat solids. A patent was issued on an "electrical" fish liver oil extractor but details were not available to the writer (Satake—*Japan 6168* [53]).

Investigations by Belousov (*Molochnaya Prom.* 14, No. 9, 28) on the butter-formation process were interpreted to support the "flotation theory." He observed that emulsifying agents, such as albumin and lecithin, interfered with adherence of the fat particles to the air bubbles and thus prolonged churning; whereas isoamyl alcohol hastened churning. These observations were said to suggest that separation of the fat was dependent on adherence to the surface of air bubbles. A new "Alfa" process of continuous butter making involved a primary centrifuging to concentrate the fat and a second reworking at 8–13° to effect phase reversal ("Hollandia" Hollandische Fabriek Melkproducten Voedings-middelen N.V.—*Dutch 73,806*). A new DeLaval-type cream separator is said to remove extra solids with the fat (Goument—*U. S.* 2,694,520). A concentrate of 99.5–99.9% fat was obtained from cream by centrifugal separation at 130–140° F., dilution with water to fat content of 40–50% and reseparatoration (Weinreich—*Dairy World* 33, No. 2, 10). A newly patented butter churn is tilt-able and is supplied with a heat exchanger for control of temperature (Thorstensson-Rydberg—*U. S.* 2,688,468).

**VEGETABLE OIL EXTRACTION.** General descriptive and review publications on vegetable seed processing pertained to: pneumatic transport of oil seeds (Mascarenhas—*Olearia* 7, 246), problems in receiving, storage, and preparation of oil seeds (Quinson—*Rev. Francaise corps gras* 1, 275), processing European seeds by pressing (Rentenberger—*Seifen-Öle-Fette-Wachse* 80, 27, 51, 75), recent developments in oil extraction (Varma—*Oils & Oilseeds J., India*, 5, No. 10/12, 42), history of pressing methods (Laisney—*Rev. Francaise corps gras* 1, 287), plant operation data for high-capacity expeller operations (Dunning—*Oil Mill Gaz.* 58, No. 12, 11), solvent losses in solvent extraction (Helme—*Rev. Francaise corps gras* 1, 305), processing olives for oil (Luque & Nieto—*8th Congr.*

*intern. inds. agr. Brussels* 4, 139), processing castor beans (Dunning—*J. Am. Oil Chemists' Soc.* 31, 290), extraction of castor oil through aqueous medium (Verma & Sastry—*Oils & Oilseeds J., India*, 4, No. 9/10, 26), detoxifying cottonseed and preparing for oil extraction (Sergeev—*Masloboino-Zhirovaya Prom.* 19, No. 2, 5), improvement of cottonseed quality (Goldovskii—*Ibid.* No. 4, 8), processing of ucuhuba fat (Martinenghi—*Olearia* 7, 290, 295; 8, 47, 50), a flow sheet of the Tucker Products edible oil processing plant (anon.—*Food Eng.* 26, No. 3, 140), and the effect of processing conditions on the nutritive value of cottonseed meal for poultry (Altschul—*Poultry Sci.* 33, 180).

Attention was given to handling and storage of seeds. Van-neck (*8th Congr. intern. inds. agr. Brussels*, 4, 306), in investigations on handling palm fruit, found less acidity in the final oil from mechanically picked than from hand picked fruit. Milner & Thompson (*J. Agr. & Food Chem.* 2, 303) determined the progressive changes in composition resulting from the spontaneous heating of soybeans. They concluded that the exothermic nature of the sugar-protein interactions (Maillard reaction) was a major cause of spontaneous chemical heating in agricultural materials. Among 23 chemicals investigated for the inhibition of oil decomposition in stored rice bran, formalin was fairly effective, benzyl chloride and thiophenol were effective for one week, and all others tested were ineffective (Katayama & Tamaki—*J. Oil Chemists' Soc., Japan* 2, 156). Six different varieties of olives showed better storage stability, with respect to development of free acidity, when dipped in five per cent salt solution for 48 hours before storage (Castorina—*Olivicoltura* 6, No. 7, 12). Ventilation of seeds with forced air reduced storage temperature of sunflower seeds more efficiently than did conveyor rehandling (Golik—*Masloboino-Zhirovaya Prom.* 18, No. 11, 5). Zhitkov (*Ibid.* 19, No. 1, 12) published diagrams and descriptions of drum drier and seed cleaning equipment.

Seed treatments and extractions were studied with regard to producing high quality oils and meals. In processing tung nuts, a detoxified meal was obtained by a commercial expeller pressing which involved exposure to high temperature, and subsequent extraction of the meal with ethanol (Mann *et al.*—*J. Agr. & Food Chem.* 2, 258). In cottonseed processing, alkalies, among the various chemical agents tested, most effectively reduced toxicity of the by-product meal (Eagle—*J. Am. Oil Chemists' Soc.* 31, 121). In this work, the residual toxicity could not be explained on the basis of free gossypol content since meals with high values gave better rat growth performance than did some with lower levels of free gossypol. Thurber *et al.* (*Ibid.* 384) reported that a low cooking temperature (200–211° F.) followed by evaporative cooling seemed most desirable in cottonseed expeller milling from the viewpoints of quality of the meal, quality of the oil, and smoothness of operations. Condon *et al.* (*J. Agr. & Food Chem.* 2, 822) recorded the relationships of extent of autoclaving cottonseed meal to the gossypol content and nutritional value of the meal as fundamental data for processing the solvent meal for livestock feeding. Plyushkina (*Masloboino-Zhirovaya Prom.* 18, No. 10, 7) preferred cooking cottonseed of high moisture content so as to produce light colored oil. With crushed soybeans, Semenenko (*Ibid.* 19, No. 4, 25) recommended passing air through the charge during cooking to reduce moisture so as to produce a better quality soybean cake or flour. Pasch (*Span.* 204,645) subjected the cooking charge to dielectric heating after the steaming step in order to reduce moisture before pressing.

Prepressing of soybean flakes down to less than 10% oil content did not increase the rate of subsequent extraction with hexane over unpressed flakes (Dunning & Terstage—*J. Am. Oil Chemists' Soc.* 31, 28). However, a three "Rotocel" system solvent plant showed successful commercial operations in extracting cottonseed presscake (Anderson & McCubbin—*Ibid.* 475). With sesame seed, decoction extraction followed by expeller pressing of the dried solid was said to have some advantages (Kruchenskii—*Masloboino-Zhirovaya Prom.* 18, No. 7, 28). A double decoction extraction process was patented for extraction of palm oil (Depiesse—*Belg.* 480,722, 500,152). Cocoa butter and cocoa flavoring were produced from cocoa beans by gelatinizing the starch, coagulating the proteins, and centrifuging the oil-and-water emulsion to obtain cocoa butter and an aqueous flavoring agent (Siehrs—*U. S.* 2,687,959).

In hydraulic milling of cottonseed, the pressure should not exceed 2000 lbs. per sq. in.; each additional one quarter inch thickness of final cake from 0.25 to 1.0 inch increases residual oil three-eighths per cent; and the residual oil can be reduced

about 0.5% by heating the presses to 210°F. and maintaining the pressing moisture at six per cent (Carter—*Univ. Tenn. Eng. Expt. Sta. Bull. No. 18*, 80 pp.). In a new expeller press the extracted oil is cooled and then circulated through the shaft for cooling purposes and to remove foots (Bowman—*U. S. 2,687,084*). A new expeller makes use of a cylinder type impeller rather than an Archimedean screw to reduce heat development (MacIlwaine—*U. S. 2,697,978*).

A new solvent process, "Filtration-Extraction," based on countercurrent washing of the charge on a horizontal filter has been described (anon.—*Chem. Eng. 61*, No. 7, 324); demonstrated on cooked and uncooked soybean flakes (D'Aquin—*J. Am. Oil Chemists' Soc. 31*, 606) and used for the simultaneous recovery of wax and oil from rice bran (Pominski—*Ibid.* 451). Several new features for solvent systems were invented. Solvent, as heated vapor, was supplied to a countercurrent basket type system so that drying was accomplished during extraction (Barns—*U. S. 2,695,304*). To gain economy in power and evaporators Stapelberg (*U. S. 2,680,754*; *Brit. 707,385*) designed an operation so as to obtain miscella of 40% solute. The "DeSmet" system, based on sprinkling layers of materials on conveyors with solvents, has been patented in the United States (DeSmet—*U. S. 2,684,288*). In a similar system Bonotto (*U. S. 2,686,192*) percolated, rather than sprayed, the solvent to obviate channelling and clogging. Decossas *et al.* (*J. Am. Oil Chemists' Soc. 31*, 338) designed a new batch solvent-extraction pilot plant for use chiefly in research. There were other patents on continuous extraction but details were not available to the writer (Santelli & Viarengo—*It. 474,013*; Nabeta—*Japan 1286* ['53]; Maki—*Japan 3830* ['53]).

The effect of various soybean-flake bed properties on holdup of solvent after extraction of oil (Kocatus & Cornell—*Ind. Eng. Chem. 46*, 1219), the kinematic viscosities of benzene, carbon disulfide, and trichloroethylene solutions of olive oil (Oliver & Ramos—*Anales real. soc. españ. fis. y quim. 48B*, 431), and the viscosity of cottonseed oil-benzene solutions (Gavrilenko & Beloborodov—*Mastoboino-Zhirovaya Prom. 18*, No. 11, 13) have been recorded as fundamental data for solvent extraction processing. The extraction capacity of hexane, cyclohexane, acetone, trichloroethane, ethanol, and dichloroethane on rapeseed and peanuts at two different particle sizes were measured at 20 and at 30 siphoning in a Soxhlet apparatus (Lavenant—*Rev. mens. inform. ITERG 8*, 15). Extraction was poorest with ethanol, there were only slight differences in the efficiency of the others, and odor and color of the oil extracted with the chlorinated hydrocarbons were unsatisfactory. Paquot & Galletaud (*J. rech., cent. nat. rech. sci., Paris 1953*, No. 22, 40; No. 24, 120) also record poor odor and color in extractions with chlorinated hydrocarbon, but consider these to be very exhaustive extractants. The 1,2-dichloroethane gave higher yield and faster extraction than 1,1-dichloroethylene or light petroleum solvent. In similar work Jacini *et al.* (*Atti minerali, grassi e saponi, colori e vernici 31*, 39) tabulated the analyses of the oils extracted with the various solvents. Gupta & Aggarwal (*J. Sci. Ind. Res. 12B*, 545) listed ether, ethyl acetate, and benzene as efficient extractants for kamala seed oil; whereas petroleum ether, acetone, chloroform and carbon tetrachloride were not. However, he recommended a primary extraction with petroleum ether followed by getting the residual oil with benzene, because stability of benzene-extracted oil was very poor. In pilot plant studies with castor and mahua seeds, gasoline (boiling range 60-100°C.) was superior to benzene or petroleum ether (Aditya & Nandi—*J. Indian Chem. Soc. Ind. News. Ed. 16*, 27). Here fundamental data on the effect of flake thickness and flake-bed height on efficiency have been recorded. Data on the effect of temperature (20-110°) on extraction time and composition of the oil extracted with ligroine from olive pulp indicated that it was most advantageous, economically, to extract at 60-70° (Antonoli & Turiziani—*Ann. chim. Rome 43*, 839). A propane extraction technique has been worked out to yield an extracted oil which does not require refining (Miller—*U. S. 2,682,551*). In this process colloidal particles were said to aggregate and the aggregates were stabilized by the monoglyceride impurities causing them to precipitate from the miscelles into a dense phase.

Equations for use in trichloroethylene extraction of cottonseed were developed to calculate the residual extractables from a given flake thickness, meat diameter, extraction in hours, viscosity and temperature (Arnold & Juhl—*J. Am. Oil Chemists' Soc. 31*, 613). This and a report on the densities and viscosities of trichloroethylene miscelles of cottonseed oil, fish oil, and beef tallow (Arnold *et al.*—*Ibid.* 393) are useful for

design and control of operations with the solvent. However, the many communications on toxicity of chlorinated hydrocarbons remind the users that there are hazards involved to the processing personnel and to animals that eat the byproduct feeds (McBirney—*Arch. Ind. Hyg. Occupational Med. 10*, 130; Kleinfeld & Tabershaw—*Ibid.* 134; Coler & Rossmiller—*Ibid.* 8, 227; Yamaga & Saruta—*J. Sci. Labor, Japan 29*, 395; Friberg *et al.*—*Acta Pharmacol. Toxicol. 9*, 303; Pritchard—*Univ. Microfilms, Publ. No. 6156*, 183 pp.; Hoscheck—*Die Medizinische 1954*, 1275).

In the application of alcohol solvent extraction to cottonseed, Rao (*Oil & Oilseed J., India 6*, No. 4, 10; *Soap, India, 6*, No. 11, 12) emphasized that the meal is nontoxic because gossypol has been removed. Other advantages were that it is simpler, did not require cooking of the seed, and in India it is more economical than extraction with petroleum solvent (Satyan & Rao—*Bull. Central Food Technol. Res. Inst. Mysore 2*, 305). Technical data such as solubilities, steam and power requirements, capital investment, and operating cost for commercially processing peanut cake have been issued (Rao—*J. Sci. Ind. Res. India 12A*, 373). Optimum conditions such as amount of alcohol, temperature, and agitation have been worked out for applying this solvent for the extraction of rice bran oil (Kawai & Ukiya—*J. Chem. Soc. Japan, Ind. Chem. Sect. 55*, 381). One attempt to design a continuous system for the alcohol extraction of coconut oil was complicated by condensation of moisture, precipitation of sugars, and build-up of nonoil substances in the solvent. However, a semi-continuous system capable of extracting 71% of the total oil was developed (Gutierrez—*Philippine Agr. 34*, 133).

Puntambekar (*Paintindia 4*, 85; *Oils & Oilseeds J., India 5*, No. 10/12, 37) recommended that kamala seeds, which contain a readily polymerizable fat, be extracted with a noncongealable glyceride oil, the miscella be cooled, and the granules of kamala fat be removed by centrifuging.

Systems for desolventizing oil extraction residues differed. Belter *et al.* (*J. Am. Oil Chemists' Soc. 31*, 401) passed superheated solvent vapors into the solvent saturated flakes and conveyed them into a cyclone separator where the separation occurred. Karnofsky (*U. S. 2,691,830*) improved a continuous desolventizer and deodorizer by passing noncondensable gases through the system to help remove the solvent vapor. A combination desolventizer and toaster comprised superposed dryers of gradient temperature through which the charge passes in series (Hutchins—*U. S. 2,695,459*).

BYPRODUCT FATS. Sisson *et al.* (*U. S. 2,688,590*) recovered fatty material from tall oil by a system of distillation and redistillation of specific fractions. Potts (*U. S. 674,570*) designed a special distillation column from which fatty acids distill through the top, and rosin acids and pitch are discarded at the base. One patent included distillation of the fatty acids from rosin acids and subsequent separation of oleic and linoleic acids from the fatty fractions by fractional crystallization from acetone (Glynn & Hofferth—*U. S. 2,662,849*). Rosin acids may be removed from the fatty acids by precipitation with acetonitrile (Harwood *et al.*—*U. S. 2,672,458*). One process, which began with the crude soaps of tall oil, comprised adding rosin acids in amount equivalent to the fatty soap present, warming to cause substitution of the rosin for the fatty acids, and extracting the latter with ketones (Kokatur—*U. S. 2,662,880*).

Wolfrom (*Am. Dyestuff Repr. 43*, P372) reported that greater wool grease recovery is possible with nonionic detergent scouring agents and has described the use of alkylphenol ethylene oxide type of detergent for the purpose. Details for the flotation process of recovering wool wax from scour liquors have been published (Evans & Ewers—*Australian J. Appl. Sci. 4*, 552; Edwards *et al.*—*Ibid.* 579). This method involves aerating the scour liquid, collecting the froth, washing the froth, and separating the wax by centrifuging. A patented solvent method comprised conducting vapors of heavier-than-water organic solvent over the scouring solution; the solvents condense at the surface and drop through the liquid, extracting the wool fat (Colin—*Belg. 516,280, 521,355*). A good grade of wool grease was said to be produced by adding ionizable alkali or ammonia salt of a lower organic acid to the scour liquor, heating to darkening, settling, and centrifuging (Cabot & Cohen—*U. S. 2,692,184*). Patents have been issued on reducing the ash content of wool fat by washing with sequestering agents (Bovy—*Belg. 525,713*), and for decolorizing it with hydrogen peroxide (Lower—*Brit. 706,422*).

Bone glue extraction equipment was modified to permit skimming to recover bone grease (Mortenson—*U. S. 2,667,500*).

REFINING, BLEACHING, AND DEODORIZATION. Desliming or degumming of oils may be a primary step in production of a phosphatized by-product, a means of lowering subsequent alkali refining losses, or simply a means of producing a clear oil when alkali deacidification is unnecessary. In an investigation on the efficiencies of several detergents, acids, alkaline salts, acid salts, other salts, lignin, and commercial products for precipitating gums (phospholipides), lignin was markedly efficient (Dangoumau—*Rev. Francaise corps gras* 1, 473). In this work copper sulfate reacted or formed complexes with the phospholipides. With safflower seed oil, heating to about 200° F. in the presence of 0.6% moisture, precipitates the gums; or alternatively one can heat to 495° F. and include decomposition of the carotenoids so that a light colored filtered oil is obtainable (Christensen—*U. S.* 2,667,499). With solvent processes it is convenient to hydrate the gums in the miscella with dry steam to precipitate them (Watson—*U. S.* 2,686,193). The chemicals recommended for degumming were amino compounds or ammonia (Clayton—*U. S.* 2,686,794), successive treatments with phosphoric acid and alkali phosphates, respectively (Colomb—*Lack- u. Farben-Chem.* 5, No. 9/12, 14), and treatment with polybasic aliphatic acids (Sadler—*U. S.* 2,666,074). A continuous apparatus for degumming is based on continuously injecting medium for hydration in a stream of oil passing through a reaction zone, while maintaining the mixture in a turbulent state, and separating with centrifuges (Dron—*U. S.* 2,683,155). In such a system, a conveyance has been designed to inhibit precipitation and give even flow so that centrifuges operate at a smooth constant level (Bierke—*U. S.* 2,657,224). The mucilaginous materials have also been removed by dissolving the crude oil in liquefied, normally gaseous, hydrocarbons, in which the mucilaginous materials were not soluble (Hixson & Miller—*U. S.* 2,666,773). With crude rice bran oil, waxes and gums can be separated as a sludge by a primary centrifuge, and this sludge can be separated into wax and an aqueous gum phase with recentrifuging at 200° F. (Sterzynski & Lawatsch—*U. S.* 2,663,717). Naudet *et al.* (*Bull. mens. inform. ITERG* 8, 112) demonstrated the recovery of fatty acids from oil gums and mucilages by a system of autoclaving with soda ash, or saponification with soda lye, and acidification to release the fatty acids. A toxic oil from sikimi seed was rendered edible by treatment with inorganic or organic acid followed by neutralization with soda ash (Tabuchi—*Japan* 835 [54]).

The communications containing general descriptive information and reviews on fat refining were written on the following texts: new continuous and batch refining processes (Felix—*Seifen-Öle-Fette-Wachse* 80, 25, 49), continuous refining with the DeLaval "Short Mix" process (Braae—*Fette u. Seifen* 55, 859), centrifugal separators for refining of crude vegetable oils (Möller—*Ibid.* 56, 336), hermetic separator for vegetable oil refining (Sullivan—*J. Am. Oil Chemists' Soc.* 31, 361), a classification of methods for refining fats (Smits—*Masloboino-Zhirovaya Prom.* 18, No. 8, 10), refining with simultaneous production of a phospholipide concentrate (Sergeev—*Ibid.* 19, No. 4, 10), refining rapeseed oil (Zharskii & Romanova—*Ibid.* No. 2, 35), refining of peanut and cottonseed oils (Rentenberger—*Seifen-Öle-Fette-Wachse* 80, 436), yields in refining olive oil (Massa—*Grassas y aceites* 4, 53), refining rice-bran oil (Carola—*Olii minerali, grassi e saponi, colori e vernici* 30, 56), advantages of earth-carbon mixtures for bleaching oils (Aehmelt—*Chem.-Ztg.* 78, 766), bleaching fats and oils with hydrogen peroxide (Stein—*Seifen-Öle-Fette-Wachse* 80, 30), bleaching and deodorization of vegetable oils (Gilles—*Rev. Francaise corps gras* 1, 399), deodorization of fats and oils (Sergeev—*Masloboino-Zhirovaya Prom.* 18, No. 8, 29), theory, computation, and design of apparatus for deodorizing oils (Gel'perin & Gel'perin—*Ibid.* 19, No. 4, 12), and general principles and apparatus for deodorization of oils (Merat—*Rev. Francaise corps gras* 1, 396).

Rapidity of operation and reduced neutral oil loss occurs in a new Sharples Corp. (*U. S.* 2,663,719, *Brit.* 695,593) continuous refining system where contact of lye with oil is effected by turbulent flow rather than conventional mixing and contact is for only 0.5-5 seconds before the centrifugal separation. In a two-stage system Afzelius & Lindgren (*U. S.* 2,678,936, *Brit.* 684,035) refined similarly with insufficient lye and completed the refining in the second stage with vigorous agitation. Equipment has been designed so that multiple stage refining can be accomplished in one vessel, the mixture being impelled through the stages continuously with steam as the driving medium (Metallgesellschaft A.-G.—*Brit.* 707,470). Two methods of refining in which alkali and oil are emulsified and the emulsions

are broken to separate foams were described (Markley & Feuge—*U. S.* 2,686,796; Bortovoi & Saganskii—*Masloboino-Zhirovaya Prom.* 19, No. 3, 34). The newly patented additives for reducing neutral oil losses during alkali refining were alkali sulfate, chloride or carbonate (Aktiebolaget Separator—*Brit.* 704,591), polycarboxylic acids such as citric or tartaric (Carlson—*U. S.* 2,678,325; Ziels—*U. S.* 2,678,326), "Versene" (Unilever Ltd.—*Brit.* 708,831), and soap or soapstock (Samsi—*Indian* 49,358). Improved stability toward oxidation was obtained in solvent extracted oil by bleaching the oil in the diluted miscella stage and alkali refining of the concentrated miscella (Ziegler—*U. S.* 2,670,362). A refining method for rice bran oil comprised precipitation of waxes with acetone, alkali refining and bleaching (Martinenghi—*Chimica e ind., Milan*, 36, 467). For highly acid dewaxed rice bran oil a combination of neutralization, selective hydrogenation of the soaps formed, and salting out of the hardened soap was suitable (Nishimura—*Japan* 2736 [53]). Elimination of chlorophyll from rapeseed oil by acid treatment before alkali refining was necessary to prevent production of dark colored hydrogenated products (Kaminskii—*Masloboino-Zhirovaya Prom.* 19, No. 3, 10).

Other means of removing free fatty acids from fats and oils involved fractionation with liquefied propane (Hixson & Miller—*U. S.* 2,666,773; Mattikow—*U. S.* 2,652,412), esterification with propylene oxide (Takao & Tomiyama—*Japan* 5685 [53]), extraction with various lower alcohols (Gomez & Cartaya—*Grassas y aceites* 4, 176; Odagiri—*Japan* 978 [54]; Toyama & Toyama—*Rept. Nagoya Ind. Sci. Res. Inst.* No. 4, 61), and various means of evaporation or distillation (Salganskii & Shvetsov—*Masloboino-Zhirovaya Prom.* 18, No. 8, 24; Yoshida—*Japan* 5186 [53]; Council Sci. & Ind. Res.—*Indian* 48,530; Nakajima & Kobayashi—*Japan* 636 [53]).

A pilot plant which was constructed to develop new absorbent clays for bleaching fatty oils was described by Rich (*Ind. Eng. Chem.* 46, 2272). The complete plant includes units for neutralizing, bleaching, hydrogenating and deodorizing oils which are miniature counterparts of the commercial units. A substantial improvement in batch decolorizing of tallow by activated absorbents was obtained with addition of one per cent moisture (Rich—*J. Am. Oil Chemists' Soc.* 31, 374). A bleaching method for soybean oil comprising in succession acid treatment, neutralization, treatment with active carbon and steam at 290° F., cooling, adding bleaching earth and heating to 150° F. was said to inhibit color and odor reversion (Metallgesellschaft A.-G.—*Brit.* 707,454). Heating with a small amount of hypophosphorous acid before decolorization with liquefied, normally gaseous hydrocarbons also prevented color reversion of refined oils (Hlavacek—*U. S.* 2,673,868). Rzhikhin's (*Masloboino-Zhirovaya Prom.* 19, No. 2, 8) investigations on the browning of refined cottonseed oil indicated that condensation and interaction of gossypol with phospholipides was the cause, and the process was brought about by the action of heat and air through changes in the functional groups of gossypol. Dechary *et al.* (*J. Am. Oil Chemists' Soc.*, 31, 420) inhibited the browning of cottonseed oil by precipitation of the gossypol and some other materials with *p*-aminobenzoic acid. This work suggests that the inhibition of color reversion during storage should be approached through removal of gossypol, but an economical reagent suitable for commercial application is required. Dark green rice bran oil should be treated with inorganic acids before bleaching with clay to obtain a light oil (Seto—*Japan* 5286 [52]). A similar process was required for rapeseed oil intended for hydrogenation to a solid fat (Zharskii *et al.*—*Masloboino-Zhirovaya Prom.* 18, No. 7, 16). Methods of activation and a method of use for bleaching oils has been recorded for certain Russian clays (Kats—*Ibid.* 19, No. 5, 36), Indian bentonite (Chakrabarty & Pal—*Indian Soap J.* 18, 311), and earths of the state of Hyderabad, India (Joshi & Saletore—*J. Sci. Ind. Res., India* 12B, 381). Details were written for the application of hydrogen peroxide to the bleaching of wool fat (Mikumo & Goto—*Res. Rept. Nagoya Ind. Sci. Res. Inst.* No. 1, 29), rice bran oil (Toyama—*Ibid.* No. 3, 46), sperm-whale oil (Moldavskaya & Dmitrieva—*Masloboino-Zhirovaya Prom.* 19, No. 2, 14), monoglycerides (Al-sop—*U. S.* 2,684,971), and fats, oils, and waxes in general (Wachi—*Japan* 4933 [53]).

A newly patented oil deodorizing apparatus comprises a series of superimposed heatable trays in a shell, each tray-cell having communication to vacuum independently of the other cells except the bottom tray which has means for cooling the oil (Bailey—*U. S.* 2,691,665). Beal & Lancaster (*U. S.* 2,674,609) patented a steam deodorization process in which 0.5 vol-

ume per cent of ethanol was added to the oil entering a falling-film-type column. Another new system was based on deaeration, heating and atomizing into a vacuum chamber by means of water vapor (Ballestra—*Rev. Francaise corps gras* 1, 562). New processes for deodorizing fish and marine animal oils were based on heating in the presence of nickel-carbon catalyst (Tshichiya *et al.*—*Japan* 2490 [’53]), electrolyzing opposite a diaphragm containing salt solution (Itakura—*Japan* 1592 [’53]) or solution containing sodium chloride and potassium sulfide (Itakura—*Japan* 6184 [’53]), and subjecting to the action of supersonics (Agawa *et al.*—*J. Chem. Soc. Ind. Chem. Sect.* 55, 399).

**BYPRODUCTS OF REFINING.** Reviews were prepared on the properties and uses of phospholipides (Merat—*Rev. Francaise corps gras* 1, 27; Mathur—*Oils & Oilseeds J. India* 5, No. 10/12, 124) and on properties and uses of cholesterol (Lower—*Chem. Products* 17, 300).

In directions for production of phospholipides from sunflower oil, by Lesyuis (*Masloboino-Zhironaya Prom.* 18, No. 10, 9) the oil is filtered hot, cooled to precipitate the phospholipides, refiltered, the precipitate is diluted with sunflower oil and re-separated as above. A fluid phosphatide product was dry and contained soybean oil as a diluent (Myers—*U. S.* 2,686,190). Toyama & Toyama (*Res. Rept. Nogoya Ind. Sci. Res. Inst.* No. 4, 56) refined crude phosphatides, obtained from foots of petroleum naphtha extracted soybean oil, by steaming and treatment with hydrogen peroxide. According to Scholfield & Dutton (*J. Am. Oil Chemists' Soc.* 31, 258), the peroxide bleaching is effective in destroying carotenoids, water washing removes xanthophylls, and a residual brown color is probably due to an aldehyde amine reaction product. This brown is increased by heating the phosphatides at 100°, and its development is not prevented by removal of free sugars or by hydrogenation.

Hydrated gums obtained from an oil in a degumming operation were subjected to treatment with a liquified, normally gaseous hydrocarbon for the purpose of recovering oil (Clayton—*U. S.* 2,678,327). Foots from the acid refining of sardine oil was distilled to recover 60% fat acids and some pitch (Sudo—*Japan* 3682 [’53]).

Two pyrethrum synergists, sesamin and sesamolin, were extracted by chromatographic fractionation from sesame oil; and in entomological tests, the latter was found to be five times more active than the former as a pyrethrum synergist (Beroza—*J. Am. Oil Chemists' Soc.* 31, 302). On the basis of chemical tests and ultraviolet absorption, a tentative structure has been suggested for sesamolin.

Sperm whale head oil was saponified, the fatty alcohol was separated; and on extraction of the alcohols at zero degrees with liquid ammonia, oleyl alcohol was removed leaving a good grade of cetyl alcohol (Itai—*Bull. Res. Ind. Non-aq. solns. Tohoku Univ.* 3, 97). Cholesterol was isolated from wool-wax alcohols by crystallization from lower hydrocarbons of the benzene series and methanol, and separation by selective crystallization from acetic and propionic acids (Hewett—*U. S.* 2,688,623). Soybean oil sterol concentrates were produced by saponifying the oil, adding an alcohol-water mixture to the soap, followed by liquid extraction with naphtha (Christenson—*U. S.* 2,679,503). Other methods described for producing sterols involved molecular distillation of tocopherols from linseed oil (Komori *et al.*—*J. Chem. Soc. Japan Ind. Chem. Sect.* 56, 433), rice bran oil (*Ibid.* 55, 466, 468), and rice germ oil (Komori—*J. Oil Chemists' Soc., Japan* 2, 190), and vitamin A from whale oil (Yamakawa—*Bull. Japan Soc. Sci. Fisheries* 18, 675). Molecular distillation equipment of Raoul & Meunier, Hichman, Sutton, Röhm & Haas, and Pingris & Mollet-Fontaine were illustrated and their applications described (Paquot—*Rev. Francaise corps gras* 1, 73).

Wax was separated from glycerides in sperm blubber oil by molecular distillation (Fujii—*Repts. Res. Lab. Nippon Suisan Co.* 6, 24).

**WINTERIZATION, SPLITTING AND FRACTIONATION.** Phase relations in the solvent winterization of crude and refined peanut oil in 85-15 acetone-hexane mixtures were developed to indicate the conditions necessary for removal of the required amount of stearin (Boucher & Skau—*J. Am. Oil Chemists' Soc.* 31, 268). Skau (*U. S.* 2,684,377-8) patented use of this system with chilling to -13° for peanut oil and -8° for cottonseed oil. Paquot & Galletaud (*Oleagineux* 8, 839) winterized peanut oil by crystallization from pure dichloroethane or in a 4:1 mixture of dichloroethane-ethanol with chilling to -15°. A two-stage cooling method of winterizing comprised dissolving the oil in solvent, crystallization at 5°, and completing the crystalliza-

tion at 15° below this temperature (Brennan *et al.*—*U. S.* 2,678,937).

Seal oil of iodine value 148, heated with a like volume of furfural and allowed to cool, permitted recovery of a separated layer containing an oil fraction of iodine value of 183 (Dugal—*Fisheries Res. Board Can. Progr. Repts. Atlantic Coast Sta. No. 57*, 3). A technique for fractionating fatty oils with liquefied gaseous hydrocarbons was patented (Palmer—*U. S.* 2,658,907). A means of removing more saturated constituents with such a system included subjecting the oil to interesterification before fractionation (Miller—*U. S.* 2,688,626).

General informational literature written on fat splitting was: a review on continuous hydrolysis (Burrow—*Trans. Inst. Chem. Engs., London* 31, 250), principles and newer developments in fat splitting (Schlenker—*Seifen-Öle-Fette-Wachse* 79, 179, 223, 247, 271, 295, 361, 387, 409, 435, 458, 511), and new designs for small scale operation (Berger—*Soap, Sanit. Chemicals* 30, No. 3, 93). Fat splitting agent preparation by Bespyatov (*Masloboino-Zhironaya Prom.* 18, No. 7, 21) from petroleum sulfonates involved forming the calcium and barium salts and separating the fractions most soluble in water. In comparative fat splitting tests the barium salt of dibutyl biphenyl sulfonic acid was a more efficient reagent than the barium salt of dibutyl-naphthalene sulfonic acid (Fukuzumi *et al.*—*J. Chem. Soc., Japan, Ind. Chem. Sect.* 55, 405; 56, 114). A patented method for hydrolysis of whale oil was based on autoclaving with an aqueous salt solution (Murata & Higo—*Japan* 3681 [’53]). One for nim oil involved saponification, and release of fatty acids with an inorganic acid. It included fractionation of the fatty acids by crystallization technique (Council Sci. & Ind. Res.—*Indian* 46,713). Splitting of sperm whale oil by saponification was catalyzed with sodium or magnesium ethylate (Fujii—*Repts. Res. Lab. Nippon Suisan Co.* 6, 24). Controlled heating of sperm oil with water permitted selective splitting of glycerides so that the natural wax esters could easily be segregated (Grunthal & Mannes—*U. S.* 2,686,191).

Tests on preparation of splitting enzymes from seven species of castor beans indicated that the product from a red, triple bloom spiny variety was most active (Nizamuddin & Kulkarni—*J. Sci. Ind. Res., India* 12B, 390).

The physical chemistry fundamentals of fractionating fatty acids by distillation, crystallization, chromatography, extraction with solvents, and precipitation with urea were discussed by Rigamonti (*Fette u. Seifen* 56, 1). A technique involving crystallization from acetone was demonstrated with a description on the preparation of fractions with iodine values up to 256 from safflower, sunflower, and niger seed oils (Patel—*Oils & Oilseeds J., India* 4, No. 9/10, 41). Directions for a double graining technique to produce stearic acid concentrate of definite setting points from tallow fatty acids were published (Juillard—*Bull. mens. inform. ITERG* 7, 485). The characteristics of fractions obtained by crystallization of whiting fatty acids from acetone at various temperatures from -40 to -10° were recorded as fundamental information for segregating concentrates of unsaturated and lauric acids from the mixed fatty acids of the oil (Frolova—*Rybnoc Khozyaistvo* 27, No. 2, 59). A combination of crystallization and solvent partition technique for separation of fatty acid mixtures comprised graining to form finely divided crystals and washing out the liquid portion with solvent (N. V. Vereenigde Stearine Kaarsenfab. "Gouda-Apollo"—*Brit.* 700,775).

Solubility and selectivity diagrams were prepared for methanol-castor oil methyl esters-heptane systems at 8.4 and 24° as fundamental information for liquid-liquid extraction of methyl ricinoleate (McCormack & Bolley—*J. Am. Oil Chemists' Soc.* 31, 408). Rice oil fatty acids, dissolved by heating in a mixture of four parts of furfural and four parts of 80% methanol, were cooled to 10° with separation of a solid fraction, principally palmitic acid. These unsaturated acids were separated from the solution by addition of water (Nakajima & Kosuge—*Japan* 6634 [’53]).

The fundamental principles and applications of extractive crystallization of fatty material with urea were discussed by Truter (*Chem. & Process Eng.* 35, 75). The technique was demonstrated for the segregation of iso-acids from other straight chain acids resulting from paraffin oxidations (Runge & Laske—*Fette u. Seifen* 56, 145), the separation and identification of components of oxidized methyl oleate and methyl linoleate (Castravas & Knafo—*Oleagineux* 8, 79), fractionation of safflower fatty acids (Narayan & Kulkarni—*J. Sci. Ind. Res., India, 13B*, 75), obtaining fatty acids with iodine value of 294-356 from the liver oil of cod, shark, pollock, menhaden, and other fish (Abu-Nasr *et al.*—*J. Am. Oil Chemists' Soc.* 31, 16),

separation of binary mixtures comprising a saturated and an unsaturated acid (Michel & Desbordes—*Bull. soc. chim. France* 1954, 913), segregating unsaturated glycerides and waxes from the saturated components of ecalot oil (de Ursinos *et al.*—*Anales real soc. espan. fis. y quim.* 49B, 645), partial separation of abietic acids from the fatty acids of olive oil (Moreno *et al.*—*Ibid.* 639), fractionation of rice bran oil fatty acids to obtain concentrates of saturated, oleic, and linoleic acids, respectively (Sakurai—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 56, 118), production of a palmitic acid-rich fraction from distilled rice-bran oil fatty acids (*Ibid.* 501), and preparation of soap stock and film-forming materials from cottonseed oil (Kats & Vlasova—*Masloboino-Zhirovaya Prom.* 18, No. 11, 16). Applications of urea-complex segregations which were patented were on preparation of concentrates of high iodine value from rice oil fatty acids (Sakurai—*Japan 6635* ['53], 979 ['54]), and separation of short chain, unsaturated and iso-alcohols from saturated alcohols of 10 or more carbon atoms (Bengen—*Ger.* 869,070, Cl. 120).

Descriptive information on fatty distillation was published by Ayerbe & Suarez (*Gras y aceites, Spain*, 4, 191). A new patented technique for fatty acid distillation involved preliminary aerating at 240-260°F. to prevent distillation of latent color-forming materials (Reinsh & Caldara—*U. S.* 2,664,430).

A new technique of fractionating oils involved dialyses through polar rubber diaphragms (Bolding—*Dutch* 72,285).

**HARDENING OF OILS.** General information communications on hardening of oils were on the kinetics of hydrogenation (Swicklik—*Univ. Microfilms Publ. No. 8913*, 93 pp.), hydrogenation and hydrogenolysis (Keely—*Ind. Eng. Chem.* 46, 1846), hydrogenation of mustard oil (Prakash *et al.*—*J. Proc. Oil Technol. Assoc. India, Kanpur* 8, 67), and elaidinization (Cruz & de Ursinos—*Grasas y aceites, Spain*, 4, 128).

Some reports were from investigations on the course of the hydrogenation reactions. A spectrophotometer study of tung oil during hydrogenation showed that dienes with maximum absorption at 271.5  $\mu$  decrease rapidly whereas those with maximum at 232 decrease less rapidly (Hashimoto—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 56, 123). Similar work by Catravas (*Compt. rend.* 236, 935) showed that as much as 9.3% conjugated dienes and traces of trienes and tetraenes from polyunsaturated constituents develop but the higher conjugated polyenes were rapidly hydrogenated. Increasing agitation when hydrogenating soybean oil improved selective saturation of the most unsaturated components (Beal & Lancaster—*J. Am. Oil Chemists' Soc.* 31, 619). A method was patented for improving selectivity of hydrogenation by adding 0.01-0.5%, based on oil, of an ethanol soluble reaction product of a polyhydric alcohol partial ester of phosphoric anhydride and an alkyloamine (Royce & Haskell—*U. S.* 2,671,097). Catalysts made by the reduction of nickel carbonate at high (90-156 atmospheres) hydrogen pressure (Fujii *et al.*—*Japan 3831* ['53]) and reduction of a mixture of copper and calcium nitrates (Ueno—*Japan 5027* ['53]) were said to induce highly selective hydrogenation of glycerides. Elovich (*Masloboino-Zhirovaya Prom.* 19, No. 3, 21) developed an equation to numerically evaluate selectivity.

Hydrogenation of vegetable oils in solvents was much more rapid and was possible at lower temperature than with the oil alone (Sokol'skii & Melekhina—*Izvest. Akad. Nauk Kazakh. S.S.R. No. 123*, No. 7, 9, 20). Thus the optimum temperature in benzene was 30° and in toluene 60-70°. Promotion of hydrogenation of oils with nickel catalyst was also obtained by the presence of platinum or palladium (Sokol'skii *et al.*—*Ibid.* No. 7, 30), and with the presence of carbon, titanium oxide, and diatomaceous earth (Tyutyunnikov & Fraier—*Masloboino-Zhirovaya Prom.* 18, No. 10, 12).

The method of hydrogenation of oil by using hydrogen released from ethanol by dehydrogenation was investigated (Mahnala—*Suomen Kemistilehti* 26B, 57). The kinetics of the reaction at higher temperatures suggested that the acetaldehyde formed in the process further decomposes and leads to the poisoning of the catalyst by carbon monoxide. Simultaneous splitting and hydrogenation of oils by adding water to the reacting mixtures was patented (Ueno—*Japan 4231* ['53]). Hydrogenation was used as a means of removing aldehydes and ketones from fatty alcohols (Miyake & Fujita—*Japan 1069* ['53]).

A method of measuring degree of unsaturation of fat in the course of hydrogenation was based on measuring the dielectric constant of the oil at a frequency below that which produces

relaxation of the dipoles of its molecules (Goldsmith *et al.*—*Brit.* 708,940).

Descriptive communications on the preparation of a hydrogenation catalyst were on catalyst for vanaspati production (Nanavati—*Oils and Oilseeds J., India* 4, No. 9/10, 32; *Rev. Francaise Corps gras.* 1, 565), nickel formate catalyst (Kaminskii—*Masloboino-Zhirovaya Prom.* 19, No. 4, 31) and copper nickel catalyst (Zaks & Liberman—*Ibid.*, 27). The use of mixed chromium-copper-manganese catalyst (Takumi & Kuwada—*Japan 1367* ['53]) and fatty acid salts of nickel and copper (Ueno—*Japan 4083* ['53]) in hydrogenations of oils was patented.

In tests on the activity of hydrogenation catalysts, those prepared as mixtures of nickel and copper were more active than nickel from reduced nickel formate (Delgado—*Rev. cienc. apl. Madrid*, 7, 152). An equation for numerically evaluating a catalyst was based on time required for a certain decrease in iodine during hydrogenation of a standard oil under specific conditions (Zinov'ev—*Masloboino-Zhirovaya Prom.* 19, No. 3, 17).

**INTER- AND TRANSESTERIFICATION.** The interesterification of fats and oils was reviewed under the subtitles: general ideas, interesterification course, interesterification of mixtures, glycerol monoesters, interesterification between monoesters, and migration of fatty chains between free alcoholic groups (Naudet—*Rev. Francaise corps gras* 1, 129). Interesterification of lard improved its ability to retain air, making it comparable to hydrogenated vegetable oil for shortening uses (Bailey—*Proc. Res. Conf. Council Res., Am. Meat Inst.* 5, 11). In a study on industrial conditions for interesterification of cuttle fish oil, descriptive data on products produced at various temperatures between -5 and 50° and with 0.1-1% sodium methoxide catalyst were recorded (Marumo & Tomiyama—*J. Oil Chemists' Soc. Japan* 2, 232). Holding the cuttle fish oil at 10° with 0.5% catalyst for 80 hours increased its cloud point from 2.0° to 35°. Using tin chloride as the interesterification catalyst was said to induce stability in products during storage (Paquot—*Bull. mens. inform. ITERG* 7, 387).

Fats containing acids of 6-10 carbon atoms were reacted with fatty acids of 12-18 carbon atoms under conditions for interesterification and for volatilization of the freed short acid to give products more suitable for candy coatings (Barsky—*Brit.* 706,562). Other procedures for the same purpose comprised converting the fats to free fatty acids and reesterifying with 95% of the glycerol required for reconstitution (Barsky & Zinzalian—*U. S.* 2,685,592), blending free fatty acids to minimize content of lower members, reconstituting to glycerides, and hydrogenating (Barsky & Zinzalian—*U. S.* 2,667,418), and removing lower fatty acids from the free fatty acid mixture by distillation and reconstituting to glycerides (Imhausen—*Brit.* 694,970, 694,983).

The effect of ethanol, catalyst and moisture concentrations, and temperature in the ethanolysis of coconut, castor, mohua, sesame, linseed, tung, and mustard oils has been determined to serve as fundamental data for ethanolysis of oils (Choudhury & Mukherji—*J. Indian Chem. Soc.* 31, 116, 125, 129; *Sci. & Culture, India* 19, 309). With mustard oil, removal of allyl thiocyanate by extraction with ethanol increased the reaction rate. Alcoholysis processes were described in which the catalysts used were alkali earth oxides (Hunn—*U. S.* 2,654,767), alkyl carbonates or sulfites (Anglaret & Maubec—*Brit.* 707,005), and *p*-toluene sulfonic acid (Perron—*Bull. mens. ITERG* 8, 63). Dihydroxy stearic acid, esterified with methanol as a terminal group and esterified at a hydroxy group with formic acid, was heated with a lower aliphatic alcohol to replace the lower fatty acid with hydrogen by alcoholysis without disturbing the terminal group (Logan—*U. S.* 2,669,572).

Experience on glycerolysis of vegetable oils with excess glycerol was recorded as fundamental data for the commercial manufacture of monoglycerides (Chinoy & Kamath—*Paint-india* 3, No. 5, 27; No. 6, 27). Data included properties, yield, and ratio of  $\alpha$ - to  $\beta$ -monoglycerides of products derived from linseed, castor, and dehydrated castor oils. Reacting a mixture of glycerides with glycerol in a homogeneous solution with a tertiary aromatic nitrogenous base solvent produced products of high monoglyceride content (Mattil & Sims—*U. S.* 2,691,664). Excess glycerol was recovered from monoglyceride preparations by dissolving the mixture in hexane and extracting with water (Kurita—*Japan 1982* ['53]). Monoglycerides were freed of flavor reversion material by dissolving in warm lower alkyl esters of phosphoric acid and chilling to a point where two phases form; one of the phases contains the refined monoglycerides (Young & Black—*U. S.* 2,682,550).

Partial glycerides were also prepared by hydrolysis of tri-glycerides with lipase prepared from castor beans (Rose & Balls—*U. S.* 2,676,906, 2,680,090).

Various natural fats, oils, and waxes were transesterified with ethylene oxides in the preparation of emulsifiers (Sundberg & Chiddix—*U. S.* 2,678,935).

A substitute for cacao fat was made by reacting stearyl monoglyceride with a coconut oil fat acid fraction boiling at 140-165° at 4-mm. pressure (Kawamura & Fujita—*Japan* [1953] Nov. 30).

### Fatty Products (Except Detergents)

**HOUSEHOLD AND OTHER EDIBLE FATTY PRODUCTS.** The role of mono- and diglycerides in baking was comprehensively treated by Coppock *et al.* (*J. Sci. Food & Agr.* 5, 8, 19). Their communications contain historical information, suggestions for specifications, illustrations of effects in bread, sponges, and Madeira cakes, theories on mechanism of action, information on natural occurrence of monoglycerides in flours, method of estimation, and pharmacology. An investigation on the possibility of eliminating glycerol in the manufacture of superglycerinated shortening by replacement with sodium or calcium glyceroxide indicated that a shortening prepared with the sodium compound was the more active of the two; but the best products were obtained by using a combination of one percent glycerol and calcium glyceroxide as the catalyst (Privett—*Ann. Rept. Hormel Inst.* 1952-3, 21). Subsequent work in the same laboratory showed that the emulsifiers improved the shortening properties of lard regardless of whether the crystal structure of the lard was modified, and that hydrogenated lard flakes appeared to give the best product of all the fats used in the preparation of the mono- and diglycerides (*Ibid.* 1953-54, 17). The newly described shortening improvers were: calcium salts of a homologous series of stearyl lactic acids (Thompson & Buddemeyer—*Cereal Chem.* 31, 296), polyethylene glycol esters containing one fat derived acid, and one short chain acid (Valko—*U. S.* 2,666,706), reaction products of phospholipides with lactic or similar acid (Glade—*U. S.* 2,666,704-5), esterification product of glycerol with fatty acids and lactic acid (Iveson *et al.*—*U. S.* 2,690,971), and esters of acetyl polycarboxylic acid with a fatty acid partial glycerol ester (Joffe—*U. S.* 2,689,797). New dry, readily dispersible shortenings were made, respectively, by encasing fat in homogenous mixture of sugar and gelatin as the main constituents (Robinson *et al.*—*U. S.* 2,694,643), and by mixing lard with natural gelatin from squash, with sugar, spice, and coloring as optional ingredients (Monti—*Ital.* 478, 754).

Polyethylene type emulsifiers were added to choline and inositol preparations to improve their effectiveness in the treatment of atherosclerosis and reduction of blood pressure (Maiese—*U. S.* 2,694,664). Such emulsifiers were not beneficial for improving intestinal absorption of food in ulcerative colitis (Ueyama *et al.*—*Gastroenterology* 23, 143), did not increase fat absorption in normal adults (Tidwell & Nagler—*Ibid.*, 470), were considered of questionable importance for improving fat and vitamin A absorption in premature infants (Snyderman *et al.*—*Pediatrics* 12, 158), but increased gastrointestinal iron absorption in hamsters (Wissler *et al.*—*Proc. Soc. Exptl. Biol. Med.* 86, 170). In clinical tests the compounds produced no toxic effects on feeding to infants (Preston *et al.*—*J. Clinical Nutr.* 1, 539), to old people (Waldstein *et al.*—*Am. J. Dig. Disease* 21, 181), or to normal individuals (Janowitz *et al.*—*Gastroenterology* 24, 510). They promoted skin tumor production by carcinogenic agents (Setälä *et al.*—*Science* 120, 1075). Diethylene glycol, which may be used in the manufacture of the emulsifiers, has a stronger diuretic effect than glycerol and appears in the bile and urine after ingestion (Loeser *et al.*—*Naunyn-Schmiedeberg's Arch. Exptl. Pathol. Pharmacol.* 221, 14). In this work, pathological changes caused by administration of lethal doses of diethylene glycol to rats were described.

Mixed "aceticin fats" made by random interesterification of soybean, cottonseed, coconut, and hydrogenated oils with tri-acetin had a lower melting point, improved stability, large plastic range and were as good or better shortenings than the original fats from which they were derived (Baur—*J. Am. Oil Chemists' Soc.* 31, 147, 196). Various properties, including spacings obtained by x-ray defraction, were recorded, and the inedible uses suggested for them included: plasticizers for polymers, replacement for palm oil in tinning, and as hydraulic oils. Gros & Feuge (*Ibid.* 377) evaluated the ability of aceticin fats made from natural oils and olein to plasticize fats, as

fundamental information for their use in margarine manufacture. Expansibilities, melting dilutions and temperatures, and x-ray data of the polymorphic forms of 1,2-diaceto-3-stearin and 1-aceto-3-stearin were recorded by Vicknair *et al.* (*J. Phys. Chem.* 58, 64). The x-ray diffraction patterns of the three forms of each fat were given and the microstructures were described.

Burke (*Fette u. Seifen* 56, 309) illustrated and described modern apparatus and techniques for margarine manufacture. A margarine production process patented by Teramoto (*Japan* 188 [1954]) contained the step of anaerobically fermenting the fat and oil raw material and the milk with *Lactobacillus bulgaricus* or *Streptococcus lactis*. A stabilized margarine contained isoamyl gallate as the stabilizing agent (Tomiya—*Japan* 5782 [1953]). Addition of a small amount of the methanol soluble fraction of oil-free vegetable oil phosphatides to margarine to reduce spattering was patented (Mattikow—*U. S.* 2,640,780). Another patent on margarine pertained to location of the coloring pellet in the packaged product (Hensgen—*U. S.* 2,668,114).

A fat satisfactory as a replacement for cocoa butter in confectionery products was made by hydrogenating refined hazelnut or almond oil to solidifying points of 17-20° and 10-21°, respectively (Calafell—*Span.* 200,164). A coating composition for frozen confections comprised vegetable oil and an aqueous phase containing sugar, flavor, and color emulsified with a tetraurate of 20 polyoxyethylene sorbitol (Carter—*U. S.* 2,674,534). A food preservation coating was a paste containing vegetable wax, vegetable oil, extract of chicory and extract of "creosole" (Rizzardi—*U. S.* 2,668,121). Partial esters of glycerol and fatty acids were added to fat intended for pan frying to inhibit adhesion of proteinaceous material to the pan (Edgar—*U. S.* 2,685,521).

Solubility data of almost completely hydrogenated peanut oil in refined and bleached peanut oil as related to freedom from oil separation on storage has been developed as fundamental information important to the problem of oil separation in peanut butter manufacture (Magne *et al.*—*J. Am. Oil Chemists' Soc.* 31, 113). In this work best prevention of oil separation involved shock chilling to molten mixture to produce fine crystallization, followed by tempering at a temperature that permits transformation of the crystals into more desirable higher melting forms. A patented process of this type comprised solidifying the peanut butter containing hard fat below the lowest temperature of the plastic range while agitating, raising the temperature to just below the highest temperature of the plastic range, and reagitating (Avera—*U. S.* 2,688,554).

Good quality oleo fat was said to enhance stability and resist "churn-out," when used in making non-butterfat frozen milk dessert products (Hull—*Food Eng.* 26, No. 8, 133).

**GENERAL EMULSIFIERS AND DEMULSIFIERS.** General descriptive communications on emulsifiers were written on: lanolin and cholesterol in emulsions (Hadert—*Seifen-Öle-Fette-Wachse* 30, 502), emulsifying agents in washable ointments (Münzel & Ammann—*Pharm. Acta Helv.* 29, 1), stearate ointments (*Ibid.* 91), surface behavior of  $\alpha$ -monoglycerides of various fatty acids (Perez & Santos—*Anales real soc. espan. fis y quim* 49B, 723), and associations between lipides and compounds, such as lecithins, saponins, etc., which may favor dispersion of the lipides in an aqueous medium (Dervichian—*Bull. mens. inform. ITERG* 8, 9).

A hydrometer method was designed for measuring stabilities of heavier-than-water emulsions (Sanders *et al.*—*Soap & Chem. Specialties* 30, No. 5, 99). A stability method for water-in-oil type emulsions was based on applying a directionalized potential between a pair of electrodes, at least one of which is capable of releasing gas when contacted by water, to determine the ionic charge on the dispersed phase (Chittum—*U. S.* 2,678,911). The Powers-Cataline method of comparing emulsifiers was modified and applied for the evaluation of the emulsifying capacity of 24 derivatives of 5-cholestene (Worrell & Sinsheimer—*J. Am. Pharm. Assoc.* 43, 562).

Addition of the emulsifier, Tween 61, to cacao butter yields a pharmaceutically useful plastic material that will take up aqueous solution, but its consistency becomes unsuitable for making suppositories (Kettlitz *et al.*—*Boll. chim. farm.* 93, 83). Emulsifiers were prepared by condensing fatty acids or organic bases with products of hydrolysis of alginic acid (Abe & Ihara—*Bull. Japan Soc. Sci. Fisheries* 18, 47, 51, 55). Partial oxidation of wool grease with an aqueous acid chlorite oxidizing agent improves its emulsifying capacity for weakly alkaline aqueous solutions (Stanley—*U. S.* 2,665,282). New emulsifier patents were: on polyethylene glycol ethers of phe-



nolic compounds for general purposes (Hoffman-LaRoche & Co. A.-G.—*Swiss 238,413 Cl. 36e*; Sanders *et al.*—*U. S. 2,696,453*), on carboyclic monocarboxylic acid salts of glyoxalidines (Luvisi—*U. S. 2,659,731*) for formulation of toxicants used in agriculture, on reaction products of cation-active detergent and anion-active compounds of wax-like structure for making wax emulsions (Götte—*Ger. 859,468*), and for a mixture of soap, organic polyhydroxide compound, an alkyl naphthalene, and fatty acids for emulsification of paraffin wax (McGowan & Conley—*U. S. 2,684,338*).

Flocculation and coalescence of oil-in-water emulsions were studied to gain fundamental knowledge regarding the stability of Hevea latex by van den Tempel (*Mededeel. Rubber-Stichting. No. 225*, 5, 20, 34, 46, 55, 75). On the assumption that flocculation is governed by electrostatic repulsion as with hydrophobic sols of solid particles and coalescence is affected by the structure, he discussed electrostatic interaction, surface potentials, relation between rate of flocculation and electrostatic repulsion of oil droplets; suggested equations relating time of coagulations to rate of flocculation and rate of coalescence; and indicated effect of emulsifier, salt, etc., on coagulation. Methods of determining surface area and particle size of synthetic latexes containing soaps, by Maron *et al.* (*J. Colloid Sci.* 9, 89, 104, 263) were based on the polymer concentration, the film molecular area of the soaps and the amount of soap required to attain the critical micelle concentration as determined by surface tension at 50° or conduction at 50°. Fermor & Peizner (*Kolloid Zhur.* 16, 297) related the rate of polymerization of styrene in soap solutions to the concentration of ionic micelles of the emulsifier. They suggested that initiator molecules break down in the electric double layer surrounding the micelles, and the radicals formed start the polymerization chain. With slightly water soluble monomers such as vinyl acetate, in contrast to insoluble monomers the amount of detergent absorbed at saturation is independent of the concentration of the detergent and the size or surface area of the polymer particles (Okamura & Motoyama—*Mem. Fac. Eng. Kyoto Univ.* 15, 242). The use of alkali metal soaps of a mixture of petroleum naphthenic acids as the emulsifier at the rate of 2.5–3.5%, based on monomers, in diene elastomer polymerizations was patented (Sweely—*U. S. 2,667,471*).

The newly patented surface active agents used as demulsifiers in the production of petroleum were a mixture of oxypropylated amines, polycarboxylic acids, fat acids, and polyhydroxy compounds (DeGroote—*U. S. 2,679,510-29*; *U. S. reissue 23,851*; Smith—*U. S. 2,695,909*), diethers of polyoxyalkylene aliphatic diol (Kirkpatrick—*U. S. 2,662,859*), and oil soluble neutralized sulfonated mixture of polyalkylated benzenes obtained from "bottoms" used in the production of dodecylbenzene (Wisher—*U. S. 2,652,370*, *2,671,762*). An investigation on the ability of polyoxyethylated detergents for displacement of petroleum from sand surfaces indicated that for each type, the maximum displacement was a function of the oxyethyl content and that this property can be correlated with emulsifying capacity, solubility, and hydrophilic-lipophilic balance (Dunning *et al.*—*Ind. Eng. Chem.* 46, 591).

ACID, ALCOHOL, ALDEHYDE, NITROGENOUS, AND OTHER FAT DERIVATIVES. The general informative communications on these materials were on: preparation of alcohols, aldehydes, acid anhydrides, acid chlorides and various nitrogen and sulfur containing compounds from fats (Sethi—*Oils & Oilseeds J., India*, 5, No. 10/12, 65), production of fatty acids and their nitrogen derivatives (Schwitzer—*Rev. Francaise corps gras* 1, 5), properties of nitrogen derivatives of fats (Kalbag—*Bombay Technologist* 1, 18), isolation of fatty acids for use in laboratory studies (Hilditch—*Chemistry & Industry* 1954, 1382), manufacture of dicarboxylic acids by oxidation of natural fatty acids (Kirjakka & Nieminen—*Teknillisen Kem. Aikakauslehti* 11, 299), specifications for butyl acetylricinoleate (*Brit. Standard* 1992, 11 pp), preparation and properties of oleyl alcohol (Hembrough—*Chem. Products* 17, 378), production of fatty alcohols (Martens—*Seifen-Öle-Fette Wachse* 78, 601, 629), review of high pressure, sodium, and lithium aluminum hydride reduction, "oxo," "synol," and electrolytic oxidation process in the preparation of fatty alcohols (Kulkarni—*Bombay Technologist* 2, 37), alcohols by catalytic hydrogenation (Barroso & Ayerbe—*Grasas y aceites* 4, 133), and simultaneous preparation of fatty alcohols and sodium cyanate (Blazot & Servant—*Oleagineux* 3, 564).

Synthetic fatty acids were prepared for various purposes. Palmitoleic, gadoleic and 12,16-tetra-cosadienoic acids were synthesized to confirm the identity of an unsaturated acid iso-

lated from *Galeocedror tigrinus* oil (Gupta—*Proc. Natl. Inst. Sci. India* 19, 519). Linoleic acid labeled in the one position with isotopic carbon was made for biochemical studies (Howton *et al.*—*J. Am. Chem. Soc.* 76, 4970). Vaccenic acid was isolated from hydrogenated tung oil and found to be a trans acid (Hashimoto—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 56, 178). A fatty acid with terminal carboxylic groups,  $\alpha$ -kamloleic acid, was separated from the seed oil of *Mallotus philippinensis* and converted to the  $\beta$ -form by irradiation to serve as an intermediate for the preparation of various commercial products (Aggarwal & Chandra—*U. S. 2,685,593*). A laboratory method of preparation of elaidic acid was based on isomerizing oleic acid with selenium catalyst (Swern & Scanlan—*Biochem. Preps.* 3, 118). Elaidic acid was partially hydrogenated and partially polymerized with atomic hydrogen (van Steenis & Waterman—*Rec. trav. Chem.* 72, 563). A procedure for preparation of brassidic acid involved isolation of erucic acid from rape oil, its isomerization to brassidic acid, and purification (Skellon & Taylor—*J. Chem. Soc.* 1953, 1433). Several branched-chain fatty acids were synthesized and their properties recorded (Cason *et al.*—*J. Org. Chem.* 18, 842, 850, 857; *J. Biol. Chem.* 205, 449). Teramura *et al.* (*Bull. Inst. Chem. Res., Kyoto Univ.* 31, 223) prepared and described  $\alpha$ -formylstearate. In a study on the structure of lecithin of eggs, distearyl-L- $\alpha$ -lecithin was prepared by hydrogenation of the chromatographically purified lecithins of hen eggs (Hanahan—*J. Biol. Chem.* 211, 321). Glycerophosphatidic acids were prepared starting from diglycerides (Uhlenbroek & Verkade—*Rec. trav. chim.* 72, 395).

Equipment to chlorinate shark liver oil was patented (Aimi *et al.*—*Japan 841* [54]). A study of the chlorination process for fatty acids showed that solvents have no beneficial effect (Vidwans—*Bombay Technologist* 2, 82). In the same study it was demonstrated that dechlorination with heat and without an acid acceptor yields products of poor film-forming properties. Investigations on various catalysts for dechlorination of chlorinated methyl stearate at 300° indicated that 0.5% cobalt chloride or oxide was efficient without inducing polymerization of the product; iron and zinc chloride were very efficient but the dechlorination was accompanied by strong polymerization (Naudet & Desnuelle—*Bull. mens. inform. ITERG* 7, 490). The reaction of Zetzsche; *i.e.*, heating a fatty acid chloride with excess acetic anhydride, was used to make aliphatic acid anhydrides (Sonntag *et al.*—*J. Am. Oil Chemists' Soc.* 31, 151). Pentadecyl bromide was prepared by treating silver palmitate with a solution of bromine in carbon tetrachloride (Adachi & Hirao—*J. Oil Chemists' Soc., Japan* 1, 167).

Oleic acid of high purity was obtained by heating a preparation of unsaturated fatty acids with maleic acid and fractionally distilling (Komori *et al.*—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 55, 739). Palmitic acid of about 90% purity can be obtained by selective hydrogenation of cottonseed oil to convert polyunsaturated acids to oleic acid, heating this product with excess caustic alkali at 320° and separating the solid acids (Kirschenbauer—*U. S. 2,682,549*). Dilution of linseed oil to 10% concentration in mineral oil permitted polymerization of fatty acid groups without interglyceride reaction (Sims—*J. Am. Oil Chemists' Soc.* 31, 327). Efficient and compact equipment was designed for the manufacture of dimerized acids (Goebel—*U. S. 2,664,429*).

Methods for preparation of dibasic acids from fatty acids were described. Yields on fusing hydrogenated castor oil with sodium hydroxide were recorded by Kobayashi (*J. Oil Chemists' Soc., Japan*, 2, 183). The use of cadmium metal or compound as catalyst in such a process for manufacture of sebacic acid from castor oil was patented (Henkel & Cie G. m. b. H.—*Brit. 698,154*; Stein—*U. S. 2,696,500-1*). Permanganate oxidation of silkworm chrysalis oil yields more azelaic acid than the same oxidation of castor oil (Imai & Ohira—*Res. Repts. Fac. Textile & Sericult. Shinshu Univ.* 3, 112). Diacids higher than sebacic are obtained by oxidation of methyl stearate with nitric-sulfuric acid mixtures (Perron & Petit—*J. recherches centre natl. recherche sci. Labs. Bellevue, Paris*, No. 24, 122).

Fatty materials were also oxidized to produce hydroxy- and epoxy-compounds. The methods described for hydroxylation involved: addition of formic acid at the double bond followed by hydrolysis of the formate ester (Knight *et al.*—*J. Am. Oil Chemists' Soc.* 31, 1), autoclaving fatty acids in the presence of caustic alkali and manganese dioxide (Tsuchikawa—*Japan 2737* [53]), and subjecting 60–75% sulfuric acid solution to anode oxidation in an electrolyte cell, followed by reacting this with the fatty material (Logan—*U. S. 2,688,031*). Details and equipment for epoxidation of fatty material have been de-

scribed in a communication (Schmitz & Wallace—*J. Am. Oil Chemists' Soc.* 31, 363) and in a patent (Greenspan & Gall—*U. S.* 2,692,271). A report of investigations on such a method in which the peracetic acid reagent is made *in situ* contains data on the influence of sulfuric acid, acetic acid, and moisture in varying amounts on the reaction (Naudet & Carrera—*Rev. Francaise corps gras.* 1, 478). Oxidation of linoleic acid with one mole of peracetic acid yields monoepoxystearic acid and with two moles of peracetic acid the diepoxy compound forms (Swern & Dickel—*J. Am. Chem. Soc.* 76, 1957). In the same investigations, performic acid formed the expected hydroxyformoxystearic acid due to opening of the oxirane rings of diepoxystearic with formic acid. Hydrolysis of this hydroxyformoxy compound and diepoxystearic acid, or the hydroxyacetoxystearic compounds formed by opening the oxirane rings with acetic acid, resulted in poor yields of tetrahydroxystearic acids. McKay *et al.* (*Ibid.* 2383) in similar work demonstrated that such oxidations of  $\alpha$ -linoleic acid gives rise to two new compounds besides the 9,10-dihydroxystearic acid and the sativic acid which were already identified. The two new compounds were only partially characterized. A study of the oxidation of methyl linoleate and methyl linolealaidate with di-*t*-butyl peroxide indicated that the products were largely mixed isomers of the dehydro dimers of the fatty esters (Harrison & Wheeler—*Ibid.* 2379).

Various methods of manufacture of fatty alcohols were studied. An investigation on cost, by Hill *et al.* (*Ind. Eng. Chem.* 46, 1917) indicated that the advantages of the sodium reduction method are: production of both saturated and unsaturated acids, lower initial investment, simpler maintenance, and superior products; and advantages of hydrogenolysis are: cheaper raw materials, wide choice of suitable feed stock, and wide choice of location. A comparison of these two methods on the basis of yields from several oils favored sodium reduction (Kane & Kulkarni—*Oils & Oilseeds J., India*, 5, No. 10/12, 52). In this work the effect of catalyst, hydrogen pressure, and temperature in relation to yields of alcohol and production of hydrocarbons by the hydrogenolysis method was recorded. The new catalyst demonstrated for the hydrogenolysis process of alcohol production comprised mixtures of copper and chromium oxides (Haefeli—*Chemica, Switz.* 7, 255; Takao *et al.*—*Japan 4221* [53]) and zinc containing some aluminum (Kobashi *et al.*—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 54, 581). Fatty alcohols in 85% yield were obtained by hydrogenating the lead soaps of sperm oil (Komori *et al.*—*Ibid.* 55, 680). With the electrolytic oxidation of soaps process, use of acetone as the solvent; presence of chlorates, bicarbonates and fluorides; and low current densities were associated with good yields of alcoholic products (Kalbag—*Bombay Technologist* 3, 81). Yields of fatty alcohols, glycerol, and cyanate have been recorded on reducing seven fats with sodium and methyl isobutyl carbinol in xylene (Barrett *et al.*—*Ind. Eng. Chem.* 45, 1114). Some fatty alcohols and fatty acids were synthesized for analytically confirming identity of some components of wool-wax (Milburn & Truter—*J. Chem. Soc.* 1954, 3344).

Kaufmann *et al.* (*Fette u. Seifen* 55, 847) prepared stearyl, oleyl, and elaidyl aldehydes by the Rosenmund method and characterized them. He demonstrated that these readily polymerize to trimers through a mechanism involving development of a ring structure of  $-C-O-$  linkages. These trioxane derivatives have been characterized spectroscopically. Subsequently Kaufmann & Kirschnek (*Ibid.* 851) reviewed methods of preparation of aldehydes from the standpoint of reducing loss by polymerization of the product and designed a preparation procedure based on reduction of fatty amides with lithium aluminum hydride. Lauryl alcohol was converted to dodecanal in 34% yield by heating 30 minutes at 250° with copper chromite (Halasz—*Can. J. Chem.* 31, 297). Distillation of castor oil in vacuum yields about 33% undecylenic acid and 17% heptaldehyde; the latter is useful for the preparation of vulcanization accelerators (Qureshi—*Paintindia* 2, No. 6, 13; No. 7, 29). With the same method Gupta & Aggarwal (*Ibid.* 4, No. 1, 133) obtained a 21% yield of heptaldehyde.

Heating ricinoleic acid at 225-350° with lime converts it to a mixture of 2-octanone, 2-octanol,  $\omega$ -hydroxydecanoic acid and sebacic acid (Haury—*U. S.* 2,693,480). Fatty ketones suitable as solvents for wax were made by contacting fatty acids with alumina catalyst at 300-400° (Ohlson & Hoerr—*U. S.* 2,697,729). Polyketones, suitable substitutes for waxes, were formed from fatty acids and  $\alpha,\omega$ -polymethylene dicarbocyclic acids on heating to 500-715°F. with powdered iron (Watson & Mixon—*U. S.* 2,686,204). Heating cottonseed oil to 340° produced some

palmitone (Chalmers—*Acta Univ. Intern. contra Cancrum* 7, 595).

Data on destructive distillation and cracking of nim oil for the production of solvents for agricultural toxicants and thinners for paint were published in a patent (Council Sci. & Ind. Res.—*Indian* 48,529). Best yields, 80%, were obtained on cracking in the presence of one per cent zinc chloride. Vapors of vegetable or mineral oil with carbon tetrachloride and hydrogen were passed through a high-frequency electromagnetic field for the production of lower boiling hydrocarbons and/or rubberlike residues (Wilkinson—*Brit.* 697,223).

Nitrogenous derivatives of fats were investigated for various purposes. Stumpf (*Am. Paint J.* 38, No. 45, 60) prepared the ammonium salts of 12 different fatty acids and recorded their physical properties and solubilities in many solvents. These may be used for waterproofing stone, paper or textiles, in lubricants, or as detergents in dry cleaning. Racemic  $\alpha$ -amino derivatives of  $C_7$  to  $C_{11}$  fatty acids were prepared in a study of the action of the enzyme acylase (Birnbaum *et al.*—*J. Biol. Chem.* 203, 333). Erythro- and threo-2-amino-3-hydroxystearic acids were synthesized to study the stereochemistry of dehydrosphingosine (Carter *et al.*—*J. Am. Chem. Soc.* 75, 4705). *n*-Octadecylamine hydrochloride was prepared from stearyl alcohol *via* stearyl iodide by the Gabriel synthesis and its properties recorded (Wood—*J. Chem. Soc.* 1953, 3327). In a demonstration on the preparation of fatty monoamides of ethylene diamine by aminolysis of triglycerides, data are given on the course of the reaction and the products formed (Baldy *et al.*—*Rev. Francaise corps gras* 1, 552). Here, a method of making *n*-lauryl-*n'*-dimethylbenzethylethylene diamine is given in detail. The Wagner potentiometric salicylaldehyde method for quantitatively determining amines was modified for application to fatty amines by using chloroform instead of alcohol as the solvent (Jackson *et al.*—*Anal. Chem.* 25, 1764). A process for converting fatty nitriles to amines by hydrogenation was patented (Renfrew & Warner—*U. S.* 2,690,456). Another method involved reduction of the nitrile with sodium in a mixed butanol-xylene solvent (Sakakibara—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 54, 594).

METAL SOAPS, WATER PROOFERS, WELL DRILLING FLUIDS, FLOTATION AGENTS, FLUSHING COMPOUNDS, DEFOAMERS, GERMICIDES, AND RUST INHIBITING COATINGS. In a general communication on metallic soaps, Licata (*J. Am. Oil Chemists' Soc.* 31, 204) described commercial practices in the manufacture of various metal oleates, linoleates, resinates, stearates, hydroxystearates, etc., and pointed out that the various acids play an important function in determining the method of preparation, the physical properties, and ultimately the use. Two stearates of 23 polyvalent metals were carefully prepared and their melting values recorded (Stumpf—*Am. Paint J.* 38, No. 15, 60). Aluminum soap-mineral spirits gel peptized with butanol had a markedly low gel time with high gel consistency (Rodriguez—*Ibid.* No. 31, 86). Aluminum stearate for paint and enamel uses was made by melting stearic acid with aluminum distearate to avoid a grainy texture (Ashley—*U. S.* 2,681,291). Analytical methods for analysis of metal soaps and for control of composition in manufacturing were published (Nebbia—*Pittura e vernici* 7, No. 11, 41; No. 12, 43).

A review on waterproofing of fabrics contains information on the use of metallic and other derivatives of fats for this purpose (Tara—*Industrie textile* No. 809, 280). Stearato chromic chloride is soluble in water but when absorbed on many polar surfaces is hydrophobic. This property renders it suitable for waterproofing fiber and siliceous, and proteinaceous materials (Der—*Ind. Eng. Chem.* 46, 766). The water-repellency of stearyl isocyanate is said to be due to its decomposition on fabrics to insoluble distearylurea (Hamalainen *et al.*—*Am. Dyestuff Repr.* 43, 453). Water repellency produced by this process was inferior to that produced by stearamidomethylpyridinium chloride. Other waterproofing agents described for use on fabrics or paper were: a mixture of water-insoluble metal soaps and alkylolamide (Cunder & Licata—*U. S.* 2,660,567), condensate products of a fatty acid amide and formaldehyde (Yoshizaki—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 54, 777), mixtures of water-insoluble metal soaps of tall oil and waxes (Jihoceske papirny, narodni podnik—*Austrian* 176,548), and water-insoluble soaps prepared *in situ* during dry cleaning of fabrics (Shields & Piepmeyer—*U. S.* 2,695,250).

A slippery type of oxidation product of fish oils was prepared for use in leather tanning (Sagoschen & Czepelak—*Österr. Leder-Ztg.* 8, 270). Half esters and half soaps of succinic acid containing fatty chains were introduced into leather to

improve water resistance (von Fuchs—*U. S.* 2,693,996). A waterproofing composition for cement comprised a compatible mixture of an alkyd resin and an organo-polysiloxane resin (Kennedy & Weigand—*U. S.* 2,679,491).

Patents were issued on various oil well drilling fluids or muds which contained fat derived soaps or emulsifying agents as important components (Dawson—*U. S.* 2,675,352-3; Fischer & Rogers—*U. S.* 2,679,478, 2,687,375; Menaul—*U. S.* 2,689,219; Fischer—*U. S.* 2,696,486; Salathiel—*U. S.* 2,697,692).

Use of fatty materials or their derivatives for many other purposes was described. Application of fatty chemicals to flotation was reviewed (Baarson & Parks—*J. Am. Oil Chemists' Soc.* 31, 261). A cleanser for paint brushes contained organic solvents and polyoxyalkylene polyhydric alcohol fatty esters (Eisen—*U. S.* 2,697,674). Solutions for flushing gum, sludge, etc., from engines contained isopropanol, water, and soap (Brandes & Pattinson—*U. S.* 2,678,920), and an aromatic solvent plus a propane insoluble fraction of crude fatty oils (Kalinowski & Feller—*U. S.* 2,671,761). The latter named material (Walker & Farbak—*U. S.* 2,668,138) and condensation products of ethylene oxide and abietic acid were patented for depressing foaming in fermenting media. A mixture of fatty acids, wax, polyoxyethylene glycol dilaurate, and polyoxypropylenediol was patented as a general defoamer (Luvisi—*U. S.* 2,668,150). A "Lumetron" colorimeter has been applied for evaluation of the effectiveness of defoamers, determination of their optimum concentration, and investigation of synergistic antifoaming mixtures (Ross *et al.*—*J. Phys. Chem.* 58, 247). Caprylimidazolone, *N*-2-pyridyl derivatives of fatty acid amides, and *N*-6-quinolyl derivatives of fatty acid amides were prepared and their germicidal capacity evaluated (Takase—*J. Chem. Soc. Pure Chem. Sect.* 74, 59, 60, 62). A new fat derived quaternary ammonium germicide was patented (Harris—*U. S.* 2,673,316). Fatty compounds containing a thiirane group were made for use as fungicides and antiseptics (Dearborn—*U. S.* 2,695,286). Gels of esters of  $\alpha$ -hydroxy acids and their fatty acid estolides were useful as linoleum-cementing compounds (Cunningham & Polly—*U. S.* 2,652,410).

Several patented rust proofing compositions contained fatty materials. A thixotropic composition that spread easily and did not drip from the surfaces contained fatty and mineral oils and a sulfonate emulsifier (Veatch & Persing—*U. S.* 2,673,838). A composition containing dibutyl sebacate, and palm oil was made for application to strips of metal by atomizing and electrostatically causing the particles to fall and adhere to the strip (Kadell—*U. S.* 2,666,716). Ebony fat plus triethanolamine "bottoms" were useful for inhibiting corrosion by carbon dioxide, hydrogen sulfide, and brine in well casings (Lytle—*U. S.* 2,675,355). Rusting in fuel lines was inhibited by adding small amounts of sulfated tall oil to gasoline, kerosene, fuel oil, and other liquid fuels (White *et al.*—*U. S.* 2,686,713). Other rust preventive compositions contained fatty soaps or emulsifiers together with mineral oil and other material (Bishop—*U. S.* 2,665,995; Wasson & Bonham—*U. S.* 2,672,444; Dieman & Lindert—*U. S.* 2,677,618; Eby—*U. S.* 2,680,718).

COATINGS, RESINS, AND PLASTICS. General informative communications regarding coating oils and resins derived from fatty oils were: theories on drying of oils (Weiss—*Seifen-Öle-Fette-Wachse* 79, 581, 670), improving drying oils (von Mikusch—*Ibid.* 533, 565, 589, 641), processed oils for paints (Henderson—*Can. Chem. Processing* 38, No. 5, 26), heat polymerization of oils (Brushwell—*Am. Paint J.* 38, No. 12, 74; No. 13, 68; Walter—*Paint & Varnish Prod.* 44, No. 7, 21), alkali-induced isomerism of linseed oil (Slansky—*Paint Manuf.* 24, 121), various drying oils in the paint and varnish industry (Mistri—*Oils & Oilseeds J. India* 5, No. 10/12, 118), carilla-seed oil gel (Airan—*Ibid.* 4, No. 9/10, 43), cyclization and stereochemistry of methyl eleostearate (Chen—*Chem. Ind. & Eng., China* 2, No. 3, 93, 98), use of safflower seed oil in paint (Prane—*Paint, Oil & Chem. Rev.* 117, No. 4, 18; *Paint Ind. Mag.* 69, No. 3, 15; *Am. Paint J.* 38, No. 26, 76), uses for castor oil (Rao & Rao—*Paint India* 3, No. 7, 32; No. 8, 33), manufacture and properties of dehydrated castor oil (Thaker—*Oils & Oilseeds J., India* 4, No. 7, 13; Sivasamban *et al.*—*Ibid.* No. 9/10, 35; Dole—*Ibid.* 34; Dole & Keskar—*Proc. Indian Acad. Sci.* 38A, 135; *J. & Proc. Oil Tech. Assoc. Kanpur, India* 7, 49; Slansky—*Paint Manuf.* 24, 45), improving drying properties of oils with pentaerythritol (Moreno *et al.*—*Grasas y aceites, Spain* 5, 11; Gourley—*Paint Manuf.* 24, 147), composition, compatibility, and formulations with epoxy-modified rosin esters (Austin & Drew—*Paint, Oil & Chem. Rev.* 117,

No. 11, 15), vegetable oils in alkyd resins (Prakash—*Oils & Oilseeds J., India* 4, No. 9/10, 38), trends in fatty acids used in alkyd resins (Earhart—*Paint & Varnish Prod.* 44, No. 4, 27; *Am. Paint J.* 38, 74), styrenation of alkyds (Hempel—*Paint Ind. Mag.* 69, No. 5, 21; *Am. Paint J.* 38, No. 32, 72), metallic soaps in the paint industry (Morley-Smith—*Paint Manuf.* 24, 224; Wendt—*Off. Dig. Fed. Paint & Varnish Production Clubs No. 344*, 604), isotopic and chromatographic techniques in protective-coating technology (Heiberger—*Paint & Varnish Prod.* 44, No. 2, 21), analytical methods for varnish resins (Poluzzi—*Ind. vernice, Milan*, 8, 61), cohesive properties of baked, pigmented soybean-oil films (Carrick & Trease—*Paint, Oil & Chem. Rev.* 117, No. 8, 12), and microstructure of paint films (Bobalek *et al.*—*Ind. Eng. Chem.* 46, 572).

Hanson (*J. Oil & Colour Chemists' Assoc.* 37, 143) devised a system of graphs relating specific refraction to molecular weight of hydrocarbons of varying number of rings and used them for analysis of rings in polymerized and dried oils. Ayengar (*Oils & Oilseeds J., India*, 4, No. 9/10, 44) demonstrated the use of dielectric constants to differentiate oxidation from polymerization in oils, and to measure the degree of dehydration of castor oil. A procedure for analysis of alkyd resins modified with vinyl chloride-acetate copolymer was based on saponification, fractionation with solvents, and determination of vinyl chloride by means of a chlorine determination (Swann & Esposito—*Anal. Chem.* 26, 1054).

Various old and new means were used to study the reactions that occur during oxidation and polymerization of oils. Displacement chromatography along with other techniques was used to study the oxidation of methyl linoleate (Khan *et al.*—*J. Am. Chem. Soc.* 76, 1179) and methyl linolenate (Khan—*J. Chem. Phys.* 21, 952). The linoleate on autooxidation in the dark, with copper catalyst, or with ultraviolet light yielded two major dienoic hydroxy-products exhibiting cis,trans- and trans,trans-conjugation; whereas with chlorophyll photooxidation four products were found, one of which exhibited no conjugation. Similar patterns were observed with methyl linolenate. Similar work by Privett *et al.* (*J. Am. Oil Chemists' Soc.* 31, 23) has shown that oxidation of methyl linolenate at 0° to a peroxide value of 600-700 milliequivalents of oxygen per kilo yields 60% cis-trans-conjugated diene methyl octadecatrienoate-mono-hydroperoxide. Privett (*Ann. Rept. Hormel Ind.* 1953-4, 37) also described preparation of all cis-linoleate by urea complex fractionation for studies as reviewed above. Cattravas (*Oleagineux* 8, 677) subjected methyl esters of linseed oil to catalytic isomerization and analyzed the product by urea complex fractionation and chemical and spectroscopic means. His data show that the dienes as well as the trienes formed are different spectrally and in their behavior with urea precipitation. He suggested that separation of the different types of each could be made by urea precipitations.

O'Neill (*Chemistry & Industry* 1954, 384) examined the products of autooxidation of methyl  $\alpha$ -eleostearate. In the non-conjugated acid, hydroperoxide was said to be formed with development of conjugation, then dimerization, decomposition of hydro-peroxides with further dimerization, and scission together with bonding by secondary valence forces, follow. His mechanism for conjugated acids involves direct attack of oxygen at the double bond system in the 1:4 or 1:2 position with competitive production of monomeric, dimeric, and higher polymers, mainly carbon-carbon linked peroxides. Oxidations on methyl oleate and linoleate by Willits *et al.* (*J. Am. Oil Chemists' Soc.* 31, 420) and by Ricciuti *et al.* (*Ibid.* 456), respectively, have demonstrated that initially absorbed oxygen forms hydroperoxides whereas in later stages the oxygen is consumed to form non-hydroperoxide material. Similar work on oleic acid and methyl oleate with oxidation at 65° in the presence of a copper catalyst gave yields of 12-17% of 9,10-hydroxystearic acid and 64-8% of cleavage products (Knight *et al.*—*J. Am. Oil Chemists' Soc.* 31, 93).

Oxidized linseed oil was separated into polymeric and monomeric glycerides and each was analyzed (Paschke & Wheeler—*Ibid.* 208). Intradimerization occurred slightly (1.3-6%) in the monomeric glycerides, but was appreciable (10-20%) in the polymeric glyceride fraction. In a kinetic study on the oxidation of oils, Georgiadis & Gaillard (*Chim. & industrie* 70, 383) developed equations to represent the rate of formation of intermediate products and the uptake of oxygen.

Several investigations pertained to the structure of dimers formed in drying oils. According to Boelhouwer *et al.* (*Res. Correspondence Suppl. to Res., London* 6, 55S) thermal polymerization of methyl linoleate and methyl linolenate leads

chiefly to dimers containing approximately 1.3 and 2 rings per molecule, respectively. Analyses of dimerized compositions from oxidized drying oils have indicated that such scission, decarboxylation, and possibly other reactions occur for monoacids of  $C_{19}$  to  $C_{20}$  and diacids of less than  $C_{38}$  are among the normal dimers (Petit & Cazes—*Peintures pigments, vernis* 29, 636). Clingman *et al.* (*J. Chem. Soc.* 1954, 1088) explained the mechanism of dimerization of  $\beta$ -elaeostearate on the basis of a Diels-Alder type union. Dimerization and polymerization in rapeseed oil was accelerated by addition of cumene hydroperoxide (Zuckerman *et al.*—*Can. J. Technol.* 32, 10).

Trilinolein and trilinolenin films were analyzed at two different stages of drying for a number of functional groups (Chipault—*Ann. Rept. Hormel Inst.* 1953-4, 15). The data shows that films became tacky when about one-half of the unsaturation had disappeared and a good share of the remaining double bonds have been changed to conjugated trans configuration. Earlier work in this series contained similar data on glycerol and pentaerythritol alkyd oils (*Ibid.* 1951-2, 15). Films of elupanodonic acid do not develop hydroperoxides but rather intramolecular peroxides of the dialkylperoxide type (Becke—*Fette u. Seifen* 56, 503). Drier action in film formation was explained by Mueller (*Ind. Eng. Chem.* 46, 562) on the basis of a mechanism that they produce free radicals and continue to do so during the entire course of the autoxidation.

Heat bodying an oil under vacuum in laboratory apparatus yields a product with physical properties similar to products obtained in commercial heat bodying but having different chemical compositions (Petit—*Bull. soc. chim. France* 1954, 679). It is suggested that the difference may be due to formation of supplementary double bonds in the laboratory test. Heat polymerized oils have greater wetting power and dried faster than blown bodied oils (Tyutyunnikov & Goldberg—*Masloboino-Zhirovaya Prom.* 18, No. 7, 22). New patent literature contains descriptions of improved bodying treatments obtained in the presence of *p*-benzoquinone derivatives (Young & Davy—*U. S.* 2,673,209), hydrogen fluoride (Croston *et al.*—*U. S.* 2,670,361), and activated bauxite (Council Sci. & Ind. Res.—*Indian* 45,840). Serra (*Span.* 204,444, 204,623) patented a process in which the bodying of an oil is accelerated with photochemical and thermochemical radiations, and a process of improving polymerized oils by distilling off some of the unpolymerized constituents. Ponomarev (*Masloboino-Zhirovaya Prom.* 18, No. 7, 24) called attention to the usefulness of volatile wastes from manufacture of bodied oils. These can be fractionally distilled to aldehydes, alcohols, fatty acids, and possibly other useful materials.

Various methods for improving the drying capacity of oils were investigated. A comprehensive study on improving grape seed and soybean oils by isomerization showed that nickel catalyst supported on a very dense carbon carrier was the best of five nickel catalysts investigated, and good results were also obtained with iodine as the catalyst (Rigamonti & Grossa—*Olearia* 7, 183). The newly patented catalysts for isomerization of oils were: nickel-cobalt catalyst containing silicates of these metals and some sulfur (Albert—*U. S.* 2,692,886; Lever Bros. & Unilever Ltd.—*Brit.* 693,981), nickel catalyst containing minor proportions of selenium or tellurium (Unilever Ltd.—*Brit.* 703,826), and activated bauxite (Council Sci. & Ind. Res.—*Indian* 45,841). Converting castor oil into a drying oil by dehydration with sodium sulfate catalyst resulted in products with a remarkably high per cent of conjugation (Narayanan & Jatkar—*Paintindia* 4, No. 1, 131). A low degree of conjugation results from dehydration under nitrogen without catalyst (Kissel—*Off. Dig. Federation Paint & Varnish Prod. Clubs* 26, 59). "After-tack" from dehydrated castor drying oil was inhibited by solvent removal of the nonricinoleate components before the dehydration (Choudhury *et al.*—*J. Indian Chem. Soc. Ind. News Ed.* 16, 24), and by dehydration with sodium bisulfate catalyst followed by the addition of two parts of slaked lime (Sivasamban *et al.*—*Paintindia* 4, No. 1, 132). Copper sulfate plus carbon catalysts were used to obtain light colored dehydrated oil (Ando—*Japan* 2232 [53]). A continuous system of dehydration of castor oil involved passing the oil with 0.8% concentrated sulfuric acid through a zone heated at 285° (Carter *et al.*—*Brit.* 703,363). A varnish was made from tall oil by blending with dehydrated castor oil and heating with pentaerythritol, maleic anhydride and phenolic resin (Patton & Lindlaw—*Paint Varnish Prod.* 44, No. 1, 21). A laboratory method for the evaluation of catalysts used in the dehydration of castor oil is based on the measurement of rate of thermal polymerization of test samples of dehydrated oils (Dole—*J. Proc. Oil Technol. Assoc. India Kanpur*, 8, 23).

Saturated fatty acids were condensed by heat in the presence of aluminum alcoholate catalysts to yield products suitable as coating films (Weiss—*Paint Manuf.* 24, 5, 98). Polycondensation of oleic acid by heating at 120–160° on clean plates was said to yield films similar to those formed by the drying of linseed oil (Taratenko—*Zhur. Priklad. Khim.* 27, 794). Cottonseed oil was made suitable for drying usages by oxidation in the presence of pentaerythritol, lead-manganese resinate, rosin, and sodium bisulfate (Ivanova—*Masloboino-Zhirovaya Prom.* 19, No. 5, 22). Tall oil was esterified with glycerol and blended with alkyd resins and tung oil to yield suitable varnishes (Patrick *et al.*—*Tappi* 36, 561). Rice-bran oil was conditioned for drying purposes by combined saponification and isomerization and reconstituting to sorbit esters (Nakanishi & Shioimi—*J. Chem. Soc. Japan Ind. Chem. Sect.* 56, 940), and by polymerization followed by washing successively with dilute sulfuric acid containing potassium dichromate and with 95% methanol (Koyama—*Japan* 1680 [53]). A drying product is derived from cuttle fish oil by reconstituting its more highly unsaturated fatty acids as mannitol esters (Mori *et al.*—*Japan* 993 [53]). The unsaturated fraction is isolated by fractionation of the methyl esters of the oil by the urea-complex method. Another method comprises partial saponification to remove saturated and low molecular weight unsaturated glycerides (Shibayama & Tomioka—*Japan* 1287 [53]).

New polyhydroxy compounds for the coating industry are described and demonstrated. Pintol and quebrachitol esters of linseed fatty acids have greater viscosities than comparable pentaerythritol esters; they dried at about the same rate as monopentaerythritol esters; and their film toughness was like that of tripentaerythritol esters (Rheineck & Brice—*J. Am. Oil Chemists' Soc.* 31, 306). The fatty acid esters of 1,1,1-tris (hydroxymethyl)-ethane exhibited properties intermediate between those of glycerol and pentaerythritol in alkyd formation (Balgley—*Am. Paint J.* 38, No. 24, 65).

Products ranging from improved drying oils to resinous solids suitable for protective coating compounding are made by copolymerizing fatty material with: cyclopentadiene (Jakob—*U. S.* 2,667,463), vinyl aromatic hydrocarbons (Brunner—*Brit.* 698,621), styrene (Sample—*U. S.* 2,650,907; Gleason—*U. S.* 2,652,342; Carlick—*U. S.* 2,665,283; Armitage—*Brit.* 701,441; Union chim. belge, soc. anon.—*Belg.* 524,673; Adriaan Honigs Kunstshars Ind. N.V.—*Dutch* 72,595), and straight chain aliphatic diolefin (Marhofer & Hillyer—*U. S.* 2,653,956). A packed column reaction chamber was used to experimentally styrenate drying oils continuously (Boelhouwer *et al.*—*Chemistry & Industry* 1954, 240). Reactions of styrene with sorbic acid and drying oils in copolymerizations have been explained on the basis of formation of cyclic products by a Diels-Alder reaction mechanism (Kut—*Paint Varnish Prod.* 43, No. 11, 28). In reaction of styrene with erythyl dilinoleate polymers containing 2.8–28 mole per cent of the latter were formed and 90% of the linkage with styrene involved erythryl rather than linoleic unsaturation (Weisgerber & Dyer—*J. Am. Chem. Soc.* 76, 1784). Tests on the ability of styrene to polymerize with various oils showed that with linseed oil, preoxidation of the oil with air was necessary; there was no polymerization with sunflower oil; and the reaction was quite successful with tung oil when benzoyl peroxide was present (Drinberg *et al.*—*Zhur. Priklad. Khim.* 27, 618). Graphs have been developed which permit calculations of the degree of styrenation of linseed oils from density and refractive index-measurements (Boelhouwer *et al.*—*Anal. chim. acta* 11, 74).

Styrene esters of bisphenol-epichlorohydrin condensates were esterified with linseed oil fatty acids and the mixed fatty acids of soybean and castor oils (Tess *et al.*—*Ind. Eng. Chem.* 46, 385). In many respects the coating characteristics of the products were superior to comparable styrenated alkyds. Methyl stearate converted into 2-methyl-2-nonadecene by reaction with methyl magnesium iodide followed by hydrolysis and dehydration. This product was copolymerized with drying oils (Boelhouwer *et al.*—*Rec. trav. chim.* 73, 143). Similar reactions were carried out starting with methyl oleate, methyl linoleate, and methyl linolenate, and their polymerization products were evaluated on the basis of increase in weight of unsaponifiable matter.

Wrinkle-textured films were produced from coating compositions containing vinyl and other resins by differential heating of the film (Toulmin—*U. S.* 2,670,337), by presence of vinyl resins containing hydroxy groups in the coating composition (Waldie—*U. S.* 2,671,062), by special vinyl resin-alkyd-drying oil compositions (Waldie—*U. S.* 2,671,062), and with the use of oils bodied by passing an electric current through a mixture

of oil, organic diluent, and conductive metal salts (Pawlyk—*U. S. 2,676,918*).

New information on alkyd resins pertains to: properties of alkyds made from linseed oil mono-, di-, and triglycerides (Reiser & Wekua—*Ind. Vernice, Milan* 7, 209), silicone containing alkyd resins (Libbey-Owens-Ford Glass Co.—*Brit. 694,716*; Millar—*U. S. 2,663,694*), acrylate modified alkyd resins useful as softeners for lacquers (Seifert—*Farbe u. Lack* 60, 187), fireproofing alkyd resins compositions with chlorinated aromatic radicals (Baker—*U. S. 2,680,105*), incorporating inorganic phosphorous oxy-acids to reduce their color (Dazzi—*U. S. 2,661,359*), addition of calcium salts of fatty acids to produce haze (Gourley & Purvis—*Brit. 697,318*), and a mineral oil modified alkyd resin useful as a linoleum cement (Elliott—*U. S. 2,670,782*).

Epoxide resins were blended or copolymerized with fatty oils or acids for making coating or molding materials (Rinse—*U. S. 2,652,376*; Greenlee—*U. S. 2,668,805, 2,668,807*; Newey—*U. S. 2,682,514*; McLean—*U. S. 2,687,396*; D'Alerio—*U. S. 2,695,894*; Crecelius—*U. S. 2,698,308*; Jaffe—*Belg. 520,976, 522,407*). General information on esterification of epoxy-resins with fatty acids and properties and merits of the resulting products were discussed by Narracott & Nielsen (*Fette u. Seifen* 56, 92). Heat and light stability were induced in chlorine containing vinyl polymers by incorporating the polyvalent metal salt of epoxy fatty acids (Greenspan & Gall—*U. S. 2,684,353*).

Other communications on fatty material containing resins were on: resinous esters of unsaturated alcohols and certain alkylidene bis-phenoxy fatty acids (Rust & Canfield—*U. S. 2,672,478*); condensation products of hydroxylated soybean oil and diisocyanate (Senda *et al.*—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 55, 609), resins containing ethylenediamine polymers of vegetable oils (Winkler—*U. S. 2,663,649*); a blend of polyamides derived from polymeric fatty acids and a phenol-formaldehyde resin (Witteoff & Renfrew—*U. S. 2,695,908*); and a linoleum composition containing a filter and the polymerized product of cashew oil, vegetable drying oil, resin, and formalin (Schimizuya—*Japan* 91 [53]).

Fatty materials were investigated for use as plasticizers in resinous materials. The diethylene glycol monobutyl ether esters of epoxidized soybean fatty acids were found to be equal to or better than dioctyl phthalate as plasticizers for vinyl chloride polymer (Greenspan & Gall—*Ind. Eng. Chem.* 45, 2722). In this work, these and many other fatty acid esters were investigated to determine their compatibility and usefulness as plasticizers for many polymers. Similar work was done by Saito & Imoto (*Chem. High Polymers, Japan*, 10, 19) and their results are tabulated. The newly patented plasticizers for vinyl chloride resins are tall oil esters of monohydric phenols (Pollack—*U. S. 2,695,897*), condensation products of certain fumarates with oleic acid or its esters (Butler—*U. S. 2,637,421*), and polyoxy alkene and sorbitan esters of fatty acids (Klein & Curgan—*U. S. 2,657,186*). In an investigation of a large number of plasticizers for nitrocellulose lacquers many fatty derivatives were tested (Kraus—*Farbe u. Lack* 60, 185; *Fette u. Seifen* 56, 377). Among the fatty products castor oil gave good stability against after-yellowing and butyl stearate was observed to be stable only at low temperatures.

**FATTY MATERIALS IN LUBRICATION, TEXTILE OILING, AND METAL WORKING.** Information suitable to plant engineers on lubricant equipment, types of lubricants available, lubricant grease, additives, and use schedule was published by Clark *et al.* (*Chem. Eng.* 61, No. 7, 211). Pethrick & Wood (*Gov. Res. Repts., Gt. Brit., Lubricants & Lubrication* 2, No. 5, 33) recommended that selection of greases for lubrication of magnetos and generators should be based on a torque test at  $-10^{\circ}$  with a limit of 20,000 on the plasticity number. A specification for wide temperature range lime and soda soap grease stipulated that the ratio of sodium oxide to calcium oxide should not exceed 5.0 (Kinner *et al.*—*Ibid.* No. 16, 184).

Some fundamental studies on properties of metal soaps and their gels were pertinent to their use in lubrication. An infrared spectra study of several aluminum, gallium and indium soap gels in hydrocarbons indicated that gelation is independent of bonded hydroxyl groups (Scott *et al.*—*J. Phys. Chem.* 58, 61). A modification of absorption at  $10.14 \mu$  is associated with changes in viscosity of the gels. Electron microscopic and x-ray studies have indicated that lithium 12-hydroxystearate greases have oriented fibers joined or superposed at distances of 0.5-1  $\mu$ ; calcium tallow soap greases have some coherent structure in which very fine fibers exist along with broader fibril bundles; soda grease soap forms elongated rib-

bons; and barium soap greases stabilized with barium salts contain matted broad bands of fiber bundles (Vold *et al.*—*Inst. Spokesman* 18, No. 5, 8). A study on the structure of aluminum stearate greases indicated that it is essentially a metastable jelly at temperatures below the transformation temperature, but transforms slowly to a paste on aging; the rate of transformation being accelerated by shear (Evans & Matthews—*J. Colloid Sci.* 9, 60). Another study of this gel produced data on the effect of temperature and concentration of soap on viscosity, orientation, polarization, thixotropy, osmotic pressure, and surface pressure (Inoue & Iida—*Bull. Aichi Gakuzei Univ.* No. 1, 72). These show that maximum viscosity of 1-1.5% concentrations of the soap in benzene occurs at  $30^{\circ}$ ; and thixotropy occurs at concentrations 1.5-4.0% in fresh samples and at 2-5% a month after its preparation. A study of water vapor sorption by aluminum soaps has indicated that the process involves monolayer and multilayer absorption with capillary condensation, and that part of the sorbed water swells the aluminum soap crystallites, attaching to the soap polymer chains by hydrogen bonding (Gross & Bauer—*J. Phys. Chem.* 58, 877).

The formation of cuprous stearate in the presence of oxygen but not with a hydrogen atmosphere when stearic acid is absorbed from benzene solution on a copper foil was interpreted to indicate that fatty acids act as boundary lubricants for copper and its alloys only in the presence of oxygen (Dobry—*Lubrication Eng.* 10, 210). Monolayers of pure compounds whose structures are related to those of lubrication additives were studied by pressure-area isotherm investigations (Ries & Cook—*J. Colloid Sci.* 9, 535). Stearic acid and octadecylphosphonic acid form strong films; together the films show the properties of the latter at low pressure, but at high pressure it is expelled from the films which then show the properties of stearic acid films.

Several patents on lubricating grease manufacture pertained to compounding, working, and temperature treatments to induce suitable texture and stability (Sproule & Gray—*U. S. 2,657,180*; Moore & Wilson—*U. S. 2,652,365*; Entwistle—*U. S. 2,695,878*). Another patent dealt with the necessary treatment for making stable grease structures continuously from lithium 12-hydroxystearate (Jones & Wall—*U. S. 2,652,366*).

Several patents on lubricating greases pertained to the composition of the soap used for thickening the mineral oil. One grease contained calcium soaps of a blend of tallow and peanut oil with an iodine value of 55-60 (Tech. Development, M. G. O. Branch—*Indian* 46,816). A special grease contained lithium soap of hydrogenated castor oil (Browning *et al.*—*U. S. 2,697,693*). A soda base "bleedless" lubricant grease contained soaps of hydroxy acids and polyalkylene glycol (Bondi—*U. S. 2,678,918*). Soaps of hydroxy phenyl fatty acids as thickeners improved stability and induced high drop points in greases (Bartlett *et al.*—*U. S. 2,692,232*). Soaps of fatty acids produced by oxidizing petroleum were used in greases (Hirsh—*U. S. 2,669,543*; Kirk & Nelson—*Oil Gas J.* 52, No. 36, 97). A high temperature grease contained soaps of lower molecular weight oxy acids and natural fatty acids (Morway & Smith—*U. S. 2,690,429*). A grease compounded with five percent lithium stearate and one percent aluminum stearate in mineral oil of pour point  $-60^{\circ}$  and blended with 30-40% hydraulic oil of pour point  $-60^{\circ}$  was suitable for lubricating slow speed aircraft mechanisms operating at temperatures between  $-65$  and  $100^{\circ}$  (Pethrick & Wood—*Gov. Res. Repts., Gt. Brit., Lubricants & Lubrication* 2, Rept. No. 2, 11). A hydroxystearate soap constituent of a grease was made with lithium and sodium in ratios between 95:5 and 90:10 (N. V. de Bataafsche Petrol. Maalschappij—*Dutch* 73,006). Several patented soap greases contained fine carbon in suspension (O'Halloran—*U. S. 2,653,131, 2,696,469-71*). A patented method of lubricating metal surfaces comprised applying metal stearate by dry rubbing to the metal and thereafter lubricating with oil (Woog—*U. S. 2,673,818*).

New metal soap greases contained additional thickeners such as esters of dibasic acids with alcohols derived from the oxo process of catalytically treating monooleins with carbon monoxide and hydrogen (Morway & Smith—*U. S. 2,653,132*), soaps of dimerized fatty acids (Morway *et al.*—*U. S. 2,673,184*), waxes (Reudink—*Dutch* 73,989), cellulose (Siriani & Puddington—*U. S. 2,682,506*), pectic acid salt (Morway *et al.*—*U. S. 2,694,683*), reaction product of copolymer of styrene and maleic anhydride (Giammaria—*U. S. 2,698,297*), copolymer of maleic anhydride and allyl esters of fatty acids (Giammaria—*U. S. 2,698,298-9*), octadecanoyl thiourea (Hotten—*U. S. 2,698,300*), organic silicon compounds (Hotten & Houston

—U. S. 2,680,095; Woods & Bollinger—U. S. 2,652,364; Zajac—U. S. 2,684,944; Hain & Zisman—U. S. 2,693,449; Kather & Wiener—U. S. 2,681,313; inorganic siliceous gels (Iller—U. S. 2,676,148; Skinner & Savage—U. S. 2,681,314; N. V. de Bataafsche Petrol. Maatschappij—Dutch 74,490; Woods & Bollinger—U. S. 2,652,361; and bentonite (McCarthy—U. S. 2,662,056; O'Halloran—U. S. 2,677,661).

Several compounds were added to greases in small amounts to induce specific properties. The addition of certain polymerized methacrylate esters improved noise-suppression (Dilworth—U. S. 2,666,033). Use of sulfurized metal soaps in greases increased extreme-pressure properties and antiwear characteristics while being relatively noncorrosive (Dixon—U. S. 2,666,744). Organic compounds of selenium or tellurium enhanced stability (Woods & Edgar—U. S. 2,676,149). N,N'-Diphenyl *p*-phenylene diamine improved thermal stability (Dilworth—U. S. 2,663,690-1). A mixture of multivalent metal sulfonate and partial oxidation products of petroleum wax inhibited rusting (Eckert & Langer—U. S. 2,671,759).

Lubricating oils were also improved with various fat derivatives. Vinyl esters of fatty acids copolymerized with dialkyl maleate depressed pour point and improved viscosity (Bartlett—U. S. 2,694,685). Other viscosity improvers are alkyl acyloxystearates (Teeter & Cowan—U. S. 2,652,411), and polymers of alkylene sulfones (Melstrom & Watson—U. S. 2,652,368). A detergent additive characterized by a high alkaline reserve was made by reacting phosphorus sulfide with wool fat, partially saponifying with alkali metal base, and completing the saponification with a mixture of alkyl phenol and alkali (Muselman & Knowlton—U. S. 2,698,296). A mixture of wool fat and a polyisobutylene (Bartleson—U. S. 2,664,202) and compounds formed by sulfurizing fatty alcohols and neutralizing with metals of group I to III (Mikeska—U. S. 659,705) were patented as giving general improvement in color, inhibition of varnish formation, oxidation protection, detergency and inhibition of corrosion. The fatty additives patented to inhibit corrosion by lubricant oils were: reaction product of diallylcyanamide and fatty amine (Boyle—U. S. 2,666,745), reaction product of dioctyl acid pyrophosphate and primary amines derived from soybean fatty acids (Woodstock & Beck—U. S. 2,664,400), and fatty alcohol ester of ethylene bis-imino-diacetic acid (Bartlett *et al.*—U. S. 2,680,094). Good color sulfur additives were made by sulfurizing lard in the presence of water (Beretvas—U. S. 2,644,825). Inhibition of hydrogen sulfide liberation from lubricants containing sulfured products was obtained by addition of soaps of 9,10-epoxystearate (Baker—U. S. 2,684,943), and sulfites (Corcoran & Cashman—U. S. 2,690,445). An extreme pressure additive was a blend of sulfurized sperm oil and chlorinated paraffin wax (Sokol—U. S. 2,696,473). An antirust compound for demulsified turbine oil was produced by reacting oleic acid with triethylene tetramine and then reacting the product with succinic acid anhydride (Landis *et al.*—U. S. 2,693,448). A mixture of tin and anti-mono soaps of fatty acids plus aromatic secondary amine was added to castor oil lubricant to inhibit gumming, drying and hardening (Evans *et al.*—U. S. 2,692,853).

Synthetic lubricants prepared from polyhydroxystearic acids were an improvement over materials prepared earlier from higher fatty acids, but efforts to make them suitable for use at temperatures as low as  $-65^{\circ}\text{F}$ . did not succeed (Gast *et al.*—*Ind. Eng. Chem.* 46, 2205). A lubricant oil for watches and fine instruments comprised a blend of dibutyl phthalate, tritoly phosphate, and castor oil (Tech. Development M.G.O. Branch—*Indian* 47, 273). Sulfurized sperm oil was added to a patented hydraulic transmission fluid to improve oiliness (Jennings *et al.*—U. S. 2,683,120).

A lubricant useful for application as a high-speed jet during metal working operations was a special blend of certain mineral oil fractions and fatty oil (Ambrose & Brandes—U. S. 2,658,870). In new metal cutting oils of the emulsion type the emulsifiers used were: phosphatides (Clark—U. S. 2,670,330), soap made by saponifying wool wax with excess alkali (Roden—U. S. 2,697,072), a mixture of oleyl acid phosphate, and a fatty acid ester of hexitol anhydride (Nichols & Schroeder—U. S. 2,695,877), and synthetic detergents which may or may not be derived from fatty oil (King & Sproule—U. S. 2,695,272; Henkel & Rapp—*Ger.* 821,208 Cl. 12s; Badische Anilin- & Soda Fabrik—*Ger.* 848,956, Cl. 12q; Quaedvlieg & Schneider—*Ger.* 821,820 Cl. 23c).

Salz (*Wire & Wire Products* 28, 1056) described wire-drawing soaps and the oils and fats used in their manufacture. A newly patented composition for this purpose contained non-

aromatic paraffin, sperm and vegetable waxes plus a methyl ester of a chlorinated fatty acid (N. V. de Bataafsche Petrol. Maatschappij—*Dutch* 73,931). A solution of soap, borax, and rust inhibitor was sprayed on metal stock to rust proof it during storage and to serve as a surface lubricant when the metal is worked (Kluender—U. S. 2,664,399).

Chabrand (*Ind. textile* No. 812, 495) listed and discussed the specific properties most desirable in a textile lubricant. New and old tests for evaluating the scourability of wool-spinning oils were discussed by Leonard *et al.* (*Am. Dyestuff Repr.* 43, P263). An emulsion type textile lubricant contained mineral oil emulsified with polyoxyethylene stearyl amine and polyoxyethylene ether of sorbitan monooleate (Jefferson & Pine—U. S. 2,690,426). Fatty acid derivatives of morpholine induced antistatic properties in such textile lubricants (Jefferson & Riley—U. S. 2,695,270).

## Deterioration of Fatty Materials

REVIEWS. Communications containing general information and reviews pertaining to the deterioration of fatty material were written on: olefin oxidation (Bateman—*Quarterly Revs.* 8, 147), oxidative changes in fatty bodies (Paquot—*J. Sci. Food & Agr.* 2, 200), mechanism of fat oxidation in its relation to rancidity (Morris—*Ibid.* 126), recent advances on the stability of foods (Lundberg & Chipault—*Food Tech.* 8, 541), factors affecting the decomposition of frying fats (Carlin *et al.*—*Ibid.* 161), stability of natural fats as affected by the interaction of phospholipides, carotenoids, and tocopherols (Wingerd—*Univ. Microfilms Pub.* No. 7009, 74 pp.), detection of peroxides in fats (Braeckman & Deprez—*Pharm. Tijdschr. Belg.* 29, 139), autoxidation and enzymatic oxidation of unsaturated acids (Franke—*Ergeb. Enzymforsch.* 12, 89) new antioxidants (Kraybill & Dugan—*J. Agr. & Food Chem.* 2, 81), expanding uses of antioxidants (Tappel—*Food Eng.* 26, No. 6, 73), economic, legal, and chemical aspects of the use of antioxidants (Reith—*Conserv.* 2, 133), autoxidation of fats and application of antioxidants (Janecke—*Arzneimittel-Forsch.* 3, 574), considerations on the permissibility of adding antioxidants in foodstuffs (Tollenaar—*Fette u. Seifen* 56, 41), inhibition of the autoxidation of fish oils (Shu—*Formosan Sci.* 7, 1), antioxidants (Kapeller—*Zucker- u. Süßwaren-Wirtsch.* 3, No. 22, 41), experiences with antioxidants (Curli—*Olearia* 8, 100), vitamin E as an *in vivo* antioxidant (Dam—*Experientia Suppl.* 1, 1952, 195, 208), and fishiness in butter (Demeter—*Deut. Lebensm.*—*Rundschau* 50, 169).

TESTS FOR DETERIORATION, STABILITY, AND ANTIOXIDANTS. An investigation of the thiobarbituric acid test for measuring oxidation of fats showed that higher values are obtained for soybean oil than for cottonseed oil of comparable peroxide values (Sidwell *et al.*—*J. Am. Oil Chemists' Soc.* 31, 603). The test has been applied to measuring the rancidity of frozen pork (Turner *et al.*—*Food Tech.* 8, 326) and frozen herring (Fridriksdotter—*Student Rept. on Spec. Problems, Cornell Univ.* 1953, 33 pp.).

The rancidity test based on determining traces of carbonyl compounds in aqueous and alcohol solution was applied to benzene extracts of foods for evaluating the rancidity of the fats in the foods (Henick *et al.*—*J. Am. Oil Chemists' Soc.* 31, 88, 447). Estimation of the acetyl value was recommended for evaluating the deterioration of ghee (Godbole—*Oils & Oilseeds J., India*, 4, No. 4/10, 44).

A new procedure for determining peroxides in fats, similar to the Lea method, avoided the necessity for de-aerating the reagents and working in a current of inert gas by mixing all the reactants in a boiling acetic acid-chloroform solution (Sully—*Analyst* 79, 86). Modified Lea methods for determination of peroxides in fats and oils were published by Hadorn & Jungkuntz (*Mitt. Lebensm. Hyg.* 44, 495) and by Bronisz & Raciborska (*Roczniki Panstwowego Zakladu Hig.* 5, 115). The use of a nonionic detergent for breaking dairy product emulsions has been found to be a satisfactory means of isolating the fat for estimation of peroxide value by the ferric thiocyanate method (Stine *et al.*—*J. Dairy Sci.* 37, 202). The dichlorophenol-indophenol method for fat peroxides has been modified by the substitution of glycol-xylene with five per cent acetic acid mixture as the fat solvent and calibrating the results against the ferric thiocyanate method (Hartman *et al.*—*New Zealand J. Sci. Technol.* 35B, 307; *J. Sci. Food & Agr.* 5, 476). A method for determining peroxides by means of quaternary titanium is based on formation of pertitanic acid under the influence of active oxygen (Furmanek & Monikowski—*Roczniki*

*Panstwowege Zakladu Hig.* 1953, 447). A new method of determining active oxygen is based on reaction with dry hydrochloric acid under anhydrous conditions and determination of unreacted acid (Drozdov & Materanskaya—*Myasnaya Ind. S.S.S.R.* 25, No. 3, 50).

Ahlers & McTaggart (*Analyst* 79, 70) demonstrated how hydroxyl, ketone, and ester groups in autoxidized fats may be determined by infra-red spectroscopy. The accuracy of each determination was similar to that of the corresponding conventional chemical method. Similarly Wolff (*Rev. Francaise corps gras* 1, 214) illustrated the spectroscopic quantitative and qualitative determinations of ketones, hydroperoxides, and peroxides of linoleic acid in rancidifying oils. The effects of refining and other treatments on the evolution of these products was also shown. Obata & Matano (*Bull. Japan Soc. Sci. Fisheries* 18, 506) used spectroscopic means to identify three carbonyl compounds in autoxidized cuttlefish liver oil.

An investigation of stability of oils and fats with the Swift Stability Test showed that the correlation between composition and induction period is 90%; that correlation of induction period to stability is about 90%, and that stability can be predicted with about 70% accuracy from the composition (Becker *et al.*—*Fette u. Seifen* 55, 880). According to Bill & Sandell (*Farm. Revy* 53, 413) stabilities run by the "hot oven method" at 100° for oils and 80° for lard should be rated on the time required to attain a peroxide number of 2.0 ml. of 0.01 N sodium thiosulfate per gram, which is considered the end of the induction period.

Parmelee & Babel (*Indiana Agr. Expt. Sta. Bull.* 603, 4) investigated the water-insoluble acids, butyric acids, and fat acidity tests of butter as related to quality. Neutralization of cream reduced these acids, whereas use of increasing amounts of sodium hydroxide to neutralize fat-water-ether mixtures in the test increased the acids. Cream inoculated with *Pseudomonas fluorescens* yielded butter with a higher water-insoluble acid content than those from cream inoculated with *Streptococcus lactis* or with *P. fluorescens* plus *S. lactis*.

A collaborative study of the method of Mahon & Chapman for the determination of propyl gallate, butylated hydroxyanisole and nordihydroguaiaretic acid has indicated that when either is present alone the methods are fairly reliable; less reliable when two or more antioxidants are present; and when no antioxidant is present, the methods give a clear indication of the fact (Kahan—*J. Assoc. Offic. Agr. Chemists'* 37, 828). The method for determining butylated hydroxyanisole antioxidant in fats and oils by the use of 2,2'-bipyridine and ferric chloride has been adjusted for application to paper and paper-board packaging materials (Austin—*J. Am. Oil Chemists' Soc.* 31, 424). The polarography of propylgallate, nordihydroguaiaretic acid, and butylated hydroxyanisole has been described with a view of using polarographic measurements for their quantitative determination (Baltes—*Fette u. Seifen* 56, 484). Titration of phenolic antioxidants in a 72% alcohol extract with cerium sulfate either potentiometrically or by using an oxidation-reduction indicator permitted determination of concentrations as low as 0.003% but did not identify the antioxidant (Wenger—*Mitt. Lebensm. Hyg.* 45, 185).

**MECHANISM OF DETERIORATION.** Feuill & Skellon (*J. Chem. Soc.* 1954, 3414) identified 9,10-epoxy- and 9,10-dihydroxystearic acids, unsaturated keto esters, and the scission fragments nonanoic, decanoic, suberic and azelic acids among the products of catalytic oxidation of *n*-propyl oleate at 55, 85, and 120°. At the higher temperatures the keto esters dimerize and form oils and resins that still retain their ketonic character. These and other observations were compatible with the mechanism involving direct attack on ethenoid linkages by free hydroxyl radicals generated by thermal homolytic fission of initially formed hydroperoxides. The formation of ketol derivatives and formic acid on oxidation of elaidic acid was confirmed by King (*Ibid.* 2114). From low temperature photochemical oxidation tests of methyl oleate, Khan *et al.* (*J. Am. Oil Chemists' Soc.* 31, 460) confirmed that the principal products are trans hydroperoxides and also found that the conversion from cis to trans double bonds occurred at the same time as hyperoxide formation. Their tests on linoleate showed that cis, trans conjugated hyperoxides form with visible light and that copper catalyzed oxidation induced trans,trans conjugated hyperperoxide formation. Photochlorophyll oxidations of linoleate lead to the formation of some unconjugated hyperoxides, some of which contain trans double bonds. Ricciuti *et al.* (*Ibid.* 456) used polarographic methods to confirm that hydroperoxides form on oxidation of linoleate. In later stages of

oxidation they found that half the oxygen can be accounted for as free acid and half other than ester, hydroperoxide or free acid.

Spectral and polarographic analyses of products of lipoxidase catalyzed oxidation of linoleate showed that cis,trans diene-conjugated isomers form, that polymers appear to be formed by oxidative reaction, that the enzyme is involved in the formation of each peroxide molecule, and that hydroperoxides are formed initially (Privett—*Ann. Rept. Hormel Inst.* 1953-4, 7). A trans,trans conjugation observed in the work was believed to occur as secondary reactions in the process of recovery and isolation. The lipoxidase showed no activity on cis-9,trans-12-linoleate.

**FACTORS AFFECTING STABILITY OF FATS AND OILS.** Less hydrolysis of lard occurred with rendering by a centrifuge method than with the horizontal vacuum autoclave method (Drozdov & Materanskaya—*Myasnaya Ind. S.S.S.R.* 25, No. 1, 54). Maximum temperature attained in both tests was 80°. Colors of off-flavored stored lards after deodorization were considerably darker than those of fresh lard and stability of the flavor was poor after the deodorization (Sims & Hilfman—*J. Am. Oil Chemists' Soc.* 31, 211). Partial hydrogenation did not stabilize the aged lards nearly as markedly as it did fresh lards. Storage tests by Berezina & Komarova (*Myasnaya Ind. S.S.S.R.* 24, No. 5, 53) indicated that a fat made of good grade cottonseed oil, 70%, and beef fat, 30%, will keep for 16 months at -5 to -12°.

Tests on nigerseed (Rao & Swaminathan—*J. Sci. Ind. Res., India* 12B, 454) and safflower (Rao & Swaminathan—*Bull. Central Food Technol. Res. Inst.* 2, 211) oils showed that they were less stable than peanut oil.

Butter, unlike other fats, contains an unsaturated fatty acid with two bonds in conjugation whose content in the butter changes with the time of year as do the oxidative defects (Thome & Mattsson—*Proc. 18th Intern. Dairy Congr.* 3, 1056). The Wollny value, Polenske value, and refractive index of rendered butterfat increase more on storage than in butter (Cerutti—*Ann. sper. agrar., Rome* 8, 781). Mitra (*J. & Proc. Inst. Chem., India* 25, 174) demonstrated that butterfat in containers stored better when air was excluded from the head space. Similarly, Palii (*Masloboino-Zhirovaya Prom.* 13, No. 9, 9) recommended vacuum storage of margarine.

Based on bioassays, retention of vitamin A on storage in margarine is better than in butter (Deuel & Greenberg—*Food Res.* 18, 497). Destruction of carotene is greater in refined than in crude peanut oil, and least in the hydrogenated oil (Roy—*J. Indian Chem. Soc., Ind. & News Ed.* 16, 129). Use of low temperature, vacuum, and a carbon dioxide atmosphere during rendering of fats protect the vitamin A (Zinov'ev & Zakharova—*Myasnaya Ind. S.S.S.R.* 24, No. 6, 57). The presence of refined sesame oil accelerates deterioration of hydrogenated oil and also of added carotene (Roy—*Ann. Biochem. & Exptl. Med., India*, 12, 63).

Tung oil has been stored in clean, well-filled, tinned gallon containers for three years with retention of quality sufficient to meet American Society for Testing Materials specifications (Holmes & Pack—*J. Am. Oil Chemists' Soc.* 31, 96). Likewise, reduction of head space in jars of peanut butter inhibited deterioration of the oil (Willich—*Food Tech.* 3, 101).

Rates of oxidation of isomers of oleic acid were found to be in the increasing order of oleic, elaidic, 12-octadecenoic and 15-octadecenoic (Toyama & Yamamoto—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 55, 164).

The presence of one per cent chlorophyll in oleic acid accelerated its oxidation in the dark as well as in the light (Kehren—*Anais fact. farm. e odontol., Univ. Sao Paulo* 10, 93). At elevated temperature zinc chloride acted as a catalyst for the oxidation of oil (Babin & Plyusnin—*Priklad. Khim.* 27, 463; Urs *et al.*—*Bull. Central Food Tech. Res., Mysore* 3, No. 1, 17). When present, unsaponifiable matter with high iodine value should be removed from oleins to improve stability (Kehren & Keutmann—*Z. ges. Textil Ind.* 55, 26).

Some communications on deterioration of fats pertained to the stability of the color. Beef fat stored at 0-5° darkened from light yellow to yellow in 2-3 months whereas samples stored at -16 to -18 remained light yellow throughout a 10-month test period (Grechko & Karachevtseva—*Myasnaya Ind. S.S.S.R.* 25, No. 3, 51). Reversion of color in beef fat that is decolorized by treatment with liquefied, normally gaseous hydrocarbons is inhibited by incorporating a small amount of a compound containing an activated sulfhydryl group as the only sulfur group (Hlavacek—*U. S.* 2,680,121). Several observa-

tions were recorded on the reddening or rusting of fish oils on aging. Nonaka (*Bull. Japan Soc. Sci. Fisheries* 18, 105, 653) observed that this occurs on oxidation of the fatty acids and not in the separated unsaponifiable matter or glycerol. His observations that the fish oils readily discolor in contact with ammonium salts and crude casein but not with purified casein led to the suggestion that ammonia liberated by nitrogenous material is involved in the reddening. Similar results by Suzuki (*J. Chem. Soc. Japan, Ind. Chem. Sect.* 56, 20) were interpreted to indicate that the reddening is due to a reducing substance as well as peroxides. In other work, a combination of aldehydes produced by oxidation and trimethylamine was said to be involved because purified fish oils readily reddened when aerated in the presence of purified trimethylamine (Obata *et al.*—*Ibid.* 17, 349). With crude nigerseed oil the natural red and yellow color decreased with simultaneous increase of peroxide value (Rao & Rao—*Oils & Oilseed J., India* 5, No. 10/12, 92).

**ANTIOXIDANTS.** Behavior of antioxidants during baking and storage of pie crust has shown that acidic synergists do not improve keeping quality; propyl gallate or nordihydroguaiaretic acid with citric acid is ineffective; lauryl gallate plus citric acid increases stability; and the addition of butylated hydroxyanisole plus citric acid to the dough or addition of "Ver-sene" to the dough followed by spraying the pie crust with solutions of lauryl or propyl gallate plus citric acid resulted in the greatest stability (Mahon & Chapman—*J. Am. Oil Chemists' Soc.* 31, 108). During heat treatment propyl gallate protects hydrogenated fats against deterioration to some extent (Roy—*Ann. Biochem. and Exptl. Med., India*, 12, 75). An investigation of 11 antioxidants at 0.05% concentration in six edible fats showed that at boiling water temperature pyrogallol and L-ascorbic acid were excellent inhibitors, but at room temperature the latter was not (Valpola—*Teknillisen Kemian Aikakausilehti* 10, 461). The antioxidants  $\alpha$ -tocopherol, nordihydroguaiaretic acid and hydroquinone markedly accelerated the thermal decomposition of fat peroxide in vacuum, but this effect was suppressed by synergists (Privett & Quackenbush—*J. Am. Oil Chemists' Soc.* 31, 281, 321). Data from this work support the concept that the peroxide radical is the point of intervention by the antioxidant in the chain reaction of autoxidation. Also it was suggested that ascorbic and citric acids function as synergists by inhibiting the antioxidant catalysis of peroxide decomposition.

Other tests on antioxidation pertained to deterioration during storage. An investigation on 15 antioxidants for preventing storage defects in butter showed that at five parts per million tetramethylthiuran disulfide, tetraethylthiuran disulfide, and sodium diethyl dithiocarbamate were good; gallates retarded formation of peroxides but did not prevent the fishy odor; and vitamin C retarded peroxide formation but adversely affected taste (Tollenaar—*Conserva* 2, 304). Yoshikawa & Nonaka (*J. Oil Chemists' Soc., Japan* 2, 186) recorded the protective ability of 39 common antioxidants on lard and soap under influence of light, aeration, and presence of copper catalyst, respectively. In this work all amine antioxidants darkened the lard. In a similar study on antioxidants for lard and for olive oil, using the Schaals' oven method of acceleration of oxidation, the alkyl gallates plus citric acid were effective in decreasing order with increase in molecular weight, and the commercial product, Tenox II, was most effective for lard (G. Quijano *et al.*—*Grasas y aceites, Spain*, 4, 119). Butylated hydroxyanisole was more effective in preventing rancidification of walnut meats than nordihydroguaiaretic acid, propyl gallate, and a commercial antioxidant salt (Musco & Cruess—*J. Agr. & Food Chem.* 2, 520). Test on the behavior of antioxidants in methyl linoleate during irradiation show that vitamin A, ascorbic acid, glutathione, and cysteine were largely destroyed; catalase had no effect, and tocopherol and a commercial antioxidant, "Lonol," were effective antioxidants (Polister & Mead—*Ibid.* 199).  $\alpha$ -Tocopherol, propyl gallate, and nordihydroguaiaretic acid inhibited the action of peroxidase, catalase, and ethanol dehydrogenase (Tappel & Marr—*Ibid.* 554).

Several antioxidant studies pertained to natural materials. Among 17 spices tested in oil-in-water emulsions cloves were unusually effective, oregano had the highest protective index in mayonnaise, and none of the spices was prooxygenic (Chippault—*Ann. Rept. Hormel Inst.* 1953-4, 23). In similar work on animal fat, several chemicals and extracts of cinnamon, allspice, red and white thyme, cayenne, clove, rosemary, sage, nutmeg, and parsley were antioxidant (Egli *et al.*—*Intern. Z. Vitaminforsch.* 25, 311). In this work eugenol and isoeugenol

were considered the active principles of clove and nutmeg, capsaicin of cayenne, and alkali soluble phenolic compounds of sage and rosemary. The antioxidant properties of black pepper were attributed to the tocopherols present (Hasselstrom *et al.*—*Food Res.* 19, 373). Caffeic acid, dihydrocaffeic esters, and many derivatives of hydroxycoumarin are antioxidant but much less effective than hydroquinone or pyrogallol (Tamura *et al.*—*J. Agr. Chem. Soc., Japan*, 26, 410). Among antioxidant flavones, structures with ortho hydroxy groups in a phenyl side ring considerably increases antioxidant properties, meta position hydroxyl in a chroman ring reduces antioxidant effect, and an  $\alpha,\beta$ -unsaturated ketone structure in a pyrone ring or the corresponding chalcone is responsible for the antioxidant effect (Heiman & Reiff—*Fette u. Seifen* 55, 451). Aca-catechin extracted from crude katha inhibited oxidation of vegetable oils (Husaini & Saleto—*J. Sci. Ind. Res., India*, 12B, 408). Gossypol or dianilinosgossypol at 0.5% concentration considerably increased the stability of lard but had only slight protective influence on cottonseed oil (Bickford *et al.*—*J. Am. Oil Chemists' Soc.* 31, 91). Milk products such as cream, skim milk, and fermented skim milk protected vitamin A in margarine, whereas butterfat did not (Mori *et al.*—*J. Japan Soc. Food Nutr.* 5, 180). Compounds which have *in vivo* vitamin E antioxidant activity or their structural analogs, strongly inhibited hemin-, hemoglobin-, and cytochrome c-catalyzed oleic acid oxidation (Tappel—*Arch. Biochem. Biophys.* 50, 473). The antioxidant activity of liquid smoke flavors were shown to vary from zero to a profound effect (Watts & Faulkner—*Food Tech.* 8, 158; Erdman *et al.*—*Ibid.* 320). Ascorbic acid was considered unsuitable for stabilizing butter because a malt-like flavor developed in the butter during storage (Sabatschka—*Milchwissenschaft.* 8, 300). Addition of soybean phosphatides to soybean salad oil improved its stability and initial flavor but caused darkening of the oils and the introduction of undesirable storage flavors when added at levels which improved the oxidative stability (Evans *et al.*—*J. Am. Oil Chemists' Soc.* 31, 295). In this work it was suggested that phosphatides are the precursors of melony, bitter, cucumber flavors frequently encountered in aged soybean salad oils. This flavor response was the same as that produced by phosphoric acid. Privett & Quackenbush (*J. Am. Oil Chemists' Soc.* 31, 169, 225) attributed the protective action of phosphatides and phosphoric acid to complex formation with fat peroxides.

Two communications on preservation of fats pertained to deactivation of prooxidant metal compounds. Hartman & White (*New Zealand J. Sci. Technol.* 35, 254) demonstrated increased stability of iron-containing beef and mutton fat by removal of the metals with tannin or deactivation with citric and tartaric acids. The effectiveness of carboxymethyl mercapto succinic acid for the same purpose was demonstrated on various oils and shortenings (Evans *et al.*—*J. Am. Oil Chemists' Soc.* 31, 9).

Rac (*Seifen-Öle-Fette-Wachse* 80, 181) recommended oat extracts plus citric or tartaric acid for the stabilization of rancid fats that have been regenerated by refining. Vahlteich *et al.* (*Food Tech.* 8, 6) recommended that the citric acid ester stabilizer be added after deodorization. Privett (*Ann. Rept. Hormel Inst.* 1953-4, 41) found the selachyl alcohol fraction isolated from unsaponifiable material of fish oils to be an ideal solvent for incorporating antioxidants into fat.

Chronic toxicity studies on conidins and conidins indicated that they were safe for use as food fat antioxidants (Wilson & Cox—*Proc. Soc. Exptl. Biol. Med.* 86, 247).

Patents have been issued on use of the following antioxidants: solutions of phosphoric acid and glycine (Kuhrt—*U. S.* 2,665,991, 2,681,281-3), alkoxy derivatives of biphenyl (Bell & Knowles—*U. S.* 2,697,111), derivatives of *p*-alkoxyphenols (Bell *et al.*—*U. S.* 2,682,474, 2,682,563), a combination of monoalkyl ester of citric acid and a phenol antioxidant (Embree & Kascher—*U. S.* 2,686,751), lecithin citrate in combination with other antioxidants (Hall—*U. S.* 2,677,616), 3,3,5,5-tetraalkyl diphenolquinones (Jones—*U. S.* 2,686,814), acylated *p*-aminophenols (Young & Cottle—*U. S.* 2,654,722), esters of gallic acid (Ohshima—*Japan* 3329[1953]), *tert*-alkyl-4-alkoxyphenol (Chenicek—*U. S.* 2,666,708, 2,686,723-4, 2,690,396; Rosenwald & Chenicek—*U. S.* 2,666,709, Rosenwald—*U. S.* 2,679,459), 4-alkoxyphenol having at least one ring hydrogen substituted by an alkylthioalkyl group (Chenicek—*U. S.* 2,668,768), and special mixture of butylated hydroxyanisole and propyl gallate (Hoffman *et al.*—*U. S.* 2,683,694). Pasteurizing of cream or milk after addition of sugar preserves the fresh flavor of butter made therefrom (Turnbow—*U. S.* 2,673,155).



Compounds of the structure like 2,4-HO(MeCH:CH)<sub>2</sub>H<sub>3</sub>OEt were patented for the preservation of soap (Tomiyama *et al.*—*Japan 5432*[1953]).

**FLAVOR REVERSION.** Some of the investigations on flavor reversion of oils were attempts to identify the compounds causing the odor. Formic acid, acetic acid, butyric acid, enanthic acid, acetaldehyde, butyraldehyde and enanthole were identified among the products volatilized on aeration of the C<sub>20</sub> and C<sub>22</sub> acids of fish oils and were assumed to be the causes of the flavor reversion (Toyama & Matsumoto—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 56, 972). In similar work on cuttlefish liver oil C<sub>1</sub> to C<sub>6</sub> acids and 12 amino compounds were isolated (Obata & Matano—*J. Oil Chemists' Soc., Japan*, 2, 112). An odorous fraction collected in the condenser during commercial deodorization of peanut oil contained 2,4-decadienal and a strongly smelling substance which was not precipitated by bisulfite (Lefort—*Bull. mens. inform. ITERG* 7, 383).

Isolated polymers from soybean oil were further oxidized at 30° to yield various aldehydes like those already identified in whole reverted soybean oil (Chang & Kummerow—*J. Am. Oil Chemists' Soc.* 31, 324). The work suggested that oxidative polymers could be unintentionally incorporated into oils in various ways from equipment and then serve as precursors of reversion compounds. Certain fractions derived in the refining of soybean oil with liquefied propane were returned to the refined oil to improve the flavor stability (Passino—*U. S.* 2,664,431). Another patented means of inhibiting reversion of fats and oils involves partial hydrolysis and removal of some of the freed fatty acids (Metallgesellschaft A.-G.—*Brit.* 707,454).

With butters reversion to fishy flavors correlated well with a peroxide value of 0.5 by Leas' method and 1.0 by the Loftus-Hills method (Jamotte *et al.*—*Proc. 13th Intern. Dairy Congr.* 3, 1079).

[Part II will follow in June issue.]

## Polarographic Studies of Fat Oxidation<sup>1</sup>

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EVER SINCE the importance of peroxides in the autoxidation of fats was recognized, attempts have been made to identify and study the different peroxides involved. For lack of better methods, most of the evidence was based on analogy with simpler processes and on the analysis of breakdown products. During the autoxidation of asymmetric diphenylethylene Staudinger (1) showed that two peroxides of differing stability were formed. By analogy and from variations in the different analytical constants of oxidized fats, formation of several types of peroxides in oxidized fats was inferred. Farmer and co-workers (2) were the first actually to isolate and identify a peroxide, that is, the hydroperoxide. Since then methyl oleate hydroperoxide has been isolated in purer form, and it is now generally accepted that the hydroperoxide is one of the first and major products of autoxidation of unsaturated fatty acids. Even after the isolation of the hydroperoxide, there was no method available for detecting and estimating hydroperoxide in the presence of other peroxides.

Lewis and Quackenbush (3), using a polarograph for the study of autoxidized fat, obtained three waves which they showed were due to peroxides and which were not parts of the same wave. They did not however identify the peroxides responsible for the three waves. They used a mixture of methyl alcohol and benzene as solvent and lithium chloride as supporting electrolyte. Willits and co-workers (4) with the same solvent-electrolyte combination studied polarograms of a large number of oxygen-containing organic compounds having the same functional groups as were believed to occur in autoxidized fats. They observed that the acyl peroxides were reduced in the range 0–0.2 volts, and 2-diketones and hydroperoxides between 0.6–1.0 volts, and the unsaturated aldehydes and ketones around 1.5 volts and beyond; methyl oleate hydroperoxide was found to give a wave around 0.8 volt.

The present work involved a study of the polarographic behavior of peroxides formed in fats during autoxidation at 60°C. in the presence and absence of a catalyst.

### Experimental

The autoxidations were conducted at 60°, by bubbling dry air through the fat or methyl esters and exposing to a 275-watt sunlamp. The polarograms were carried out in a 0.3 M solution of lithium chloride in a solvent consisting of equal proportions of methyl alcohol and benzene. The sample size varied from 0.01 g./100 ml. to 0.40 g./100 ml., chosen so as to give complete solution. The polarograms were obtained on a Sargent model XXI recording polarograph, using an H-type cell maintained at 30°. A saturated calomel electrode was used as reference electrode. The capillary used had a drop time of 1.5 seconds and mercury flow rate of 4.71 mgms./sec. The cell had a resistance of approximately 1,000 ohms, and the polarograph was used at a sensitivity of 0.04 microamperes per millimeter.

The peroxide value, expressed as milli equivalents per kilogram was determined on 0.1–0.5 g. of the sample, using a reaction time of 15 min. The solubility was tested by determining whether 0.2 ml. of the sample in 10 ml. Skellysolve F gave a clear or turbid solution.

The methyl esters used for comparison with soybean oil were prepared from fatty acids obtained by saponification of soybean oil. The methyl esters were distilled before use and had an iodine value of 127.3. The soybean oil used was a commercial, refined, and deodorized sample with an iodine value of 133.1.

### Results and Discussion

As a first step in this investigation soybean oil was autoxidized at different temperatures. In the autoxidation at 0° and room temperature the samples were soluble in Skellysolve F even after oxidation for 20 days and showed a small wave at 0.2 volts and a prominent wave around 0.7 volts. The sample oxidized at 60° was however sufficiently polymerized at

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