Annual Review of Literature on Fats, Oils, and Soaps. Part 1

Report of the Literature Review Committee*

M. M. PISKUR, Swift and Company, Chicago, Illinois

Introduction

In the year 1947 the literature contributions on the subject under review were numerically about the same as during the preceding year. However, there has been a slight shift in interest. Published works on analyses and processing may have decreased while the biochemical, physiological, and physical phases of fat chemistry have attracted slightly more attention. The number of patents on synthetic detergents appears to have declined during the past several years, while technical uses for fat derivatives as lubricants, anticorrosives, emulsifiers, demulsifiers, etc., were attracting more interest.

STATISTICS AND OUTLOOK. This information was most comprehensively prepared by the Outlook and Situation Board of the U. S. Department of Agriculture, Bureau of Economics (*Fats and Oils Situation FOS 122, 1947,* 22 pp.). According to this publication, disappearance of food fats in the United States in the year beginning October, 1946, for both civilian and armed forces totaled 42 pounds per person. This was two pounds per person above the unusually low level of a year earlier but four pounds below the 1937-41 average. Domestic disappearance of food fats per person in 1947-48 may be moderately less than in 1946-47.

The 1946-47 export of food fats was substantially below wartime level but about 250 million pounds above pre-war. Imports, excepting coconut oil, totaled only 35 millions. In 1937-41, the imports of edible fats averaged 191 million pounds annually. About 120 million pounds of coconut oil were used in food products during the fiscal year, compared with 15 million pounds a year earlier.

There was very little change in the supply of soap fats, and prospects for 1947-48 will be about the same as for the previous year. Approximately 900 million pounds of oils and fats were used in paints, varnishes, floor coverings, oilcloth, printing inks, core oils, resins, caulking compounds, etc., in the year beginning October, 1946. This was about equal to the wartime average and about 60 million pounds above the 1937-41 average.

Prices of fats and oils have fluctuated widely since decontrol. The index of wholesale prices of food fats (1935-39 = 100) for the first 12 months following removal of price ceilings (Nov. '46-Oct. '47) averaged 254. This was 109 points, or 75% higher than the average of the index for most of the war. In regard to soap fats, tallow averaged 19 cents per pound after a ceiling of 8.6 for the previous year. The price of coconut oil followed closely the movement of tallow prices. Prices of drying oils averaged 32 cents as compared to 14.3 cents during the price-control period of the previous year. The supply outlook indicated that drying oil prices for the 1947-48 period will average somewhat less while other fats may not change in price.

Several other reports of general nature were of interest principally because of their economic aspects. The subjects treated were fats and oils from 1841 to 1941 (Hilditch—*Ind. Chemist 23,* 415), an inventory on sources, application, and properties of 31 oils and fats of commerce (Dean—*Soaps, Perfumery, Cosmetics 19,* 927; *20,* 54), edible oils of Germany (Goss—*Food Industries 19,* 184, 320; Anon.—*Manuf. Chemist 28,* 154), vegetable oil production in British African colonies (Keen *et al.*—*Oleagineux 2,* 475), oil industry of Argentina (Ferrara—*Olearia 1,* 21), oilseed production of Canada (Dougherty—*Industrial Reference Service No. 17, 5,* Pt. 5, 3 pp.), the Italian oil problem (Bandini—*Olearia 1,* 67), and fat and oil resources of Latin America (Markley—*Oil Mill Gaz. 51,* No. 6, 9).

Another group of general communications treated various aspects of the oil industry. The subject of these comprehensive papers covered soybean research at the Northern Regional Research Laboratory (Hilbert—*Soybean Digest 6,* No. 11, 33), the properties of French rape, soybean, and linseed oils (Andre & Martin—*Bull. soc. chim. France 1947,* 217), industrial uses of soybean oil (Alcala—*Ion 6,* 415), bodying oils [Paleni—*Chimica e industria (Milan) 29,* 100], oil-mill equipment [Bagot—*Inds. agr. et aliment (Paris) 64,* 27], processing (Elicegúi—*Ion 6,* 480; Bagot—Chem. & Ind. 56, 117, 238; Martinenghi—*Olearia 1,* 14), and an annual review of the chem-

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* Literature Review Committee

E. W. BLANK　W. H. GOSS
J. B. BROWN　M. M. PISKUR, Chairman

istry and metabolism of the lipids (Piskur & Schultz —*Ann. Rev. Biochem. 15,* 79).

FOSTERING INDIVIDUAL SOURCES. Monographs were written on the aleurities (Engelbeen — *Bull. Agr. Congo Belg. 37,* 256; Blackmon—*Econ. Botany 1,* 161; McKinney—*U. S. Dept. Agr., Bur. Agr. Ind., Chem. AIC-94,* 13 pp.), okra seed oil (Edwards & Miller—*Chemurgic Digest 6,* 29; Markley & Dollear—*Oil Mill Gaz. 52,* No. 6, 13), grape seed oil (Beck—*Rev. Brasil. quim. 23,* 205; Martinenghi—*Olearia 1,* 84), olive oil culture in Greece (Lychnos—*Ibid.* 106), olives in Eritrea and in Ethiopia (Pajella—*Ibid.* 96), soybean oil Cagnoni — *Ibid.* 36; Daubert — *Soybean Digest 7,* No. 11, 24; Manley—*Ibid.* 26; Eisenschiml —*Am. Paint J. 32,* No. 2, 72; Sorenson—*Official Digest Federation Paint & Varnish Production Clubs No. 267,* 238), stillingia oil (Potts—*Paint, Oil Chem. Rev. 109,* No. 25, 16), fish oils (Lovern—*J. Intern. Soc. Leather Trade's Chemists 31,* 207), rapeseed oil (Grace & Zuckerman—*Can. Chem. Process Inds. 31,* 571), British plans for cultivation of peanuts in Africa (Maugini—*Olearia 1,* 3), peanut oil (Schofield —*Food 15,* 258), crocodile fat (Dean—*Soap, Perfumery Cosmetics 20,* 262), tall oil (Hess—*Paint Tech. 11,* 299), fat production with yeast on sulfite residues (Schmidt—*Die Chemie 59,* 16), and synthetic fats (Mannes — *Die Chemie 57,* 6; Lennartz — *Die Chemie 59,* 10; Editorial—*Chem. Inds. 60,* 64; Williams—*Chemistry & Industry 1947,* 251). For further references on individual fats and oils the reader is referred to charts in Section F giving the newly recorded analytical data on oils from potential commercial sources.

Where supplies of certain oils were inadequate, some writers discussed substitutes or interchangeability of oils. Widegren (*Seifensieder-Ztg. 1943,* 76) suggested that certain combinations of tall and dehydrated castor oil could be substituted for linseed oil in the paint industry. Chatfield (*Oil Colour Trades J. 110,* 1186) listed several oils and classes of oils which in combination with resins were suitable replacements for the linseed oil. According to Schar (*Mitt. Lebensm. Hyg. 37,* 363) linseed oil was used for human consumption in Switzerland during the war. The oil was hydrogenated and mixed one part to four parts with other fats.

NEW LITERATURE. A book on *Fatty Acids, Their Chemistry and Physical Properties* by Markley (Interscience Publishers Inc., New York, 1947) efficiently fills a gap among the organized information on fats and oils. This is the first time that this information has been comprehensively organized to a readily accessible form and should shorten the literature work of that large number of investigators who are interested in fatty acids and their derivatives. Hilditch's book (*Chemical Constitution of Natural Fats,* Chapman & Hall, Ltd., London, 1947) was revised to incorporate the notable advances that have occurred during the seven years since the first edition appeared. He has described and classified about 420 fats from plant species, about 80 fats from land animals, and about 100 fats of aquatic origin.

During the past several years, a few changes occurred in the French fat and oil journals. The *Bulletin des Matieres grasses de l'institut colonial de Marseilles* and *Industries corps gras* were discontinued and the material was appearing in *Oleagineux.* The latter is now sponsored by (a) Inst. Recherches Huiles de Palme et Oleagineux, (b) Inst. Tech. Etudes et Recherches Corps Gras, and (c) Inst. Colonial Marseille. A new Italian journal was entitled *Olearia* and was sponsored by two local fat, oil, and soap associations.

Production

ANIMAL FAT. Maillet's review on rendering (*Inds. corps gras 3,* 38, 81) is well worth mentioning, for the author described and illustrated all the latest equipment and processes in use in America and in Europe for the production of lard, margarine, and tallow.

Attempts to apply enzymatic disintegration in rendering processes were described in two patents. Kiel (*U. S. 2,423,102*) digested fat tissue with proteolytic enzymes at a pH higher than 6.0 and then heated the charge to 60° to release the fat from the protein matter. Ekhard (*Ger. 707,226, Cl. 23a*) fermented fatty tissue with lactic acid-producing bacteria in the presence of carbohydrates, to release fat which was then separated and washed.

There was some interest in the selection of the optimum temperature in conventional rendering processes. When rendering herring by heating and then by pressure extraction, it was reported that the heating temperature should be above 70° or the oil will not be released during the pressing (Notevarp and Tornes—*Fiskeridirektoratets Skrifter 1,* 7). Stable chicken fat was said to be produced by vacuum rendering at 80° (Anon.—*U. S. Egg & Poultry Mag. 53,* No. 8, 7). A newly patented rendering plant comprised holding tanks and renderers between which were attached toothed milling devices (Niessen—*Ger. 728,592, Cl. 23a*).

In connection with wool grease recovery, a description and flow diagrams of the processes used in Bradford, England, were published (Hillier and Campbell —*Synthetics and By-Products 8,* 329, 375). Twenty per cent of the world's wool production is washed in this locality. Faber (*Sewage Works J. 19,* 248) found calcium hypochlorite and aeration of the wool-scouring wastes, followed by skimming, led to the most successful recovery of wool grease. The return from the grease probably does not pay for the total cost of the treatment in either of the above cases: but since waste treatment to prevent polluting streams is compulsory, the recovered wool grease aided in the economy of treatment.

Six systems of continuous butter production were described and compared by McDowall (*Food Inds. 19,* 909). The methods, in general, allowed considerable economies of labor and time, but there were operational problems, such as difficulties in handling of raw material of various fat content and acidity. The products were enough unlike butter in appearance, consistency or, in some cases, flavor that segregation or sale under a name other than butter would be necessary. Newly patented developments in continuous butter making comprised concentrating the fat by centrifuging under vacuum and in the presence of some steam (Horneman *et al.*—*U. S. 2,423,834*) and by centrifuging cream, adjusted to pH 2, at about 95° temperature (Riggs—*U. S. 2,414,837*). A recent continuous butter making machine was claimed to be quite different than the others in that the cream was churned under pressure and in an atmosphere of carbon dioxide (Perruche—*La Nature 1947,* 362).

In operation cream was churned into butter in five minutes, and the entire equipment had a production capacity of 1,000 kilograms of finished small-packaged butter per hour.

In conventional butter making Mulder (*Verslag Landbouw. Onderzoek No. 52 C,* 269) observed that, when using cream low in fat, longer churning was necessary and the butter particles were round and smooth, in contrast to flocs from richer cream. However, the processes showed no difference in the hardness of the butter produced. Petersen (*Fette u. Seifen 51,* 440) confirmed earlier work of Virtanen which indicated that the addition of special buffering salts increased the stability of butters. Pont (*J. Council Sci. & Ind. Res. 19,* 432), in studies on washing butter, recorded that fresh unwashed butter graded one point higher than washed samples, but after three months' storage, graders favored the washed samples in the majority of the cases. Theories concerning churning of butter were reviewed by Peterson (*Fette u. Seifen 51,* 59).

A new dehydrated butter was considered novel because all the non-fat constituents were allowed to remain in the butter (Jakobsen—*U. S. 2,418,645*). This process of preserving butter comprised vacuum dehydration to five per cent moisture content.

VEGETABLE FAT. Processing information on vegetable oils included information on storage and the behavior of seeds during storage. Hygroscopic equilibria data for cottonseed (Karon—*J. Am. Oil Chemists' Soc. 24,* 56) and sunflowerseed (Colvin *et al.*—*Can. J. Res. 25F,* 111) were recorded. The former varied linearly from 6.03 to 10.27% moisture at 31 to 71% relative humidity, and then the moisture increased rapidly to 22.19% as the humidity was increased to 93%. The data were interpreted with respect to their application in planning aerating procedures during storage. The moisture equilibria of sunflowerseed was found to be about two per cent below respective values for wheat, oat groats, and flaxseed; and the sunflower hulls had a higher moisture content than the meats. Other work (Sinclair & Sallans—*Ibid.* 119) showed that the moisture content of the hulls could be reduced several per cent without changing the moisture content of the meats. Such a change improved hulling efficiencies and decreased the percentage of meats broken.

Holmes *et al.* (*J. Am. Oil Chemists' Soc. 24,* 311) in studies on storing tung seeds, found that artificial drying before storage to about 10% moisture improved processing efficiency and the quality of the oil. The optimum drying temperatures were 70-78°, below or above which both the processing efficiency and the quality of oil produced were reduced.

Fundamental work on lipolysis and the respiration index (RI) of cottonseed by Altschul and coworkers (*Plant Physiol. 21,* 506, 550, 573; *Science 105,* 525) led to an application in the studies on cottonseed storage. The average RI was an exponential function of the moisture content of the seed; whereas lipolysis seemed more affected by maturity. Both reflected the vigor of the seeds and should therefore be considered in commercial storage. Ammonia inhibited both respiration and lipolysis, and reduced the color of the oil. Studies of the effects of germicides and fungicides suggested that the deterioration (lipolysis) which occurred in stored cottonseed was due to enzymes in the seed rather than to microbiological activity. Although lipolysis was experimentally controlled with several enzyme inhibitors, none of the reagents used would be applicable if the products were intended for food purposes.

There were several reports on the behavior of pigments during the processing of cottonseed (Boatner *et al.*—*J. Am. Chem. Soc. 69,* 668, 1268, *Botan. Gaz. 108,* 484, *J. Am. Oil Chemists' Soc. 24,* 97, 276-362). Gossyfulvin, a native pigment, and gossycaerulin, a blue gossypol derivative occurring in the cooked cottonseed, were isolated; and their spectral, thermal, and chemical properties recorded. The information was used to study the relationship of the processing methods to the quality of the final products. The pigmentation of the cooked cottonseed and pressure produced oil was dependent upon the moisture content and period of heating of the seed. Expeller crude oils were more deeply colored and contained one principal pigment, whereas the hydraulic-pressed oils contained two principal pigments. Alkali refining removed most of the pigments, but the refined oil still contained some of the original pigments as well as a large number of their decomposition products. The color development in the seed and crude oils on aging was found to be related to the absorption spectra of the crude oils; *i.e.,* crude oils of maximums at 368-370 mμ rapidly developed "high bleach colors"; *i.e.,* intensity of color after bleaching. Hence, processing conditions which result in the production of oils exhibiting this type of absorption should be avoided, or if production of such oils is unavoidable, the oils should be refined and bleached as rapidly as possible. Solvent extraction of oil free from gossypol and gossypurpurin was possible when moisture was excluded and water immiscible solvents were used. The pigments could then be removed from the resulting meals by a flotation process or extraction with methanol, ethanol, isopropanol, acetone, or 1,4-dioxane.

Baskervil *et al.* (*Oil Mill Gaz. 51,* No. 11, 56) graphically recorded the effect of cooking temperature, pressure, time, and thickness of cake on the amount of oil remaining in cottonseed cake. Jáky's (*Kiserletügyi Közlemények 46,* 25) processing studies on suflowerseed indicated that 70-80% of the shells should be removed before pressing. In the production of edible fat from Cacao beans, according to Schär (*Mitt. Gebiete Lebensm. Hyg. 38,* 11), the beans should be pressed in such a manner as to allow 10% fat to remain in the meal. The meal may be ground and roasted for food purposes. The residue from solvent extracted beans was useless for either human or animal consumption. A newly patented oil-seed processing method comprised pressing to a porous cake of 10-24% oil content, followed by a special granulating process, and then solvent extraction (Schmidt & Webber—*U. S. 2,430,535*).

Vanneck (*Bull. Agr. Congo Belg. 38,* 75) published a description of extraction of palm oil by the wet process. This comprised sterilization to prevent enzyme action, pulping, digestion, boiling, decantation, etc.

Two suggestions were made for the use of enzymes in vegetable oil production. Cellulose in wheat germ was hydrolyzed enzymatically and the oil separated from proteins and carbohydrates by centrifuging (Atieselscabet Niro Atomizer—*Dan. 64,815*). Fat acids were produced from ground nut cake by adding 20-30% ground castor beans, incubating 2-3 days at

35° and extracting the fat acids with weak alkali hydroxide solution (Golant—*U. S. S. R. 66,420*).

The general papers on solvent extraction included descriptions of the Allis-Chalmers plant (Bilbe—*Oil Mill Gaz. 51,* No. 7, 39, Tray & Bilbe—*Chem. Eng. 54,* 139) and the Delta Products Co. plant (Moore—*Food Inds. 19,* 471, Gordon—*So. Power & Ind. 65,* No. 7, 62), reviews of modern methods (Goss— *U. S. Dept. Agr., AIC-135,* 6 pp., Schwitzer—*Paint Manuf. 17,* 255, Markley—*Oil Mill Gaz. 51,* No. 7, 27, Bonotto —*Ibid.* 32, Antoniani—*Olearia 1,* 26) and a description of solvent extraction of grape-seed oil (Bonnet—*Bull. mat. grasses inst. colonial Marseille 26,* 186). In discussing cottonseed oil extraction methods, Cole (*Oil Mill Gaz. 51,* No. 7, 36) criticized solvent systems because of the gossypol problem, production of "fines" in the meal, and cost. Fines, *i.e.,* powdery livestock feed, is undesirable.

Some laboratory experiments were undertaken to provide the information required for the design and operation of plants. Pominski *et al.* (*Oil Mill Gaz. 51,* No. 12, 33) developed data on the behavior of hexane and ethyl ether in the extraction of cottonseed, okraseed, and rice bran oil. D'Aquin *et al.* (*Ibid.* No. 10, 17) studied the effects of processing conditions on the quality of products. Crude oil obtained by solvent extraction of either cooked or uncooked cottonseed meats compared favorably in quality and grade with oil prepared by pressing. The solvent oils appeared to refine better. Crude oil from uncooked meats degraded more in color on heating than did oil from cooked meats. McCormack (*J. Am. Oil Chemists' Soc. 24,* 299) extracted acorns with butanol, using both the centrifugal and the continuous methods. The percentage of oil extracted was greater with the former method, being 73-89.5% of that present in the acorns. Progress in the solvent extraction of cottonseed with simultaneous flotation separation of the pigment glands was recorded by Vix *et al.* (*J. Am. Oil Chemists' Soc. 24,* 228). Commercial hexane and tetrachlorethylene were used as solvents. This semi-pilot-plant process was capable of producing prime oil and light colored meal. About 60-70% of the oil content of the flakes was recovered as a miscella.

Several suggestions for improving solvent extraction processes appeared as patents. Sunflowerseed should be heated to 80-120° to partially coagulate the protein (Levin — *U. S. 2.417.507*). Accessories were designed to remove "fines" from miscella (Truax — *U. S. 2,416,421*). Vibrating the filtering screens in certain extraction equipment hastened the separation of miscella from the residue (Rose, Downs, & Thompson, Ltd.—*Brit. 584,272*).

A comprehensive review on extraction solvents by MacGee (*Oil Mill Gaz. 52,* No. 2, 17) was of interest because he described the properties and discussed the advantages and disadvantages of all solvents available for the process. The analyses of commercial petroleum solvents were also recorded.

Preliminary investigations on isopropanol as an extraction solvent for cottonseed oil indicated that 91% isopropanol efficiently extracted gossypol along with the oil (Harris *et al.*—*J. Am. Oil Chemists' Soc. 24,* 370). Thus this solvent allowed production of a meal highly superior to hydraulic meal for livestock feeding. Hexane-extracted olive oil differed from pressed oil in that it contained resins, gums, and chlorophyll (Lewis—*J. Am. Oil Chemists' Soc. 24,* 315). For edible purposes the solvent oil required refining. Mortenson (*U. S. 2,416,196*) patented an extraction process in which solvents of boiling points higher than that of water were used so that extractions could be carried out at the boiling temperature of water. Dinley (*Brit. 569,497*) designed a still adapted for the purification of extracted soybean oil incident to its separation from the trichloroethylene solvent.

TALL OIL. In a review on the fatty acid composition of tall oil, Browning and Calkin (*Paper Trade J. 123,* No. 26, 45) showed the composition to be very variable, due to the differences in methods of production. Other progress with this oil dealt with improvements in processing. It was suggested that the original black liquor skimmings of crude tall oil soap be treated with sulfur dioxide and sodium bisulfite (Pollak *et al.*—*U. S. 2.430.029.* Taussky (*U. S. 2,413,009*) improved tall oil by treatment with hydrogen under pressure and with spent hydrogenation catalyst. Several patents (Palmer — *U. S. 2,432,332-3,* Freeman and Gloyer—*U. S. 2,423,232-3*) described separating the fatty from the rosin acids by a method based on increasing the polarity of the fatty acids and separation by liquid-liquid extraction or chromatographically. The polarity of the fatty acids was increased by incomplete esterification with polyhydric alcohols to produce compounds with free hydroxyl groups. Lovas and Loughlin (*U. S. 2,412,818*), for a similar purpose, reacted the tall oil with ethylenediamine to form fat acid amide waxes which were separated from rosin acids by crystallization from solvents. Harris (*U. S. 2,419,211*) found that the rosin acids could be precipitated from solutions of tall oil as salts of primary amines.

MEDICINAL OIL. In two patented procedures for fish liver oil production, the livers were heated to 65-80° in water to coagulate proteins, the water was drained, and the livers ground. At this point one inventor (Underwood—*Brit. 585,304*) dried the material and extracted with dichloroethylene; and the other inventor (Crowther—*U. S. 2,413,692*) heated the comminuted material in water and skimmed off the oil that was released.

Buxton (*J. Am. Oil Chemists' Soc. 24, 107*) recorded data on the selective solvent fractionation of various fish-liver oils with 91-99% isopropanol, 95% acetone, and 100% methanol. All of these polar solvents extracted the more unsaturated portion of the oil along with vitamin A and antioxidants. Methanol extracted only a part of the latter, while the other solvents used removed substantially all. New patents for concentrating vitamins according to the above method were assigned to National Oil Products Co. (*U. S. 2,412,561, 2,412,766, Brit. 589,336*).

A vitamin concentration method for fish oils patented by Trent (*U. S. 2,432,181*) comprised distillation after conversion of fatty acids to esters of lower alcohols; the vitamins and sterols were recovered from the still residues. Shantz (*Brit. 588,728*) converted the fatty acids of liver oils to the ethanolamides and crystallized these from the ethanol solution. The vitamin alcohols were recovered from the ethanol on evaporation. The vitamin A precursors in this concentrate were converted into vitamin A by heating (Embree & Shantz—*U. S. 2,414,458*).

In two methods for the production of carotenoid concentrates, palm oil or other oils were concentrated by selective solvents (Larner—*U. S. 2,432,021*) and by distillation (Eckey—*Brit. 567,682*). A method for making tocopherol extracts depended on selective adsorption on special activated earth from chloroform solutions (*Bull. soc. chim. biol. 24, 365*).

HYDROGENATION. Selectivity of hydrogenation, which determines the yield of each component at a given degree of hydrogenation, was reviewed by Balandin (*J. Gen. Chem. (U. S. S. R.) 16,* 557).

A new process for hydrogenation was based on atomizing the oil and catalyst in a hydrogen atmosphere (Holmboe—*Nor. 70,486*). Special heating coils and heat exchangers for this process were also patented (Holmboe—*Nor. 70,291-2*). Harwood & Binkerd (*U. S. 2,423,236*) improved the susceptibility of tall oil to hydrogenation by pretreatment with 2-10% alkali.

Most interest on hydrogenation during the year seemed to be concentrated on catalysts. In studying Raney nickel catalyst, Schmidt-Nielsen & Spillum (*Kgl. Norske Videnskab. Selskabs Forh. 17,* No. 31, 122) prepared a needle-shaped crystalline product the color of metallic nickel and corresponding to $NiAl_3$, which on treatment with lye gave a very active catalyst. Freed (*U. S. 2,424,811*) produced hydrogenation catalyst in flaked form, by suspending nickel in hard fat and flaking on drum flakers. Levin (*J. Applied Chem. U. S. S. R. 19,* 779) and Loshkarev *et al.* (*Ibid.* 800) preferred a catalyst prepared by cathodic precipitation of nickel and subsequently annealing the product in a hydrogen current at a high temperature. A method for hydrogenating fat products to alcohols made use of a mixture of copper compounds and cadmium soap as the catalyst (Procter & Gamble Co.—*Brit. 569,923*) or copper and lead soaps (Procter & Gamble Co.—*Brit. 584,939; 585,219*).

Uyeno (*J. Chem. Soc. Japan 63,* 976) reported that one active white earth proved to be the best carrier for hydrogenation catalyst; diatomaceous earth, certain local clays, kaolin, talc, and yellow ocher showed similar activity, while bauxite was inferior.

Hardening fats by elaidinization in the presence of selenium was the subject of one patent (Industreele Exploitatiemij—*Dutch 51,865*). The residual selenium in such products was removed by treatment with hydrogen peroxide (*Dutch 55,814*).

TRANSESTERIFICATION. Desnuelle & Naudet (*Bull. soc. chim. 1946,* 90, 595; *1947,* 323) continued to report data on the course of the transesterification reaction. Using tristearin and triolein with sodium methylate as the catalyst they plotted the course of the reaction at 135, 175, and 205°. The reaction in all cases tended to go to an equilibrium of the "law of probable distribution," which in American literature has been called "random distribution." The reaction was twice as rapid at 205 as at 135°. The theoretical curves of the reactions were represented by mathematical equations. New patents on transesterification were assigned to Procter and Gamble Co. (*Brit. 575,315; 590,737*).

REFINING. Fash (*J. Am. Oil Chemists' Soc. 23,* 397) emphasized the effect of the amounts and kinds of phosphatides on the amount and concentration of caustic required, the mixing time, and the amount of oil lost into the soap stock. This information was derived from using various refining technics on cottonseed and soybean oils. The deleterious effect of gums in the refining process was further emphasized by several suggestions for their removal by washing with aqueous agents before caustic refining (Thurman—*U. S. 2,415,313;* Desneuelle & Naudet—*Bull. mens. l'ITERG No. 3,* 23; Frères—*Fr. 854,568;* Mattikow—*U. S. 2,415,301*). Some of the suggestions included information on recovery of by-products, such as phosphatides, sterols, etc., from the precipitated gums. One patented refining process including degumming, extracting free fatty acids with selective solvents, and finally an alkali treatment (Black & Bollens—*U. S. 2,416,146*). Clayton *et al.* (*Brit. 571,973*) carried out refining by impinging an alkali solution mist on an oil mist, breaking the emulsion formed and separating the refined oil.

Schlenker & Gnaedinger (*J. Am. Oil Chemists' Soc. 24,* 239) pointed out that losses in refining of high acid oils could be reduced by heating, which re-esterifies much of the free acids. Thus, a palm oil containing 30.8% free fatty acid was heated six hours at 222° under vacuum and showed a loss of 1.2 grams while the free fatty acids were reduced to 16.3%. André & Cuvier (*Bull. mat. grasses inst. colonial Marseille 29,* 152) recommended that highly acid palm oils be neutralized with sodium carbonate.

A process for refining crude wool grease comprised emulsifying with soap and water, alkali treating, and breaking the emulsion with sulfonated oil (Am. Chem. Paint Co.—*U. S. 2,417,329; Brit. 580,338*). In conventional refining one inventor (Liebscher — *U. S. 2,415,140*) suggested the addition of glycerol to break the emulsion and to aid the separation of foots.

Two non-alkali oil refining processes dealt with, respectively, selectively extracting the fatty acids with polar solvents (Rius & Moreno—*Anales fís. y quím. (Madrid) 42,* 123; Moreno—*Ibid. 43* 261), and treatment with microörganisms of the class of Saccharomyces and/or acid formers as Lactobacillus (Ekhard—*Ger. 714,119, Cl. 23a*).

In decolorization of refined oils containing residual soap as compared to oil without soap there was a difference in the samples when they were viewed in the light, although Lovibond and Wesson tintometers did not show a difference (Newby—*J. Am. Oil Chemists' Soc. 24,* 378). Amounts of soap removed by centrifuging and various washings by employing bleaching earths were also recorded.

Since the bleaching of soybean oil depended principally on removal of chlorophyll, the control of the process should be governed by the chlorophyll content. Pritchett *et al.'s* (*J. Am. Oil Chemists' Soc. 24,* 225) record of the behavior of this pigment in processing indicated that 25% was removed by refining; moderate hydrogenation gave a small reduction; and deodorization had little influence. In chlorophyll removal with earth, time, temperature, and pressure in bleaching had no material effect. It was pointed out that isotherms of adsorption power of the individual earths for chlorophyll from soybean oil could be developed and form the basis for control of bleaching procedures.

Several of the communications on bleaching earths for fats and oils were descriptions of earths of various geographical origin and comparison of these with commercial samples (Paleni—*Olii minerali, grassi e saponi, colori e vernici 24,* 56, 77; Puri *et al.*—*J. Indian Chem. Soc., Ind. & News Ed. 9,* 22; Cruz—*Philippine J. Sci. 76,* No. 3, 23; Ventura—*Rev. soc. brasil quim 15,* 11). Patent activities in connection with bleaching and deodorization were improvements of efficiency of the treatments by preliminary deaerating, drying, and/or removal of soap from oils (King *et al.*—*U. S. 2,428,082;* Dean—*U. S. 2,422,185;* Lee & King—*Brit. 589,534*), and methods for bleaching with hydrogen peroxide (Lever Bros. & Unilever, Ltd. — *Brit. 577,879-80*) or alkali chlorites (Deut. Gold-u. Silber-Scheideanstalt vorm. Roessler — *Belg. 449,997;* Mathieson Alkali Works, Inc.—*U. S. 2,431,842; 2,433,661-2*). Brucke (*Ger. 723,436, Cl. 23a*) steam deodorized and removed free acids from fats by distillation in multiple stages using lower treating temperatures as the charge progressed through the stages.

Some treatments for improving oils dealt with special aspects. Castor oil was refined for dielectric purposes by first alkali refining and then repeated treatment with active earths until the electrical resistance reached a maximum (Aerovox—*U. S. 2,418,819; Brit. 581,483*). "Winter" vegetable oils were improved in stability against clouding by a special procedure for crystallization and centrifuging out of hydrophyllic and waxy components (Parkin & Walker—*U. S. 2,425,001*) and by the addition of aluminum stearate (Royce—*U. S. 2,418,668*). Equipment for cooling fats out of contact with the open atmosphere was designed by Murray (*U. S. 2,433,475*).

FATTY ACIDS. Reviews and general discussions on fatty acid production and uses were prepared by Seaman (*Soap, Perfumery, Cosmetics 19,* 821, 1023), and Marsel & Allen (*Chem. Eng.. 54,* No. 6, 104).

Lascaray (*Anales fis. y quím. (Madrid) 41,* 878) examined autoclave splitting of fats and recorded data on the course of the reaction. An increase in the quantity of water was the only factor which altered the limits of the reaction. The activity of various splitting reagents was related to the degree of hydration of the respective metal ions and their valences. The manufacture of a splitting reagent by sulfonation of a mixture of rosin acids and phenols was patented (Petrov—*U. S. S. R. 65,887*).

Allen *et al.* (*Chem. Eng. Progress 43,* 459) described equipment and pilot plant runs of the Colgate-Palmolive-Peet Co.'s continuous fat splitter. Water and fatty oil were pumped concurrently to each other in a vertical tower at 700 p.s.i. gage pressure and 250° to hydrolyze 96-99% of the glycerides and yield aqueous glycerol of 10-25% concentration.

Lipase splitting of palm oil was studied on a laboratory scale using castor beans as the source of the enzyme (Loury & Max — *Oleagineux 1,* 24). The yield of acid was slightly less from acid oils than from neutral oils. The hydrolysis produced with various 0.1*N* solutions of acids as catalytic agents was as follows: sulfuric 78, acetic 70, and formic 72%.

In the last few years there has been considerable developmental work in interchanging the glycerol of glycerides with lower alcohols as a more convenient substitute for splitting. New improvements in the process dealing with optimum conditions of reaction, separation of esters, glycerol, and unreacted alcohol, etc. were devised and patented by National Oil Products Co. (*Brit. 579,767*), Murphy & Holt (*U. S. 2,418,898*), Colgate-Palmolive-Peet Co. (*Brit. 587,523; 578,751*), and N. V. Lever Bros. & Unilever (*Dutch 59,400*).

Three patents on fractionating fatty acids involved crystallization from solutions in organic solvents. Two of the patents (Lummus Co.—*Brit. 568,203;* Lever Bros. & Unilever, Ltd.—*Brit. 582,557*) dealt with the choice of conditions, solvent, and amount of same, etc.; and the other patentee (Emery Inds., Inc.—*U. S. 2,421,157*) suggested blowing air through the cooled solution to stimulate the formation of crystals that permit easier filtration. Operational details of a plant continuously fractionating 30-40 tons of fatty acids from 90% methanol were recorded by Demmerle (*Ind. Eng. Chem. 39,* 126). The cost of the process was said to be 65% less than for the common pressing methods. The methanol-water mixture was selected as a solvent for the system because acetone, ethyl acetate, or other solvents did not yield the desirable granular needle-like crystals which were most easily filtered from solution.

In an investigation on selection of solvents for fractionating rape seed oil, furfural in the cold and methanol in warm temperatures were most efficient (Gordon—*Bull. mens. l'ITERG No. 3,* 23). Ethanol, cold methanol, propanol, carbon tetrachloride, trimethylene, tetramethylene, trichloroethane, carbon disulfide, methylal, and mixtures of some of these were unsuccessful.

Products (Except Detergents)

TABLE AND COOKERY FATS. An interesting innovation in the manufacture of food fats was the application of ester-interchange to alter the constituent glycerides and physical properties as mentioned in the preceding section. Another process to accomplish a similar purpose comprised the steps of partial hydrolysis and reesterification (Proctor & Gamble Co.—*Brit. 571,209*). During the process lower-boiling fatty acids could be removed by distillation. Shortening having an extended plastic range consisted of a liquid oil blended with 17-33% cottonseed oil hydrogenated to a titer of over 60° and less than 65° (Ziels & Schmidt—*U. S. 2,430,596*). Two new patents on shortening in powder or granular form described making small particles of fat and emulsifier mixture provided with a coating or hull of milk solids or soybean flour (North *et al.*—*U. S. 2,431,497-8*).

In margarine manufacture, adaptation of equipment originally designed for continuous ice cream manufacture tripled production and halved labor (Slaughter—*Food Inds. 19,* 1050).

EMULSIFIERS. Among the reviews on emulsions, two communications treated the theoretical aspects (Dervichian & Lachampt — *Bull. soc. chim. 1946,* 486; Nolla & Diaz—*Afinidad 21,* 540), and two authors reviewed equipment and technic (Appell—*Chimie & industrie 57,* 241; Leslie—*Manuf. Chemist 18,* 494).

Sandelin (*Finska Kemistsamfundets Medd. 54,* 53) in studies on the structure of milk emulsion described dispersions of butterfat in water using seven emulsifying agents. He suggested that breaking fat emulsions by agitation may be due to discharge of adsorbed ions by frictional electricity and if foam was formed, breaking was assisted by passage of the emulsifying agent into the foam.

Among general purpose emulsifiers, partial esters of polyhydric alcohols and fatty acids attracted most attention. Otter (*Chem. Weekblad 43,* 345) devised analytical method for analysis of partial esters of glycol or glycerol. They depended on determining monoglycerides according to Pohle *et al.*, and determining glycerol and glycol after saponification. The composition was calculated with the use of equations developed for the purpose. In a comparison of mono- and diglycerides the latter's capacity to lower interfacial tension of oil-water interfaces was less than 1/100 that of the former (Feuge—*J. Am. Oil Chemists' Soc. 24,* 49. In this work, 0.1% monoglyceride in the oil lowered the interfacial tension of oil-water interfaces to about half that observed when no monoglycerides were present; and a lowering to 0 occurred with 6% monoglycerides. In tests on the suitability of 125 organic emulsifiers for dispersing dimethyl phthalate, six partial esters of polyhydric alcohol and fatty acids were most satisfactory (Morton — *Proc. New Jersey Mosquito Exterm. Assoc. 33,* 69). Presslie (*Pharm. J. 157,* 185) discussed the usefulness of these esters for ointment bases. Newly patented emulsifiers of the partially esterified type were reaction products of glycol, glucoside, ethylene oxide, stearic acid (Griffin—*U. S. 2,407,002*), and a condensation product of sorbitan monostearate and ethylene oxide (Johnston —*U. S. 2,422,486*). The use of emulsifiers of this general type was patented for dispersing synthetic rubber-like material in the manufacture of protective coating solutions (Holmes—*U. S. 2,414,740*), for emulsifying fat-soluble vitamins (Freedman and Green—*U. S. 2,417,299*) and margarine (Petersen—*U. S. 2,422,633*), and for improving the texture of ice cream (Brown & Phelps—*Re. 22,858* of *U. S. 2,065,398;* Landers—*U. S. 2,423,600;* Nelson—*U. S. 2,423,613*)

Several other emulsifiers were used for various purposes. A clear emulsion of soybean lecithin in 90% lactic acid solution was prepared for bakery purposes (Christlieb—*Ger. 708,805, Cl. 2c*). The use of castor oil fatty acids and organic dicarboxylic acid reaction product as an emulsifier for polyvinyl butyral was patented (Geiges—*U. S. 2,431,800*). Sodium lauryl sulfate was recommended as the most suitable emulsifier for cold creams (Macias-Sarria—*Am. Perfumer 48,* No. 9, 61). Alkali mahogany sulfonate was added to paint to inhibit thixotropic tendencies (Althouse — *U. S. 2,419,048*). An organic solvent-lactic acid-wax mixture used as a paint remover was emulsified with sulfonated castor oil (Packer—*U. S. 2,418,138*). A dry vitamin A concentrate was prepared by dispersing the vitamin A oil in molasses and dehydrating with calcium oxide (Briod & Buxton—*U. S. 2,427,520*). Another vitamin concentrate contained vitamins A and C, respectively, dissolved and dispersed in a solid fat (Chanin—*U. S. 2,426,762*).

From the mineral oil producing industry, the emulsion literature of interest to chemists in the fatty oil field pertained to using surface active fat derivatives to break emulsions formed during treatment of petroleum bearing rock strata with mineral acids to release the petroleum from the strata. The demulsifiers were subresinous amines, amides, or esters of fatty acids, particularly ricinoleic acid (Petrolite Corp., Ltd.—*U. S. 2,417,738-40; 2,422,177; 2,422,822; 2,423,364-5; 2,426,489-90; 2,429,996-9; 2,430,000-4*).

PROTECTIVE COATING PRODUCTS. Among the review papers, Sfiras (*Ind. Parfumerie 2,* 114) discussed generally the mechanism of bodying reactions and utilization of the products. Drinberg's (*J. Applied Chem. (U. S. S. R.) 19,* 251, 258) paper on the same subject also included information on the aging of films. Hilditch (*J. Oil & Colour Chem. Assoc. 30,* 1) stressed considering double bonds as systems and the importance of their positions in the fatty acids. Bradley (*Ibid.* 225) drew attention to conjugation and the Diels-Alder reaction as the principal mechanism. Champetier and Petit (*Bull. soc. chim. 12,* 680, 689) supported this theory with analyses to show that polymers of ethyl esters of linseed oil fatty acids were dimers and contained aromatic nuclei. Bernstein (*J. Polymer Sci. 1,* 495) proposed a new mechanism in which he indicated that there were reactions at nonconjugated bonds, and he assumed differences in rates were influenced by certain *cis-trans* geometric isomers. New contributions to a very comprehensive review on drying of oils have just recently become available. This series of papers, which was prepared by Schafer (*Fette u. Seifen 50,* 356, 399, 481, 522, 555; *51,* 12) was entitled *Physical Chemistry of Lacquer* and now contains 2,753 references to literature and patents. A shorter treatise on this subject was prepared by Powers (*Paint Ind. Mag. 62,* 268). General papers of limited aspects treated preparation of bodied oils with the use of sulfur dioxide (Cannegieter—*Verfkroniek 19,* 126), new equipment for bodying oils (Barnebey—*Can. Paint & Varnish Mag. 21,* No. 3, 26), and a description of a fume scrubber for bodying kettles (Dittmer—*Chem. Eng. 54,* No. 3, 110).

Lundberg & Chipault (*J. Am. Chem. Soc. 69,* 833) studied the early stages of the bodying of methyl linoleate at temperatures between 40 and 100°. A small fraction of the oxygen which did not appear in the peroxides, that were formed during oxidation, increased with increasing temperature. These secondary products showed an ultraviolet absorption at 2775Å, and the changes occurring in absorption upon addition of alkali suggested that the products were of ketonic character. In another study on the early reactions during bodying, Schauenstein *et al.* (Fette *u. Seifen 51,* 401) suggested that the mechanism of the catalyst was to accelerate formation of conjugated systems.

Because various oils behave differently during bodying, physical and chemical characteristic data and curves taken during bodying form the most suitable basis for planning the operations. In this connection Kaufmann & Keller's (*Fette u. Seifen 51,* 404) data were on dehydroxylated castor oil, lallemantia oil, and linolenic acid. They pointed out the conditions under which conjugation and polymerization occur for each product. In work on linseed and sardine oils, O'Hare & Withrow (*Ind. & Eng. Chem. 39,* 101) recorded the conventional drying constants and demonstrated a relationship of these to the dielectric constant and ultraviolet absorption measurements. They believed that the latter characteristic, when more data are developed, should aid in the elaboration of the theories on mechanism of oil oxidation. Cannegieter's (*Paint Oil & Chem. Rev. 110,* No. 4, 17) data were on polymerization of linseed oil with and without the influence of sulfur dioxide and were intended to serve as a basis for development of equations for calculating the bodying times required to reach specific viscosities. Literature data on tung and oiticica oils were used to calculate constants for the equations for application to treatment of the oils. Addition of sulfur dioxide to an oil increased the value of the constant required for the bodying equation in proportion to the amount added.

A newly developed procedure for preparing bodied oils comprised bodying a good drying oil to the consistency of a gel and dispersing it into an unbodied oil. Application of the method to castor oil (Berger *et al.*—*U. S. 2,418,921*), and oiticica oil (Berger *et al.*—*U. S. 2,418,920*) was patented. Another patent dealt with making use of the seed oil of *Sterculia foetida* by bodying it with certain other oils (Koninklijke Ind. Maatsch. voorheen Noury & v. d. Land N. V.—*Dutch 58,517*).

The methods for improving the drying qualities of oil products varied considerably. Nonconjugated double bonds in certain oils were converted to conjugated structures to improve drying properties by heating the oils with organic acids of less than five carbon atoms (Nessler & Penoyer—*U. S. 2,425,200*) or by partial saponification under anhydrous conditions and below the decomposition temperature (Auer—*U. S. 2,418,454*). Privett *et al.* (*J. Am. Oil Chemists' Soc. 24,* 204) analyzed the products produced in linseed oil under various polymerization conditions to develop data on the selectivity of the reaction. This information provided a basis for manufacture by selective solvent segregation of a series of oils with a wide range of properties. Lower saturated primary alcohols were used as solvents for isolating polymers from polymerized drying oils according to a patent issued to Bernstein (*U. S. 2,423,751*). Goebel (*Ibid.* 65), and Eckey & Taylor (*U. S. 2,413,613*) described newly improved processes in which the fatty acids were dimerized; the former gelled out the dimers by converting to polyamides with ethylenediamine, and the latter removed unpolymerized material from the dimers by distillation. The drying properties of dehydrated castor oil were improved by heat treatment with maleic anhydride and linseed oil (Bolley—*U. S. 2,414,712*). Some drying oils were improved by addition of unsaturated fatty acid esters of hydroxydihydronordicyclopentadiene (Bruson—*U. S. 2,414,089*) or pentahydric alcohols (Auer—*U. S. 2,422,175*). A novel method of improvement comprised converting the oils to mono- and diglycerides and reacting with di-, tri-, or tetraisocyanates (I. G. Farbeninds. A.-G.—*Belg. 450,537;* Rinse—*Verfkroniek 20,* 166). Two patented methods involved additions of certain synthetic resins (Pratt—*U. S. 2,422,259;* Whitmer—*U. S. 2,420,390*). Sankaranarayanan (*J. Sci. & Ind. Res. (India) 5B,* 53) recommended dissolving 15% by weight of shellac in linseed oil in order to make films that give baked finishes with good mechanical and electrical properties. Falkenburg *et al.* (*J. Am. Chem. Soc. 69,* 486) prepared baked film material by converting the oils to fatty alcohols and esterifying with orthosilicic acid. Baked films of the orthosilicates of soybean alcohols were hard and had excellent resistance to cold water, hot water, and cold dilute alkali.

The patents on converting castor oil to a drying oil by dehydroxylation dealt with heating in the presence of organic tungsten compounds (Rheineck & Crecelius—*U. S. 2,415,969*), sulfur dioxide (Dussollier—*U. S. 2,433,077*), and aluminum phosphate (Bockel—*Dutch 56,588*) as catalysts. Tall oil drying oils were prepared by fractionally distilling and then heating select fractions with magnesium metal (Berström *et al.*—*Swed. 117,543*), by esterifying with fusel oils (Järvelan Tehtaat o/y.—*Norw. 71,841*), by esterifying with pentaerythritol (Martin—*U. S. 2,421,842*), and by manufacture of the di- and tripentaerythritols, and condensing with maleic anhydride (Vander Valk & Burrell—*Paper Trade J. 123,* No. 20, 53). The drying properties of linseed oil were improved by heating with sorbic acid and glycerol (Barthel—*U. S. 2,420,694*). Two patented varnish oils were prepared by adding certain oil-derived resins to drying oils (Scott—*U. S. 2,417,327;* Balassa—*U. S. 2,424,730*).

Various treatments were used to produce coating oils that dry to a wrinkle finish. In one case special combinations of driers and china-wood oil fatty acids were added to the drying oil (Waldie—*U. S. 2,414,006*). Another composition comprised dehydrated castor oil rosin-modified phenol-formaldehyde resin subjected to oxidation bodying until a desired viscosity was attained (Waldie—*U. S. 2,419,238*). Heating oil with a small amount of sodium (Williams—*U. S. 2,428,901*) or ethyl cesium (Williams—*U. S. 2,431,357*) also induced the wrinkling characteristic.

The technics for manufacture of drying oil emulsions or coating compositions from oils that were thinnable with either water or oil were reviewed by Paxon (*Paint Manuf. 31,* 368). Some new patented products of this type were a drying oil emulsified in water with rosin soap and borax (Miller—*U. S. 2,426,277*), and some nonsoap emulsified product adjusted to a pH of 5.7 to 8.4 and bodied while dispersed in water (Auer—*U. S. 2,418,451-3*).

A classification of metal linoleates in order of decreasing activity as drying catalysts for linseed oil was as follows: cobalt, ferric, ferrous, manganese, lead, cesium, chromium, nickel, zirconium, berylium, thallium, cadmium, uranium oxide, aluminum, thorium, barium, calcium, and magnesium (Pagani—*Ann. chim. applicata 37,* 12). Anderson (*Paint & Varnish Production Manager 27,* No. 7, 178) investigated the driers from the standpoint of the film characteristics with regard to hot and cold water, alkali, and soap resistance. The use of 0.05% cobalt, and 0.50% lead, plus 0.1% calcium to stabilize the lead, based on the oil was recommended. Crandall & Schlesman (*U. S. 2,425,671*) designed apparatus for bodying oils with boron triflouride as the catalyst. The aim was to avoid local gelation due to high local concentrations of the catalyst.

RESINS. The most modern Canadian alkyld resin plant was described by Nelson (*Can. Chem. Process Inds. 31,* 210). His economic review of the industry showed that, of 808 million pounds of plastic produced in the United States, 304 million pounds were used for protective coatings, and 108 million pounds were of the alkyd type. An alkyd resin produced from mono- and diglycerides of dehydrated castor oil fatty acids, shellac, and maleic acid yielded films suitable for use as an insulating varnish (Carrick—*Am. Paint J. 31,* No. 47, 70). Another resin prepared from maleic anhydride, a drying oil, sodium silicate, and ammonia was designed for manufacture of water dispersible coatings (Ellerman—*U. S. 2,423,230*). Gerhart & Adams (*U. S. 2,423,234*) prepared alkyd resins by reacting fatty acids with the reaction product of dicyclopentadiene and maleic anhydride. Alkyds were rendered less viscous by reacting with a small excess of polyhydric alcohol and then esterifying the free hydroxyl groups consequently formed with acetic acid (Gould—*U. S. 2,418,633*).

The reaction products of sulfur and fats were the subject of three communications. Cowan *et al.* (*Ind. Eng. Chem. 38,* 1138) cured the polyesters of polymeric fatty acids with sulfur to yield a vulcanizate that was superior to factice in tensile strength and elongation. Stamberg (*U. S. 2,422,049*) described a method of partially vulcanizing fats and sulfur to yield a product whose aqueous dispersions solidified spontaneously. The sulfurized products of Church (*U. S. 2,425,597*) were obtained by reaction of fats and resins with sulfur dissolved in organic solvents.

A relatively new series of plastics was made by acylating proteins with fatty acids (Gordon *et al.*—*Ind. Eng. Chem. 38,* 1239, 1243). Thus palmitoyl casein was found insoluble in water, dilute acids, and common organic solvents but soluble in ethylene chlorohydrin and β-chloro allyl alcohol; and it was more stable to dilute alkali than acetylated casein. Similar products were made from C_8 to C_{18} fatty acids and from egg albumin, zein, wheat, gluten, and α-soybean, θ-soybean, peanut, and cottonseed proteins. Some of their characteristics were recorded. Subsequently, the products were hardened with formaldehyde. The process improved the molding and water resistance character. Paterek (*U. S. 2,433,783*) patented an emulsified mixture of protein and oil for use as a paint.

A miscellaneous group of plastics or resins of fat derivation included heat treated mixtures of allyl ester of a carboxylic acid and tall oil (Bent & Peterson—*U: S. 2,424,074*), inter-condensation products of resin acid chloride and fatty acid chlorides (Gilbert —*U. S. 2,424,026*), reaction product of polymerized fatty acid esters, rosin and trialkanolamine (Brown—*U. S. 2,416,433*), and inter-esterification products of drying oils and lower aliphatic acids, such as citric, malic, and tartaric acids (Lasher—*U. S. 2,416,485; 2,422,356*).

Also in connection with resins, fatty acid products were used as plasticizers for vinyl resins (Sorg—*U. S. 2,414,399;* Martin—*U. S. 2,426,316*), and for the rubber-like smilax resin (Muir—*U. S. 2,413,842*).

FAT DERIVED ESTERS, ALCOHOLS, KETONES, CHLORIDES, ETC. In a measure of the kinetics of esterification of fatty acids with methyl and ethyl alcohol, Loury & Mellier (*Bull. soc. chim. (France) 1947,* 349) found esterification with methyl alcohol was most rapid and that sulfuric acid was not as good a catalyst as hydrochloric or certain aromatic sulfonic acids. At least twice the theoretical amount of alcohol was required for obtaining the most efficient yields of esters. Swern *et al.* (*J. Am. Chem. Soc. 69,* 2439) prepared the vinyl, allyl, 2-chloroallyl, methallyl, crotyl, 3-buten-2-yl, furfuryl, and oleyl esters of oleic acid and recorded their properties. Ascorbic and iso-ascorbic acids were esterified with fatty acids to improve their compatability with fats for use as antioxidants (Hoffmann-LaRoche, Inc. — Brit. *579,333; 585,828*). Such esters retained antiscorbutic activity comparable to an equivalent amount of the ascorbic acid (Ambrose & DeEds—*Arch. Biochem. 12,* 375).

Hansley (*Ind. Eng. Chem. 39,* 55) described the industrial production of fatty alcohols from fats by reduction of the fats in xylene or toluene solution with metallic sodium. The process was said to compare favorably with catalytic hydrogenation because of the simplicity of operation and equipment. Palfray & Anglaret (*Compt. Rend. 223,* 860), in studying the reaction of sodium with butyl oleate in butanol, postulated that sodium adds to the ester to form the intermediate $RC(OR')ONa$, which is hydrogenated to $RCH(OR')ONa$. The latter lost $NaOR'$ to form an aldehyde which immediately reduced to a primary alcohol or underwent the Tishchenko reaction to form $RCOOCH_2R$, which yielded RCH_2OH by a repetition of the mechanism.

Kaku *et al.* (*Bull. Inst. Phys. Chem. Research (Tokyo) 22,* 357) applied Grignard's reagent in the preparation of several tertiary alcohols from fats. 1,1-Dibenzyldodecyl, 1,1-dimethyldodecyl, 1,1-diphenyldodecyl, and 1,1-dicetyldodecyl alcohols were synthesized and some of their properties were recorded.

Sulfated fatty acids and their esters were oxidized to manufacture pelargonic and azelaic acids (National Oil Products Co.—*Brit. 585,315*). Sulfation of oleic acid, followed by hydrolysis, yielded 9-hydroxyoleic acid in 86% yield (Roe *et al.*—*J. Am. Oil Chem. Soc. 24,* 45). Commercial oleic acid gave only a 72% yield in the same operations, because some polymers and dihydroxyoleic acid were formed from the linoleic acid present in the starting material. Goswami *et al.* (*Science and Culture 12,* 555) reported that passing air through peanut oil at 70° with nickel catalyst gave a hydroxylated oil similar to castor oil. Esters of hydroxy fatty acids and tetrahydrofurfuryl alcohol were prepared in good yields by Knight *et al.* (*J. Am. Chem. Soc. 69,* 717). These were hard, waxy, solids. Hargreaves & Owen (*J. Chem. Soc. 1947,* 750) recorded that ricinoleic acid, the most common natural hydroxy acid, undergoes alkali scission, probably by first forming methyl-hexyl ketone and 10-hydroxydecanoic acid, which compounds interact to give methyl-*n*-hexylcarbinol, sebacic acid, and hydrogen.

Attempts to make fatty aldehydes by reaction of soaps with formaldehyde by Reutenauer & Lacombe (*Bull. mens. l'ITERG, No. 2,* 19) were unsuccessful.

With greater interest in fatty acid derivatives more attention was paid to fatty acid chlorides which could serve in the manufacture of many derivatives. In a study of these, Bauer & Curet (*J. Am. Oil Chemists' Soc. 24,* 36) recorded that, in general, the chlorides of the longer-chain acids hydrolyzed in water at a more rapid rate than those of shorter-chain acids. Lauryl chloride, however, appeared more resistant to hydrolysis than the chlorides of C_8 to C_{10} and C_{14} to C_{18} saturated acids. The chlorides of unsaturated C_{18} acids were hydrolyzed more rapidly than stearyl chloride. Some of the structural and orientation characteristics of chloroethyl esters of C_{12} to C_{18} saturated fatty acids were elaborated from x-ray studies (Brenet — *J. Phys. Radium 7,* 139). Condensation products of C_{14} to C_{18} fatty acid chlorides and several naphthalene compounds were synthesized and their properties recorded (Desai & Waravdekar — *Proc. Indian Acad. Sci. 24A,* 332, 338, 382, 389). The manufacture of reaction products of fatty chlorides and piperazine was patented (Buck & Baltzly—*U. S. 2,415,787*). The products were useful as intermediates for the preparation of various other products.

A method of desaturation of fatty acids depending on chlorination and dechlorination was investigated from the standpoint of most suitable conditions for dechlorination (Van Atta—*J. Am. Oil Chemists' Soc. 24,* 149, 209). Vapor phase removal of chlorine was rapid and nearly complete at low pressure and temperatures of 220 to 315°. Polymerization of the liquid unsaturated material was prevented by maintaining the pressure of the hydrogen chloride liberated in the reaction at less than two millimeters. The products from dichlorinated palmitic acid contained 20% of γ-lactones and some conjugated unsaturation; and the product from chlorinated oleic acid when esterified with glycerol was capable of forming drying films.

Fat Derivatives Containing Nitrogen. Reutenauer & Paquot (*Inds. corps gras 3,* 176; *Compt. Rend. 223,* 578) contributed improvements on laboratory manufacture of nitriles and amine fat derivatives. These comprise principally the optimum conditions for best yields of nitriles from certain fatty acids. Their latest means of converting the nitriles to amines consisted of hydrogenation in alcohol solution saturated with ammonia. Reutenauer & Lacombe (*Oleagineux 2,* 500) demonstrated that the manufacture of nitriles from fats and oils instead of the fatty acid was possible. The yields were lower, but several advantages could be gained in commercial operations. Equipment for commercial manufacture of fatty acid nitriles was designed by Potts (*U. S. 2,414,393*). An improvement in the efficiency of commercial hydrogenation of nitriles to amines was obtained by addition of the high-boiling residue of the process to succeeding hydrogenation batches. (Stegermeyer—*U. S. 2,408,959*). Thus the yield of octadecylamine was raised from 64 to 84%.

Richet (*Bull. soc. chim. 1946,* 52) prepared the chlorides, amides, and amines of lauric, palmitic, stearic, and oleic acids by the usual methods and recorded yields obtained. Harwood & Ralston (*J. Org. Chem. 12,* 740) synthesized lauric acid and dodecylamine containing C^{14} in the 1-position as predecylamine containing C_{14} in the 1-position as preliminary work to the study of the mechanism of mineral flotation using radio active technic. Some of the carboxydicyanodiamides mentioned as useful as intermediates in synthesis of dyes, resins, etc., were fat derivatives (Am. Cyanamid Co.—*Brit. 586,633*). A procedure for analysis of fatty acid amides depended on the amount of potassium hydroxide required to saponify one gram of the amide (Olsen—*Die Chemie 56,* 202).

Ralston *et al.* (*J. Am. Oil Chemists' Soc. 24,* 307) suggested six procedures for preparation of Werner type complex compounds of metal salts and fatty acid amines. The products had moldicide properties and their use for treating fabrics was suggested. Reck *et al.* (*J. Org. Chem. 12,* 517) tabulated and graphically recorded the solubilities of dodecyl- and octadecyltrimethyl-ammonium chlorides in 10 organic octadecyltrimethylammonium chlorides in 10 organic solvents. No relationship was apparent between the solubilities and the polarity of the solvent. Bouquet (*Inds. corps gras 2,* 376) prepared a comprehensive review on methods of preparation of fatty acid amines, amides, and nitriles. Another review by Ralston (*Chem. Eng. News 25,* 836) on chemicals from fats dealt principally with the derivatives containing nitrogen.

Soaps of Polyvalent Metals. A hydroxy copper soap of mixed naphthenic and fatty acids was manufactured for use as a fungicide and insecticide (Minich—*U. S. 2,423,611*). One copper soap fungicide was prepared in the presence of ammonia so that it would be substantially soluble in water (Roon—*U. S. 2,423,619*).

Weber & Hamblet (*U. S. 2,416,074*) manufactured lead soaps by passing alkyl esters of fatty acids and water over fine lead while bubbling oxygen through the mixture. Gebhart & Ross (*U. S. 2,417,071*) mixed sodium soap solutions with dissolved aluminum salts in stoichiometric proportions in manufacture of aluminum soaps. Another patented process also dealt with special methods of mixing reactants (Trapeznikow—*U. S. S. R. 66,893*).

Esters of polyethylene glycol and fatty acids were used to disperse insoluble metal soaps in an aqueous medium (Retzsch & Lighthipe — *U. S. 2,425,828*). Palit & McBain (*J. Am. Oil Chemists' Soc. 24,* 190) reported that soaps of polyvalent metals were soluble in mixtures of chloroform and glycol and could be titrated directly in the mixture with acid. The remainder of the information on insoluble metal soaps pertained principally to lubricant manufacture.

Lubricants. The field of lubricant manufacture and use was enriched by new fundamental research reports on the characteristics of soaps as related to their behavior as lubricants. The densities and flow properties of sodium soaps from C_6 to C_{18} saturated fatty acids have been measured at 30-300° and the results were correlated with the properties of dispersion of the soaps in mineral oil (Southam & Puddington—*Can. J. Res. 25B,* 121, 125). The experimental results on the formation of lyophilic dispersions of the soap in mineral oil agreed with the theory that soaps giving bi-dimensional melting points were capable of forming stable emulsions. Large changes were found in the properties of stearate soap at 68 and 105°. An interesting abrupt change, loss of bi-dimensional melting point, and dispersion capacity also occurred when the number of carbon atoms in the soap was reduced below eight. The flow changes were attributed to loosening of the bonds in one dimension and the consequent provision of easier slip planes. Smith & McBain (*J. Phys. & Colloid Chem. 51,* 1189) determined the phase diagrams of sodium stearate-hydrocarbon at temperatures from 25 to 310° for 12 hydrocarbons. All phase diagrams exhibited: (a) a two-phase gel, (b) a golden or orange liquid-crystal phase, (c) a white, wax-like liquid-crystal phase, (d) an isotropic solution, and (e) an isotropic jelly, continuous in phase with solution. Smith (*J. Am. Oil Chemists' Soc. 24,* 353) also correlated the physical properties of lubricant soaps with thickening, dispersion, texture, effect of additives, and stability of soap hydrocarbon lubricants.

The structure and properties of aluminum dilaurate gels and jellies were the subject of several reports. Marsden *et al.* (*J. Colloid Sci. 2,* 265) showed by x-ray studies that gels were formed in benzene and cyclohexane without greatly disturbing the diffraction pattern of the soap; on further heating the crystals disappeared, and oriented soap layers were probably formed. McBain & Working (*J. Phys. & Colloid Chem. 51,* 974) in similar work used viscosity measurements and observed a rapid increase in molecular weight with concentration, an increase in relative viscosity with temperature, and a decrease in viscosity on aging and dilution. The observations indicated that the soap in benzene was an association colloid. Shreve (*Ibid.* 963) reported that aluminum dilaurate at 50° absorbs less than three per cent and at moderate humidities less than one per cent moisture.

Nissan & Garner (*J. Inst. Petrol. 33,* 71) compared viscosity readings of aluminum and calcium soaps in hydrocarbons by capillary, rotational, and falling-sphere methods and discussed their individual suitability for the study of greases. A viscosity study of lithium, aluminum, calcium, and sodium soaps in two mineral oils, by Roehner & Robinson (*Inst. Spokesman 10,* No. 12, 4), indicated the effect of the concentration of each soap, effect of service, and the effect of temperature.

Gregory & Spink (*Nature 159,* 403) described the lubricant properties of calcium stearate and stearic acid on metal surfaces. On copper surfaces there was an increase in the coefficient of friction constant at the melting point of stearic acid; the liquid acid reacted to form the copper soap and the friction constant fell to its original low value. The minimum number of layers required for lubrication were one for stainless steel, three for copper, and five for platinum. Calcium stearate did not lubricate copper or platinum.

Two reports described methods of examining lubricant greases by the electron microscope (Ellis—*Can. J. Res. 25A,* 119; Farrington & Birdsall—*Oil Gas J. 45,* No. 46, 268, 293). In general most of the soap fibers of the greases were in the form of twisted strands, while the others were rods or ribbons. The length-to-width ratios varied from 10:1 to 200:1.

In regard to the technology of grease manufacture, Hobart (*Inst. Spokesman 11,* No. 3, 6) briefly reviewed recent progress; and Georgi & Stucker (*J. Am. Oil Chemists' Soc. 24,* 15) discussed the properties of sodium, calcium, aluminum, lithium, and barium soap greases and recorded statistical data on the consumption of oils in their manufacture.

A small grease kettle for experimental manufacture of greases was supplied with mixing devices to improve mixing, eliminate channeling in the grease, and allow manufacture of batches in a short time (Bergmann—*Ind. Eng. Chem. 39,* 498). Houlton *et al.* (*Chem. Eng. Prog. 43,* 399) described the Standard Oil Co.'s continuous lime grease plant which manufactures the soap and blends it with lube oil at the rate of 60 pounds per minute. They claim that material, labor, and floor-space saving over batch methods were sufficient to amortize the plant in about one year's time. A similar plant for aluminum soap grease with a capacity of 1,500-2,000 pounds per hour was described by Moulton *et al.* (*Inst. Spokesman 10,* No. 9, 4). The dissolving of the soap, blending with mineral oils, and gelling to a uniform consistency were accomplished in "Votators." Houlton (*U. S. 2,417,495*) improved the mixing procedures for a continuous grease plant. A newly patented continuous process by Thurman (*U. S. 2,433,636*) included the steps of melting the soaps, dehydrating, mixing with lube oil, and cooling.

Georgi & Stucker (*Inst. Spokesman 11,* No. 3, 18) recorded optimum temperatures required for dispersion of lithium, calcium, aluminum, barium, and sodium soaps in mineral oil for the manufacture of greases. Worth & McLennan (*Oil Gas J. 45,* No. 43, 74) reported that greases made from strontium soaps were particularly water resistant, stable at high temperatures, and efficient over wide temperature ranges. A method of making aluminum soap grease with a high measure of gelling effect involved maintaining the pH below 7 during the reaction (Edwards—*Brit. 587,522*). Syneresis was inhibited in grease gels by the presence of small amounts of naphthenate soaps (Meyer—*U. S. 2,409,950*). Aromatic amines were added to lithium greases to inhibit corrosion (Standard Oil Development Co.—*Brit. 578,961*). A special patented soda grease contained 70% lube stock, 20% stearate soap, and an antioxidant (Morgan & Lowe—*U. S. 2,428,123*). A method for the manufacture of lithium grease comprised mixing a suspension of finely divided lithium in mineral oil with a solution of fatty acids in mineral oil (Bell—*Brit. 583,303*). A patented grease mixture contained lube stock, castor oil, alkyl phosphate, bentonite, and lithopone (Vande Bogart & Manuel—*U. S. 2,412,929*). Another group contained inorganic salts in addition to the soaps and lube stock (McLennan—*U. S. 2,417,428-33*). A grease for under-water crafts contained chlorinated aromatic compounds, lithium, soaps, and other metallic soaps (Morway & Zimmer—*U. S. 2,420,902*).

One series of papers reported the development of a series of organic diesters very suitable for use as synthetic lubricating fluids (Bried *et al.*—*Ind. Eng. Chem. 39,* 484; Atkins *et al.*—*Ibid.* 491; Hain *et al.*—*Ibid.* 500). Although the primary products were not fat derivatives, the articles should be of interest to the fatty oil chemist, for the compatibility of the products with lubricant soaps and technic for blending them with the soaps for manufacture of greases were given.

Many patented lubricant improvers were fat derivatives. The innovations in those dealing with sulfurized fatty derivatives dealt with technic of manufacture, use of additional additives to reduce corrosion, or the choice of the fatty raw material, i.e., soaps, lecithins, fatty alcohols, fatty waxes, and fatty nitrogen derivatives (Lincoln & Byrkit—*U. S. 2,415,296, 2,421,631;* Musselman—*U. S. 2,415,836-8, 2,422,206;* McNab & Fleming—*U. S. 2,420,893;* Yule & Moir—*U. S. 2,420,280;* Williams & Backoff—*U. S. 2,420,274;* Watkins—*U. S. 2,416,807;* Fuller *et al.*—*U. S. 2,411,153*). The patentees made various claims for these, such as: improvement of viscosity, film strength, anticorrosiveness, antisludge characteristics, oiliness, etc. The lubricant additives particularly claimed as pour-point depressives were: condensation product of fatty acid nitriles and fatty acid or aromatic halides (Lieber — *U. S. 2,415,699*); lithium, zinc, and tin soaps (Morway & Zimmer—*U. S. 2,417,264*); a sulfurized aluminum stearate and mahogany sulfonate mixture (Murphy & Foust — *U. S. 2,423,789*); and compounds formed from fatty alcohols by diene synthesis (Blair—*U. S. 2,422,881*). Hodges & Rogers (*Oil-Gas J. 46, No. 22,* 89) developed a procedure for laboratory evaluation of pour-point depressants which gave results agreeing with field tests. The following lubricant additives were used principally for inhibiting corrosion: fatty acid-piperidine salts (Barker—*U. S. 2,412,956*), a reaction product of fat and dicarboxylic acid and fats condensed with fatty acid amines (Blair—*U. S. 2,426,338*), halogenated keto acids synthesized from fats (National Oil Products Co.—*Brit. 578,945*), partial soaps of polyvalent metals and the same treated with amines or ammonia gas (N. V. de Bataafsche Petroleum Maatschappij — *Dutch 53,293-4*), mixtures of fatty thiophosphoric acid esters and oil-soluble metal sulfonates (Lewis & Schott—*U. S. 2,417,876*), mixtures of petroleum sulfonates, castor oil, castor oil acids, monoglycerides, and sulfurized terpene (Schwartz — *U. S. 2,412,633-4*), reaction products of fatty acid amines with metal salts of diene synthesis derivatives of fats (Smith & Cantrell—*U. S. 2,408,102-3*), nitrogenated cephalin (Trueger & Sprague—*U. S. 2,422,321*), and the reaction product of a fatty acid phosphate and a branched-chain alkylamine (Turner—*U. S. 2,413,852*). The viscosity of petroleum oils was improved with special fatty polyamides (Blair—*U. S. 2,412,*557), polyesters of glycol and dimerized unsaturated fatty acids (Sparks & Young—*U. S. 2,424,566*), and oxyesters such as butyl acetyl ricinoleate, methoxyethyl oleate, diethylene glycol monolaurate, etc. (Evans & Young—*U. S. 2,411,150*). Detergent properties were imparted to mineral oil lubricants by addition of a mixture of calcium octadecylate and the reaction product of *p*-cresol with isobutene (McNab—*U. S. 2,419,360*) and by derivatives containing polyvalent metals and fatty acid and phosphoric acid radicals (Farrington—*U. S. 2,416,985*). Heavy metal soaps of phosphorized wax hydrolyzates added in small amounts to lubricant oils reduced wear and lacquer deposition and increased film strength (Engelke & Odell—*U. S. 2,411,032*). The addition of a fatty acid alkylene diphosphate (Smith & Cantrell—*U. S. 2,411,671*) inhibited foam in lubricants; and fatty acid amines (Duncan & Zimmer—*U. S. 2,420,068*) imparted resistance to water, such as to prevent formation of emulsions and inhibit leaching out of certain compounding agents.

Fatty acid amides and polyamide (Robinson & Kelley—*U. S. 2,425,392-3*), as well as partial esters of polyhydroxy alcohols and fats condensed with ethylene or propylene oxide (Brown—*U. S. 2,418,752*), were recently patented as textile lubricants.

The newly patented cutting oils were a mixture of fatty oil distillation residue, pine oil alkyl phosphate, emulsifying agent and water (Shipp & Pedersen—*U. S. 2,420,328-9*), and a blend of certain mineral oil fractions and lard oil (Hunter & Hobart—*U. S. 2,413,353*). Some compositions of soap, fatty acid monoglyceride, and water (Myers & Muckerheide—*U. S. 2,421,158-9*) and a paste of finely dispersed sulfur in fatty oils (Buxbaum—*Ger. 709,289, Cl. 23c*) were patented for use as cutting oil bases. Brewington (*J. Applied Phys. 18, 260*) suggested that a relation exists between physical properties of an oil and cutting ratios in machining metals, and he indicated that studies on the surface energy and rate of diffusion of the agent should prove valuable in developing oils and for protecting cutting tools. A lubricant for cold-rolling of steel comprised a water emulsion of palm oil and mineral oil containing magnesium sulfate (Carmichael & Roehner—*U. S. 2,425,174*).

MISCELLANEOUS PRODUCTS CONTAINING FAT OR FAT DERIVATIVES. Water repellancy was imparted to textiles by treatment with fatty acid amido-methylene-quaternary-ammonium chloride (Hartsfield—*U. S. 2,419,399*), fatty acid amido-methyl-ether of glycolic acid (Imperial Chemical Industries, Ltd.—*Brit. 583,031*), a reaction product of a tertiary amine with a reaction product of a mixture of formaldehyde, a silicone halide and a fatty acid amine (MacKenzie—*U. S. 2,415,017*), a reaction product of paraformaldehyde and behenic-acid-amide (Pikl—*U. S. 2,426,790*), a water suspension of drying oil, bodying catalyst, and lime (Witbaard—*Dutch 53,616*), and a reaction product of diheptadecyl ketone and fatty acid amine (Zerner — *U. S. 2,413,024*). Reaction products of fatty acid amines, fatty acid guanidine salt of aliphatic carbamic acid, and ethylene oxide imparted a softness to textiles which remained highly permanent with laundering (Vitalis & Lynn—*U. S. 2,427,242*). Cloth treated with the germicide and fungicide, didodecylbenzotriazolium bromide retained its antiseptic properties even after three washings (Valko & Dubois —*Can. 439,923*). A new sizing and dressing for artificial silk consisted of a water solution of ethanol, abietate soap, triethanolamine, sodium sulforicinoleate, and mineral oil (Bergier & Helbronner—*U. S. 2,415,408*).

Some of the recent leather lubricants and treating agents were: fatty oils sulfured at 250° and then reacted with alkali sulfide (Pfestorf—*Ger. 709,185 Cl. 12o*), ammonia reaction products of certain by-products of oxidation of paraffin with air (Bohme Fettchemie G.m.b.H. — *Belg. 449,130*), esterification of the saponifiable and unsaponified fractions of the same oil (*Ibid.— Belg. 449,131*), or fractions of the same oil separable with triethanolamine (*Ibid.—Belg. 449,531*). A discussion of the use and role of fats in the tannery was published by Gastellu (*Inds. corps gras 3*, 102, 132).

Among the patented froth flotation agents, fatty acids and alkaline phosphates were used for non-metallic minerals (Clemmer & Rampacek—*U. S. 2,424, 552*), a combination of soap and coconut oil for phosphate ores (Crawford & Jayne—*U. S. 2,416,909*), and sulfonated oils for iron ores (Herkenoff—*U. S. 2,423,314*).

Recommended compositions for protecting metals from corrosion were: a mixture of castor oil; isopropanol; sodium, potassium, and calcium ricinoleate; and water (Doelling—*U. S. 2,420,127*); blends of lead soaps of wool grease and tall oil, lubricating oil, wax, and cobalt drier (Kollen & Flaxman—*U. S. 2,418,075;* Wilson & Dodge—*U. S. 2,421,672*); and a solution of hydrolyzed lanolin in xylene (Wells—*U. S. 2,417,028*).

Most of the patented fat derived wax-like compounds were intended for polishing and cleaning uses. These were a mixture of high molecular weight alcohols, aldehydes, ketones, and esters emulsified with a fat-derived emulsifying agent (Hawk *et al.*—*U. S. 2,409,683*); esterification products of certain fractions derived in the manufacture of synthetic fatty acids from paraffin (Bohme Fettchemie G.m.b.H. — *Belg. 449,162*); a heat treated mixture of wax, linseed oil, and alkali (Beach—*U. S. 2,423,137*); a reaction product of stearic acid and dipentaerythritol (Burrell—*U. S. 2,427,255*); and an esterification product of butane-1,2,3,4-tetracarbonic acid anhydride with fatty alcohols (Hopff & Rapp—*Ger. 718,172 Cl. 12o*). A coating emulsion for retarding decay of fresh fruits and vegetables contained soap, paraffin, candelilla wax, shellac, and water (Handy — *U. S. 2,424,952*). Two general papers, one on shoe polishes (Vallence—*Manufg. Chemist 18,* 271) and the other on fats as suspending media for polishing and grinding abrasives (Steinitz—*Ind. Diamond Rev. 6,* 330), contained information pertaining to waxes containing fats or fat derivatives.

The use of fatty oils as power fuel was of interest to investigators of regions lacking a source of mineral oils. The literature on this subject was reviewed by Otto (*Bol. divulgacão inst. oleos 1945, No. 3, 91*). Martinot-Laqarde (*J. Soc. ing. automobile 14*, 237) fostered the use of castor and peanut oils as fuels for Diesel engines. Amrute (*Australasian Engr. Mar. 1947*, 60) described as a successful adaptation of peanut oil for Diesel engines during the war. However, its use was abandoned when mineral oil again became available.

Gaseous fuels were experimentally prepared from peanut, castor, cottonseed, and coconut oils by thermal cracking and the conditions for optimum yields were determined (Mandlekar *et al.*—*J. Sci. & Ind. Res. (India) 5B*, 45). The fuel recovery was about 50% at the most.

A miscellaneous group of unrelated fat products was difficult to classify in the preceding paragraphs. A protective coating to protect the skin against flash burns contained fats, solvents, metallic soap, borax, and pigment (Fauley & Ivy—*U. S. 2,425,311*). In a reclaiming process for synthetic rubbers, saturated fatty acids and a solvent were used to swell the rubber (le Beau—*U. S. 2,423,033*). A sealing composition for food container joints contained ethyl cellulose, vegetable oil, resin, and inert fillers (Millelot—*U. S. 2,419,224*). A pressure sensitive adhesive tape was coated with a base consisting of polyvinyl butyl ether and factice (Nelson & Morris—*U. S. 2,415,901*). A cleaning composition for removing sludge from internal combustion engines was a mixture of organic solvents and a fatty acid amine (Skinner—*U. S. 2,418,908-9*). A dielectric structure comprised adsorbent cellulosic material impregnated with castor oil (Coggins & Ahearn—*U. S. 2,418,820*). Various soaps, fatty acids, and fatty amines were added to bituminous paving compositions (Allen — *U. S. 2,416,134;* Johnson—*U. S. 2,426,220*). Stearin pitch was added to bituminous adhesives (Moore & Greenfield—*U. S. 2,418,135*). Stearic acid was recommended for combating foam formation in the analytical Kjeldahl nitrogen determination (Hadorn — *Mitt. Gebiete Lebensm. Hyg. 38*, 46). Foaming and priming in steam generators were reduced with the following combinations of compounds: oleic acid and diethylenetriamine, stearamide and trioxy-methylene, castor oil and triethyltetramine, and others (Imperial Chemical Industries, Ltd. — *Brit. 568,510*). Fatty acid derivatives of piperazine were effective antifoaming compounds for steam boilers (Jacoby—*U. S. 2,428,801*). A review of fats in the pharmaceutical industry by Gauthier (*Inds. corps gras 3*, 68) included within its scope oil solutions for injections, suppository fats, fats for ointments, medicinal fatty derivatives, and soaps.

The Hydrolysis of Soap Solutions. IV. The Composition of Acid Potassium Laurates and Acid Sodium Oleates as Determined by Conductivity Measurements

LUCILLE M. JOHN* and JAMES W. McBAIN, Department of Chemistry,
Stanford University, California

ACID soaps, the characteristic product of the hydrolysis of soaps, were first described by Chevreul in 1823. He found that they were acid salts of the same nature as sodium acid acetate, $NaAc \cdot HAc$. In 1927 McBain and Stewart (1) prepared potassium hydrogen dioleate and showed that it was a definite compound containing one equivalent of acid to one equivalent of soap. Its composition over a wide range was found to be independent of the proportions of oleate and acid used in the solvent. The acid soap could be recrystallized unaltered from alcohol or from oleic acid. The existence of several other acid soaps was established by later phase rule studies by McBain.

Acid soaps have been prepared, among other ways, from neutral soap and acid in alcoholic solution, and in aqueous solution by the addition of excess acid. They are also formed by hydrolysis. Most investigators have found acid soaps of the types 2 soap · 1 acid, 1 soap · 1 acid, and possibly 1 soap · 2 acid, though other types are not excluded as was shown by Ryer's preparation of $2NaSt \cdot 3HSt$ (2).

Ekwall (3, 4) considered that he prepared the acid laurates, $2NaL \cdot HL$, $NaL \cdot HL$, and $NaL \cdot 2HL$, from alcoholic solution. By studies involving the use of excess acid, he identified $NaL \cdot HL$ as a product of hydrolysis in aqueous solutions above 0.006 *N* and $2NaL \cdot HL$ above around 0.02 *N*; $NaL \cdot 2HL$ could not be identified. Conductivity measurements and analysis of filtrates of soap solutions containing excess acid lead him to the view that $NaMy \cdot HMy$ is formed in dilute solutions of sodium myristate, and $2NaMy \cdot HMy$ in solutions of somewhat higher concentrations. $2NaP \cdot HP$ and $NaP \cdot HP$ have been shown to exist by phase studies of McBain; (5) and Ekwall (6) found $NaP \cdot 2HP$, but without critical tests. McBain, Taylor and Laing (7) observed that the equivalent conductivity of sodium palmitate fell to a very low value when one equivalent of acid was present to two equivalents of palmitate, corresponding with the formation of an insoluble undissociated acid soap, $2NaP \cdot HP$. $NaP \cdot HP$ was identified as a product of hydrolysis in dilute aqueous solutions by Ekwall (8), and also $NaSt \cdot HSt$. In phase studies McBain (9) showed evidence for the existence of $2NaSt \cdot HSt$ and $NaSt \cdot 2HSt$.

Acid potassium myristate, palmitate, and stearate containing one equivalent of acid to one of soap were prepared by Levi (10) from alcoholic solution.

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* Present address: Duchesne College, Omaha, Nebr.