

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

## Report of the Literature Review Committee \*

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### Introduction

**STATISTICS AND OUTLOOK.** Statistics and outlook on domestic and foreign production, use, demand, trade, and prices of fats and oils in general and on individual products were issued periodically by the Bureau of Agricultural Economics of the U. S. Department of Agriculture (*Fats and Oils Situation Nos. 130-9*) and U. S. Department of Commerce, Office of Domestic Commerce (*Ind. Rept. Fats and Oils, Jan. 1950*).

On the basis of available statistics, beginning with the crop year 1942-43 and extending through estimates for 1949-50, the yearly production of fats and oils from domestic materials were 10,557, 10,989, 9,599, 8,827, 9,619, 9,824, 11,251, and 11,873 million pounds, respectively.

Stocks of fats and oils were over two billion pounds at the end of the year. This was not considered excessive, because end-of-the-year holdings averaged 2.2 billion pounds before the war when domestic production was considerably lower than in recent years. Exports during 1949 were more than twice as great as in 1948 and about four times as large as before the war. The import-export balances were a 365-million-pound contribution to supplies as net imports in 1948 and more than one billion pounds net exports in 1949.

The index number of wholesale prices of 26 major fats, excluding butter, in January, 1950, was 147% of the 1935-39 average compared with 201% in January, 1949. Prices last year reflected the availability of ample supplies. Another indication of the adequacy of supplies to meet all needs was the stability in prices throughout the year as contrasted with the wide swings that characterized most of the postwar years.

The general outlook was that production of fats will continue at high levels. A 6% increase in the pig crop suggests moderate increases in lard and grease output in the fall. Acreage allotments and the market quota program for 1950 may decrease corn and cottonseed output, but the oil production lost here will be balanced by expanded soybean production.

A major disturbance was growing in the economies of soap fats. Inedible tallow and grease production in the course of the past 10 years has doubled to an expected output of two billion pounds for the current crop year. Since the rapidly increasing competition in the soap field by synthetic detergents using little or no tallow and grease has lowered the demand for these soap fats, new industrial outlets for the fats must be developed.

Many other economic treatises on fats and oils were available. The world fat situation was reviewed by a British government division (*Intelligence Branch of Commonwealth Economic Commission*) and by Faure (*Oleagineux 4, 567; Olearia 3, 647*). Economic treatises on fats of limited geographic districts discussed the production, trade, and consumption in Benelux (*Ferrara—Olearia 3, 663*), Canada and Mexico (*Ibid 98*). Czechoslovakia (Podraszko—*Chem. Obzor 23, 189*), Emilia province of Italy (*Crocioni—Olearia*

*3, 32*), Iceland (Loosen—*Oleagineux 4, 227*), Oceania (Ferrara—*Ibid. 346*), Russia (Haussmann—*Olearia 3, 24*), United States (Groggins—*J. Am. Oil Chemists' Soc. 26, 356*), and Venezuela (Jenkins *et al.*—*Food & Agr. Organization of United Nations Report, Apr. 1949*). Economic communications of limited scope told about the possibilities of oil culture in Morocco (Rostand—*Oleagineux 4, 137*; van den Berg—*Ibid. 297*), sources of minor oil crops in the United States (Kester—*J. Am. Oil Chemists' Soc. 26, 65*), production and uses of industrial oils (Plasat—*Rev. inst. franc. petrole 4, 80*), fish oils in paint manufacture (Hardy—*Paint Manuf. 19, 132*), British produced drying oils (*Ibid. 317*), and a review of current work at the University of Liverpool on potential sources of drying oils (Hilditch—*J. Oil & Colour Chemists Assoc. 32, 5*).

The treatises on specific oils had the following texts: description of avacado oil (Vergriete—*Oleagineux 4, 597*), United States castor seed yields and oil content (Weibel—*Econ. Botany 2, 273*), production, taxes, prices, etc., on coconut oil (Chase—*Soap, Sanit. Chemicals 25, No. 7, 28*), grain oils (Goss—U. S. Dept. Agr., Bur. Agr. Ind. Chem. AIC-208, 14 pp.), horse fat (Holmberg & Rosenquist—*Svensk Kem. Tid. 61, 89*), Canadian erucic acid oils (Lips & Grace—*Can. J. Res. 27F, 311*; Zuckerman—*Can. Chem. Process Inds. 33, 588*), Roumanian grapeseed oil (Alexa &

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Simionescu—*Bull. inst. polytech. Jassy* 3, No. 2, 296), grapeseed oil (Nunn—*Australia Dept. Munitions, Paints Notes* 3, 238), lanolin problem in Spain (de la Quintana & Tobio—*Ion* 8, 799), olive oil culture in the Mediterranean basin (Fantoli—*Olearia* 3, 321), in French Morocco (Elant—*Ibid.* 2, 858), in Lazio (Pajella & Gazzera—*Ibid.* 3, 113), and in Liguria (Buzi—*Ibid.* 2, 868), properties of solvent extracted olive oil (Bigoni—*Ibid.* 3, 172), osage orange pulp oil (Clopton & Roberts—*J. Am. Oil Chemists' Soc.* 26, 470), palm oil culture in Portuguese West Africa (Erhart—*Oleagineux* 4, 654), oil palms of the American hemisphere (Markley & Jenkins—*J. Am. Oil Chemists' Soc.* 26, 257), the British peanut plan (Guyot—*Oleagineux* 4, 213), South Italian Somalia peanut oil culture (Bigi—*Olearia* 3, 339), Senegal peanut oil culture (Bouffil—*Oleagineux* 4, 289), plum kernel oil (Singer—*Seifen-Öle-Fette-Wachse* 74, 197), marine oils of Iceland (Karson—*U. S. Dept. Interior, Fish & Wildlife Service, Fishery Leaflet* 345, 13 pp.), rice bran oil (Feuge & Reddi—*J. Am. Oil Chemists' Soc.* 26, 349), safflower oil (Hardy—*Paint Manuf.* 19, 239, 444; Miede—*Olearia* 3, 91), shark liver oil of Trinidad (Mayor & Pearman—*Bull. Imp. Inst.* 46, No. 1, 53), soybean oil (Heinemann—*Farben, Lacke, Anstrichstoffe* 3, 148), tall oil (Démareq—*Oleagineux* 4, 588; Young *et al.*—*Soap Sanit. Chemicals* 25, No. 12, 40; Rumpel—*Mitt. chem. Forsch.-Inst. Ind. österr.* 3, 47), tung oil culture in Russia (Tkatchenko—*Rev. intern. botan. appl. et agr. trop.* 28, 32), and hydrogenated whale oil (Merat—*Oleagineux* 4, 203).

**FAT SYNTHESIS.** Fat could be synthesized biochemically by the action of yeasts or molds on suitable culture medium. Although this process was not yet commercially significant, the new fundamental information on the process seems to bring it nearer to that realization. A patented substratum for this purpose contained various inorganic salts and hydrolyzed straw (Enebo & Berg—*Swed.* 124,071). The cultures used were *Rhodotorula gracilis*, *flava*, *suganii*, *muclaginoso*, *longissima*, *aurea*, or *sannici* and, when the nitrogen in the substratum was kept low in relation to the carbohydrate, yields of 33-44% were attained. High rates of fat synthesis with *Rhodotorula gracilis* using glucose or molasses as the carbohydrate at certain optimum nitrogen concentrations were confirmed by Pan *et al.* (*Arch. Biochem.* 23, 419). Certain substances present in molasses were believed to accelerate the sugar utilization. Berhauer & Rauch's (*Biochem. Z.* 319, 77, 94, 102) data on both protein and fat synthesis indicated that there was a reciprocal relationship between the nitrogen/carbon coefficient of the substratum and the protein and fat formed. With high nitrogen the crude protein could reach 40-50% with fat not over 5-10%; but when the nitrogen amount was very small, *i.e.* 10%, the fat attained was about 50%. These authors described a method of producing fat mycelium by "submerged cultivation," *i.e.*, the culture was agitated during fermentation. Bernhard & Albrecht (*Helv. Chem. Acta* 31, 2214) grew the mold, *Phycomyces blakesleanus*, on deuterium oxide enriched glucose containing various fatty acids and isolated various lipids from the products. The lipid products contained about 66% of the deuterium of the medium. Four lots of *Chlorella pyrenoidosa* grown under controlled environmental conditions to contain 23, 33, 63, and 76% lipids varied in fatty acid content from 6 to 66% of the

dry weight of the cells (Milner—*J. Biol. Chem.* 176, 813). Analysis of the fatty acid mixtures showed saturated acids, mostly palmitic, comprising 12-16% of the total and that the liquid acids were highly unsaturated. The fats produced by various *Fusaria* were studied from the standpoint of the mechanism of the enzyme systems (Descamp—*Arch. Biochem.* 20, 457; Weiss *et al.*—*Ibid.* 22, 314; Nord *et al.*—*Ibid.* 23, 480; Fiore & Nord—*Ibid.* 23, 473). A pigment (Solanione) from *Fusarium solani* D<sub>2</sub> purple caused changes in the fat metabolism of non-pigmented *Fusaria*, namely, desaturation of the fatty constituents. Naphthoquinones decreased the amount of fat formed in growing *Fusarium lini*, indicating that they affect the enzyme system involved in the conversion of carbohydrate to fat. Alterations in saturation in some of the fats were produced by additions of riboflavin and nicotinic acid.

The economic status of synthesis of fats from coal by Fischer-Tropsch synthesis was reviewed by several authors (Nutrition Div., Food & Agr. Organization. *Synthetic Fats* 1949, 11 pp.; Paul & Tramm—*Erdöl u. Kohle* 2, 229; Zwergal—*Kolloid-Z.* 112, 168; Kuchinka—*Pharmazie* 3, 439; Wittka—*Olii minerali, olii e grassi, colori e vernici* 25, 80, 90). The process was considered unique, in that for the first time in history it was possible to synthesize from nonbiological materials a food of calorific value. All authors were cautious regarding advocating the fat for human consumption, however, pointing out that more complete and satisfactory experimental and clinical data were needed. One suggested that since synthesis of fats from microorganisms seemed to be a more wholesome source, investigations should be directed to the development of biochemical synthesis. Apart from the direct use of synthetic fats as food the industry could contribute materially to the food supplies by producing fats for industrial uses, so that less natural fat would be diverted from human nutrition to production of soap, grease, etc. The Fischer-Tropsch synthesis was of particular economic interest to Germany, because the system contributed not only fats, but also fuel gas, liquid fuel, wax, detergents, etc., which are essential elements for German economical existence. Gall and Hall (*Fuel* 27, No. 5, 155) produced fatty acids in the C<sub>10</sub> to C<sub>20</sub> range in 50-70% yield by oxidizing Fischer-Tropsch waxes at 110° with 16.5 liters of air per 100 grams of wax. The products were suitable for manufacture of laundry soap. A process for manufacture of fatty acids from petroleum comprised making sulfurized tertiary monoolefins and hydrolyzing them (Spindt & Stevens—*U. S.* 2,470,876).

Synthetic products were also replacing fats in the soap industry (Snell—*J. Am. Oil Chemists' Soc.* 26, 338; *Chemistry & Industry* 28, 499; *Chem. Eng. News* 27, 2256; Hersberger & Neidig—*Ibid.* 1646). The largest volume of synthetic detergents was based on petroleum. It was suggested that at some future date most synthetic detergents will draw from petroleum fractions and condensed gaseous olefins for raw material instead of from fats and oils. In 1949 about 24% of the packaged household detergents marketed were synthetic.

**NEW LITERATURE.** During the year the German Society for Fat Science was reorganized and publication of their journal, "Fette und Seife" was resumed. Publication of a Journal by the Japanese Oil Chemists' Society was also initiated. Two very brief his-

torical reviews of the fat industry were published (Kunzmann—*Seifen-Öle-Fette-Wachse* 75, 9; Child—*Soap, India* 2, No. 4, 12).

Simari & Martinenghi (*Olivicoltura e oleificio*. Publ. by Ulrico Hoepli, Milano, 554 pp.) wrote a comprehensive book on olive oil culture and processing. The methods of processing from primitive technic to modern solvent methods were described.

### Production

**ANIMAL AND FISH FATS.** A new rendering process for the meat-packing industry was designed for continuous operation and to yield bland fat products (Hormel—*U. S. 2,467,529*). In this, fatty tissue was hashed to a slurry, passed through heat exchangers, and dispersed in a low pressure zone to evaporate water; and the fat was separated.

Biochemical processes were suggested as aids in rendering. Beckman (*U. S. 2,486,384-5*) comminuted the raw material, inactivated fat-hydrolyzing enzymes with heat, and subjected the material to controlled proteolytic enzyme fermentation to release the fat. Somewhat similarly, Nakamoto (*Japan 154,087*) treated eggs with papain and recovered egg oil by pressing.

Some processes were particularly designed for use in the fish industry. One patentee (Lagunov—*U. S. S. R. 69,392*) described the rendering of fish livers by a process in which the protein material was hydrolyzed in two stages; it was heated first at 50-60° with 1.0-1.5% alkali and then at 80-90° with 0.5-1.0% alkali. Shropshire (*U. S. 2,473,453*) reported that subjecting fish livers to vibrations in the lower audible frequencies disrupted the cell structure and allowed separation of oil without use of chemicals or heat. A patented fish residue plant for installation aboard ships comprised comminuters, cookers, pulverizers, skimming tanks, and other accessories arranged in convenient order to process the fish waste into oil, dry meal, and glue (Napier—*U. S. 2,468,636*). Takei (*Japan 175,035*) extracted fish entrails or other material containing water by mixing with starch or flour and extracting the fat with a solvent.

Smirnova & Zueva (*Myasanaya Industriya* 1948, No. 2, 85) recovered the small amounts of fat from the bone liquor intended for the preparation of glue by centrifuging in dairy type equipment at 2800 r.p.m. and at a temperature of 80°. A scheme for recovering fats from oil plant filter and bleach wastes comprised boiling in caustic solution, centrifuging the liquid from the solids, and treating the soap solution with inorganic acid to recover fatty acids (Jaynes & Osburn—*J. Am. Oil Chemists' Soc.* 26, 693). Fatty acids could also be recovered from laundry waste water. The process of Naldi (*Ital. 422,326*) for this purpose involved precipitation with silver nitrate, treatment of the precipitate with nitric acid to free the fatty acids, and recycling the silver nitrate solution. One waste fat recovery patent dealt with new mechanical features for a continuous sewage skimmer (Campbell—*U. S. 2,468,864*).

One investigation on butter production indicated that the best practice was to churn the butter from sweet cream and flavor it with a special mixture of acetic acid, lactic acid, and diacetyl (Bang—*Svenska Mejeritidn.* 41, 155). The advantages over starter processes were superior flavor and storing properties in the butter, and production of a sweet buttermilk

which was considered more useful than sour buttermilk. Lindgren (*U. S. 2,461,117*) produced butter by centrifugally concentrating milk or cream to 80% butterfat, adding flavor and salt, and cooling to temperatures that cause the phase reversal of cream to butter. Equipment for a similar process patented by Senn (*Swiss 238,990*) was designed so that centrifuging, cooling, washing, and printing were done under exclusion of light and in an atmosphere of carbon dioxide. Three patents issued to Horneman *et al.* (*U. S. 2,466,894-6*) described a system of filters, pasteurizers, centrifuges, and mixing, cooling, and stabilizing chambers to produce butter in a continuous manner. A process of making butter without churning involved expanding the milk or cream under pressure with an inert gas; the butter separated upon releasing the pressure and agitating (Shadwick—*U. S. 2,463,915*). A canned butter for hot climates was stabilized by reducing the moisture and adding 2% of hydrogenated peanut oil, 2% of skim milk powder, and 1.5% sodium carbonate (Coombs—*Australian J. Dairy Technol.* 4, 43). Other literature on butter included patents on molding (Givens—*U. S. 2,478,819*) and cutting (Baalbergen—*U. S. 2,479,712*; Grocoff—*U. S. 2,479,742*; Berg—*2,488,656*) devices.

Guriye *et al.* (*Indian J. Dairy Sci.* 2, 77) compared the manufacture of Indian butter oil, ghee, by boiling acidified milk or cream with the standard method of churning curded milk or cream. The former method resulted in higher yields, but the flavor was not acceptable.

**VEGETABLE FATS.** Some of the vegetable oil processing information was related to analyzing seed storage practices for conditions that produced the best quality oils. Castillon *et al.* (*J. Am. Oil Chem. Soc.* 26, 655) recorded data which showed that gossypurpurin increased in stored cottonseed in proportion to the temperature and length of storage. Color development in the extracted oil from stored seed was in part due to the formation of the purple pigment, gossypurpurin from gossypol. Christensen *et al.* (*Cereal Chem.* 26, 109) correlated increases in mold population of stored cottonseed with increased production of carbon dioxide and free fatty acids. These data indicated that molds may play an important part in the deterioration of moist stored seeds. Karon & Hillery (*J. Am. Oil Chem. Soc.* 26, 16) recorded the hygroscopic equilibria and rates of attainment of the equilibria of peanuts freshly dug, naturally cured, and artificially cured. The information was of interest for development of good curing and storage practices.

Morel (*Verfkroniek* 22, 50) compared the working method and results of the Krupp and Anderson expellers for pressing *Aleurites montana* seeds. At 33% shell content the results agreed, but, at lower shell content, the Anderson machine was superior. A new expeller patent dealt with improved design of the screw and barrel (Sizer—*U. S. 2,466,492*).

Wilbaux (*Olearia* 3, 374) described simple equipment that could be utilized for palm oil production at the plantations. This comprised hand comminuters and centrifuges to separate the oil from the dried finely ground raw material. A patented method of oil milling milkweed seed began with passing the entire pods into a centrifugal type fan blower which opened the pods and detached the seeds from the floss (Reed—*U. S. 2,480,769*). The floss was removed

by a "cyclone" separator and the pods by screening; the separated seeds were then milled and pressed.

Two reviewers of extraction methods favored the use of solvent processes. Bagot (*Oleagineux* 4, 339, 427) described and illustrated one modern expeller process and five modern solvent installations. Schwitzer (*Paint Manuf.* 19, 225) discussed the economies of solvent processes and the various techniques used.

The work on processing of cottonseed dealt principally with the behavior of the pigments. Williams & Hadden (*J. Am. Oil Chem. Soc.* 26, 28) recorded the differences caused in oil pigments by varying the amount of water and temperature during cooking of the meats. Addition of water and low cooking temperatures resulted in expressed oils of low bleached color. Three patents dealt with the problem of color materials in solvent extraction processes. Perez (*U. S.* 2,485,916) first extracted the seeds with alcohol and a little soap to remove the pigments; the cottonseed was then dried, and the oil extracted with hydrocarbons. A gravity method of removing the pigment glands by Boatner *et al.* (*U. S.* 2,482,141) comprised disintegrating the cottonseed, mixing with an organic solvent of density greater than the pigment glands, and removing the floating glands. A process by Hutchins & Williamson (*U. S.* 2,484,831) produced light colored oil and meal by extracting the seed with an alcohol-hydrocarbon mixture. The process allows extraction at temperatures below those at which the proteins of the meal were denatured and it binds the gossypol pigments into a nontoxic form with the proteins of the meal. Data on solubility and distribution in systems of isopropanol-water-cottonseed oil-oleic acid-hexane were obtained by Harris *et al.* (*J. Am. Oil Chemists' Soc.* 26, 719) to serve as a basis for separating a high quality oil from the isopropanol extract of cottonseed. The work reported from the Southern Regional Laboratory during the past several years on fractionating cottonseed into pigments, meal, and oil was reviewed by Persell *et al.* (*Oil Mill Gaz.* 54, No. 3, 11).

Equipment for extraction of soybean oil with trichloroethylene was designed at the Iowa State College Laboratories (Sweeney *et al.*—*Iowa State Coll. Eng. Exptl. Sta. Bull.* No. 165, 89 pp.; *J. Am. Oil Chemists' Soc.* 26, 697; *Proc. Iowa Acad. Sci.* 54, 189; Hollowell—*Iowa State Coll. J. Sci.* 23, 41). The extractors in these plants were inclined tubes in which flaked beans were carried by means of a screw conveyor through flowing solvent. The publications comprehensively treated the properties of the solvent and beans, toxicity of the solvent, analytical control methods, and operating cost. One of the methods described made use of a mixture of alcohol and trichloroethylene as the solvent. The extraction was carried out at 70° and the miscella cooled to cause separation into two phases; the lower phase was stripped to remove solvent while the upper phase was returned to the system without evaporation. The concentration of moisture in the solvent was inhibited by having less than 6% moisture in the beans.

Two rather unconventional methods for extracting soybeans were published. In one the finely ground beans were soaked and worked twice with 0.3% sodium sulfite solution and the oil was recovered from the warmed decanted liquid by centrifuging (Druel & Huit-Fidor—*Fr.* 933,500). In the other new process the soybeans were subjected to alkali catalyzed alco-

holysis so that the ethyl or methyl esters of the fatty acids separated with the excess alcohol, and these then were distilled and hydrogenated (Inokuchi *et al.*—*J. Soc. Chem. Ind. Japan* 47, 156, 157, 235, 236; Iguchi *et al.*—*Ibid.* 49, 31). The products of the process were a superior soybean meal and industrially useful soybean fatty acid esters. One innovation in pressing soybeans dealt with spraying the beans with 5% calcium chloride solution which permitted a better yield of oil (Suzuki—*Japan* 153,567). Gustafsson (*U. S. Dept. Agr. Bur. Agr. Ind. Chem. AIC-195*, 5 pp.) issued details for a continuous soybean processing pilot plant.

Loeb *et al.* (*J. Am. Oil Chemists' Soc.* 26, 738) determined the rate of spoilage of the oil (development of free fatty acids) in rice bran when stored at various temperatures, humidities, and moisture contents, and also after chemical treatment. Chemical inhibitors were ineffective. Dried bran maintained at low moisture content could be stored for four months. A new extraction process for rice bran yielded vitamin B concentrates and oil as its products (Meinke *et al.*—*Ibid.* 532). In this, 91-95% isopropanol extracted oil, sugar, and water-soluble vitamins, and, on concentration of the miscella a sugar-syrup containing the vitamins separated from the oil. Takeshita (*J. Nippon Oil Technol.* 2, No. 1, 9, 27) determined the effect of moisture, agitation, and temperature on the extraction of rice bran oil with solvents. At temperatures of 30-50° and with agitation, 10 minutes contact with solvent were required to obtain 19% oil from bran containing 20%. For pressing the bran, Nishimura & Nishimoto (*Ibid.* No. 3, 39) preheated at 7.5-8.5 moisture content first at 90° for four minutes and then cooked at high pressures for 15 minutes.

A new continuous solvent system for extraction of seed oils contained a series of mixers alternating with centrifuges, in which solids and miscella progress in opposite directions (Pascal—*U. S.* 2,467,404). Oil extraction equipment was improved by Langhurst (*U. S.* 2,467,435) by addition of a special column in the meal drier to reduce fire hazard and entrained dust during solvent recovery.

Wingard & Shand (*J. Am. Oil Chemists' Soc.* 26, 422) designed apparatus from common laboratory equipment to study the rate of extraction of oils in both batch and countercurrent systems. The equipment could be used for study of oil bearing material, selection of solvent, design of factory equipment and operations. Prebrzhenskii (*Bull. mens. ITERG* 3, 189) reviewed the solvents used in oil milling. A review of petroleum solvents for fatty oil extraction by MacGee (*J. Am. Oil Chemists' Soc.* 26, 176) contained the composition, distillation range, evaporation rate, and some other physical properties of several hexanetype naphthas. Berti (*Olearia* 3, 629) fostered the use of carbon tetrachloride to replace the carbon disulfide used to extract olive oil cake in Italy. The former permits better recovery and quality of the oil. Paquot & Najand (*Oleagineux* 4, 22) indicated processers could take advantage of the selectivity of extraction solvents; thus, the iodine value of sesame oil extracted with furfural was much higher than when petroleum solvent or acetone was used. When castor oil was extracted with hydrocarbons of six to eight carbon atoms, much of the oil separated from the solvent on cooling; thus, about 75% of the distillation and condensation cost could be spared (Pascal—*U. S.* 2,467,-

403). Beckel & Belter (*U. S. 2,460,117, 2,469,147*) designed equipment for continuous extraction of seeds with alcohol. The system contained two cooling stages for the recovery of products from miscella; in the first cooling period oil separates from the miscella and after further evaporation lecithin, sugar, and additional oil separate out in the second cooling stage. Other new oil extraction equipment included parts for effecting corn milling processes in which the oil was a by-product (Lloyd & Schafer—*U.S. 2,460,389*; Schopmeyer—*U.S. 2,479,519*).

**TALL OIL.** One communication dealt with recovery of tall oil from waste pulp liquor. In this the liquor was concentrated to grain out soap and agitated to maintain the soap in suspension; the tall oil soaps were then separated centrifugally (Thurman—*U.S. 2,475,361*). The remainder of the tall oil production literature treated the segregation of fatty and rosin acids. In two of the processes the fatty acids were selectively esterified with alcohol; after this the rosin acids could be separated from the fatty acids with selective adsorbents (Koonce & Perry—*U.S. 2,485,744*) or by distillation and crystallization (Taylor *et al.*—*U.S. 2,487,000*). For the same purpose Houpt (*U. S. 2,463,274*) partly neutralized the tall oil dissolved in *sec.*-amyl alcohol and dehydrated the mixture. Fatty acid soaps separated from the solvent solution while the rosin acids remained dissolved in the mother liquor. In another process the tall oil was hydrogenated, adsorbed on activated carbon, and fractionally eluted into three fractions. The first was relatively pure rosin acids, the second a mixture, and the last relatively pure stearic acid (Othmer & Papps—*U.S. 2,486,974*).

**HARDENING OF OILS.** Of two general papers on hydrogenation of oils one contained a review of the methods used (Slade—*Food Manuf. 24, 361*) and the other reviewed hydrogenation and uses of whale oil (Merat—*Oleagineux 4, 203*). Equipment was designed for hydrogenating oils by atomizing the oil and catalyst into a hydrogen atmosphere (Holmboe—*Brit. 620,043, 620,145*). Another equipment patent dealt with heat exchangers by which the heat of a previously hydrogenated fat was utilized to preheat oil for subsequent hydrogenation (Holmboe—*Brit. 619,961*).

There were a few studies on the kinetics and theories of hydrogenation. Kawakami (*J. Nippon Oil Technol. Soc. 1, No. 4, 16*) recorded that the reduction of one unit of iodine value per kilogram of fat results in the evolution of 1.6 kcal. of heat. Tsutsumi (*Ibid. No. 3, 1, 12, 16, 17*) found that in the absence of water no hydrogenation of neutral oil takes place. With 2.5% moisture the reaction proceeded most smoothly and with larger amounts of water both hydrolysis and hydrogenation took place. With oils of high acid number moisture was unnecessary and even harmful to the reaction. Analyses of the products of hydrogenation of soybean oil by Ueno *et al.* (*J. Soc. Chem. Ind. Japan 45, 206*) indicated that when 20 parts of the linoleic acid was hydrogenated 14, 4, and 2 parts were converted, respectively, into isooleic, oleic, and stearic acids. More comprehensive data of this type on cottonseed and linseed oils were recorded by Bailey (*J. Am. Oil Chemists' Soc. 26, 644*). His data on rates of reaction of linoleic to oleic acid in cottonseed oil showed variations of 4 to 1 in non-selective to about 50 to 1 in very selective hydrogenation. With linseed

oil the relative selective reaction rates of oleic, iso-linoleic, linoleic, and linolenic acids were: 1, 3.85, 31, 77, respectively. In selective hydrogenation the linolenic acid reacting went to linoleic 0, isolinoleic 54, and oleic acid 46%. The complete results were interpreted to indicate that the solution of hydrogen in the oil and the adsorption of unsaturated oil on the catalyst were two steps controlling the reaction rate. In a general discussion on selective hydrogenation Waterman (*Chimie & industrie 61, 125*) pointed out that it should be possible with low temperature, high pressure, and good catalyst to hydrogenate cod liver and palm oil without destruction of carotene, and vitamins A and D.

According to Lips *et al.* (*Can. J. Res. 27F, 28*) rape and mustard seed oils could be hydrogenated at 50 lb. pressure and 284°F. with nickel format catalyst and deodorized for one hour at 464°F. to provide a stable hard fat comparable to commercial vegetable shortening. Ziel & Schmidt (*U.S. 2,468,799*) patented the use of nickel catalyst containing small amounts of sulfur for hydrogenating oils intended for margarine manufacture. Zajcev (*Scientific Memoirs Ukrainian Tech. Univ. 1, No. 4, 123*) published instructions for the manufacture of nickel-copper catalyst. The advantages of such catalyst were listed as non-foaming, reduced consumption of nickel, long life, and good selectivity.

An entirely new hydrogenation process was patented by Callery (*Brit. 621,037*). He found that glycerides of oleic and ricinoleic acids were hardened by contact with hydrazine hydroxide in the cold and at atmospheric pressure.

Another method proposed for hardening fats was by elaidinization. Eipper (*U.S. 2,456,691*) claimed that when cacao butter, chocolate, lard, and other fats were elaidinized in organic solvent solutions with nitrous acid at room temperature the hardened fats retained their normal flavor and aroma. Confectionery made from fats hardened in this manner were resistant to fat and sugar bloom when exposed to humid summer conditions. Gordon & Pailleux (*Bull. mens. ITERG 1948, No. 8, 31*) accomplished hardening of palm oil while deodorizing in the presence of selenium as an isomerization catalyst. The process yielded a bland fat suitable for margarine manufacture. One patent on solidifying oleic acid was similar in principle (Bourdiol—*Fr. 864,987*).

**REFINING AND DEODORIZATION.** The publications on refining varied from complete methods to various steps which form only a limited part of thorough refining procedures. Metallic impurities were removed from fats and oils by washing with aqueous solutions of alkali metal salts of ethylene diamine tetra-acetic acid having at least two and not over three of the acid group neutralized by the alkali (Bersworth—*U.S. 2,463,015*). In an investigation on methods for refining rice oil, a preliminary acid wash followed by regular alkali refining gave the best results (Sakurai—*J. Nippon Oil Technol. Soc. 2, No. 1, 47*). Soybean oil was sufficiently refined for protective-coating purposes by treatment with 2-30% aqueous solutions of trichloroacetic acid (Jakobsen—*U.S. 2,448,434*). One rotary alternating, pressure and vacuum filter assembly was designed especially to separate refined cottonseed oil from refining foots (McCaskell—*U.S. 2,459,082*). The innovations in continuous refining equipment were adjustments of time of reaction and concentration of

alkali to inhibit stratification before the mixture enters a centrifugal separator (Thurman—*U.S.* 2,462,923), a continuous process in which the free fatty acids were removed by distillation after preliminary degumming operation (Clayton—*U. S.* 2,478,089), equipment for drying the refined oil by continuously flowing it through a vacuum chamber as a thin film (Clayton—*U.S.* 2,483,623), and electronic and vacuum means for drying refining foots (Clayton—*U.S.* 2,472,193).

Moreno's method of continuous deacidification of oils by liquid-liquid extraction with alcohol was successfully applied to olive oil (Moreno—*Olii minerali, grassi e saponi, colori e vernici* 25, 58). Phase diagrams were developed as a basis for applying the method to palm oil (Moreno & Paniagua—*Bull. soc. chim. France* 1949, 388), and the process was reviewed by Martinenghi (*Olearia* 3, 239). The pilot plant tests on the method by Loew (*Olii minerali, grassi e saponi, colori e vernici* 25, 5) indicated that the results were good but not economical.

When small ratios of furfural were used in the liquid-liquid extraction of degummed soybean oil, the process could serve as a means of refining the oil. (Gloyer—*J. Am. Oil Chemists' Soc.* 26, 162). The raffinate was suitable for hydrogenation without further treatment, and the furfural extract was distilled for recovery of solvent and production of a varnish grade oil.

Hightower (*Food Industries* 21, 1391; *Chem. Eng.* 56, No. 9, 102) described and illustrated the continuous vacuum bleaching process used by Mrs. Tucker's Foods, Inc. The principal advantages of the system were continuous operation and reduction of oxidative reactions, and the soap (refining residue) was precipitated by dehydration. Fundamental data for this process were recorded by King & Wharton (*J. Am. Oil Chemists' Soc.* 26, 201, 389). These showed that a better bleach was obtained under vacuum conditions and that low-pH earths responded better in the process than high-pH earths. A newly patented continuous bleaching system comprised proportioning fat and bleaching agent in a conduit and then vacuum deaerating and passing through heating stages to attain bleaching temperatures (Robinson—*U.S.* 2,483,710). Brown & Muckerheide (*U.S.* 2,475,420) bleached fatty acids immediately after distillation so that the products would be both light colored and stabilized against color development.

In an investigation of the factors influencing bleaching by adsorption, Stout *et al.* (*J. Am. Oil Chemists' Soc.* 26, 120) found that acid activated clays were 1.5-2 times more effective than natural earths, and the ranges of maximum activities were 100-106° and 118-132°, respectively. Some high silica adsorbent clays were at the height of their activity at temperatures too high for use in the edible oil industry. In a new bleaching system for paint oils, the oils were mixed with small amounts of sulfuric acid before treatment with bleaching earths (Bolley & Gallagher—*U.S.* 2,458,554). In investigations of the decolorization by acid and clay, Tsuchiya (*J. Nippon Oil Technol. Soc.* 1, No. 3, 24; 2, No. 2/3, 1) found that oxalic acids increased the decolorization more effectively than sulfuric, acetic, or phosphoric acid. The latter acids decreased green and yellow color but increased red.

Both oxidizing and reducing agents were used in new chemical methods of bleaching oils. The chlorine materials used were a mixture of sodium hypochlorite and sodium chlorite (Woodward & Malmstrom—*U.S.* 2,481,463), sodium chlorite (Mouton & Borezee—*Oleagineux* 4, 271) and chlorine dioxide (Woodward—*U.S.* 2,473,930). Hydrogen peroxide processes were recommended for bleaching lanolin (Ricerche Ind. P. P. Vaccarino & Vigna—*Ital.* 421,705), rice oil (Kawai—*J. Nippon Oil Technol. Soc.* 2, No. 1, 30), and seawolf oil (Dugal & Cardin—*J. Fisheries Res. Board Can.* 7, 471). Patents on decolorizing oils by blowing with air or oxygen in the presence of salt and acid compounds of phosphorus and silicon were assigned to Lever Bros. Co. & Unilever Ltd. (*Brit.* 612,169; *U.S.* 2,468,753, 2,483,413); and in a similar process, Sakurai (*J. Nippon Oil Technol. Soc.* 2, Nos. 2/3, 25) used air with oxalic, sulfuric, or hydrochloric acid. In one bleaching process the oils were first submitted to the reducing action of ferrous salts and then to the oxidizing action of air or oxygen (Greentree—*U.S.* 2,450,549). In bleaching lanolin, Aumarchal (*Fr.* 932,301) developed nascent hydrogen in the fat by the action of sodium carbonate on a magnesium alloy and completed the bleaching with active carbon. The purpose of the nascent hydrogen was to reduce sulfur compounds.

The new deodorizing equipment described were continuous processes (Bailey—*J. Am. Oil Chemists' Soc.* 26, 166; Bataille—*Oleagineux* 3, 532; McCubbin & Monical—*U.S.* 2,461,694), and a commercial (Technochem. A-G.—*Swiss* 249,110) and a laboratory (Barnitz—*J. Am. Oil Chemists' Soc.* 26, 104) still which could also be used for other purposes. One deodorization patent dealt with time (1-1½ hr.), temperature (255-260°), and amount of gas blown through the oil (Jakobsen—*U.S.* 2,465,969). Nakajima *et al.* (*J. Nippon Oil Technol. Soc.* 1, No. 3, 30) pointed out that a considerable decrease in the acid numbers of oils could be attained during the deodorization process. Hamashima (*Japan* 172,661) found that the presence of small amounts of tin tetrachloride during deodorization improved the products. Two methods of deodorizing fish liver oils comprised contacting with fermenting milk (Mathew *et al.*—*Nature* 162, 494) and with vegetable and fruit juices (Pollak—*Fr.* 929,804), respectively.

Various non-fatty acid ester lipids were removed from fats and oils during processing as either one of the main products or as by-products. For production of good quality phosphatides, Marmor & Moyer (*U.S.* 2,461,750-1) decolorized oil miscella, stripped it of solvent at temperatures below 50°, and added water to precipitate out the phosphatides by coagulation. In production of carotene and carotenoid pigments from palm oil, cholesterol from lanolin, vitamin E from rice oil, and fat soluble vitamins from fish oils, the oils were saponified and the soaps were extracted with benzene (Tabor *et al.*—*U.S.* 2,461,300), acetone (Am. Cholesterol Products, Inc.—*Brit.* 622,725), methyl alcohol (Sakurai—*J. Nippon Oil Technol. Soc.* 2, No. 1, 42), and mixtures of organic solvents (Kern & Tabor—*U.S.* 2,470,703). Carotene was also concentrated from oils by precipitation with strong acids (Lange & Folzenlogen—*U.S.* 2,484,040) and as a residue remaining after distillation of the methyl esters of palm oil acids (Eckey—*U.S.* 2,460,796). Vitamin A of fish oils could be concentrated as a persimmon

tannin-vitamin A complex by treating the oils with aqueous tannin preparations from persimmons (Takeuchi—*Japan* 172,364).

**ESTERIFICATION AND INTERESTERIFICATION.** The processes of esterification and interesterification were accomplished for various purposes. When methyl or ethyl esters of the fatty acids were prepared, the usual purpose of the process was to render the fatty acids into a form which gave optimum results in distillation, segregation, or other purification processes. A new continuous method of esterifying fatty acids comprised passing the acids through a tower containing alcohol and mineral acids in such proportions that the ester formed was insoluble therein and thus accumulated as a separate phase (Fish—*U.S.* 2,486,938). According to one invention the acids of castor oil were converted to methyl esters by interesterification at 20-35° when the molar amounts of alcohol were 2-4 times that of the oil, and an alkali was used as the catalyst (Smith—*U.S.* 2,486,444). One method of producing alcohol esters by interesterification was in two steps; an acid catalyst was first used and then an alkaline catalyst was used to complete the process (Lever Brothers & Unilever Ltd.—*Brit.* 612,667). In a test on many catalysts for interesterification manufacture of ethyl esters of palm oil at 100°, Twitchell's reagent was suitable; *o*-nitrophenol, aluminum, trichloroacetic acid, sulfosalicylic acid, phosphoric acid, phosphomolybdic acid, ammonium chloride, and aluminum chloride had slight catalytic action while clays and many acidic chemicals were inactive (Ueno & Manpo—*J. Soc. Chem. Ind. Japan* 47, 847).

The esterification reaction of alcohols and fatty acids and interesterification reactions of monoesters and glycerols were comprehensively studied by Gros & Feuge (*J. Am. Oil Chemists' Soc.* 26, 704). Of 18 catalysts investigated barium hydroxide, lithium hydroxide, sodium ethylate, and sodium hydroxide were most effective. With equivalent amounts of alcohol and acid reacting the rate of alcoholysis was influenced by catalyst, temperature, and pressure, but all reactions came to equilibrium at about 70% completion. Under similar conditions methyl esters alcoholized more rapidly than ethyl esters. The monoesters could be converted fairly completely into triglycerides by reaction with excess glycerol and then stripping with steam under low pressure.

Peanut oil was alcoholized with ethanol using sodium hydroxide as the catalyst under conditions suitable for large-scale operations Feuge & Gros—*J. Am. Oil Chemists' Soc.* 26, 97). Curves and a table were recorded showing the actual amount of mono-, di-, and triglycerides, ethanol, soap and alkali present in the reaction mixture at various times. The optimum temperature of alcoholysis was 50°, and the glycerol ester linkages were broken in random fashion. The data were of interest as basic information for manufacture of alcohol esters, monoglyceride, diglycerides, and some soaps.

Methyl and ethyl esters of ricinoleic acid were converted to esters of higher alcohols by heating the ester and higher alcohol with an alkali catalyst (Meade *et al.*—*Brit.* 573,202). The lower alcohols volatilized from the reaction mixtures as they were released.

It was already known that when fats were heated ester-ester interchange occurs until the triglyceride mixture corresponds with random distribution of the acid radicals, and that free glycerol undergoes ester-

alcohol interchange when heated with fats producing an equilibrium among glycerol, monoglycerides, diglycerides, and triglycerides. Eckey & Formo (*J. Am. Oil Chemists' Soc.* 26, 207) combined the two processes with simultaneous crystallization of the solid glycerides. With cottonseed oil the solid glycerides were saturated diglycerides and saturated monoglycerides. Thus it was possible to segregate the high-melting and low-melting fatty acids of the fat into two separate ester fractions.

**SPLITTING FATS.** The new reviews on splitting of fats dealt principally with continuous methods in which the fat was autoclaved with water (Seaman—*Soap Perfumery & Cosmetics* 22, 384; Rowe—*Ibid.* 257; Pujol—*Ion* 9, 143). The General Mills plant which combines hydrogenation and esterification units with hydrolysis equipment was described by Williams (*Chem. Eng. Prog.* 56, No. 7, 92). One article on high-temperature equipment for fat processes contained illustrations and descriptions of splitting, distillation, and bodying apparatus (Barnebey—*J. Am. Oil Chem. Soc.* 26, 493).

The new inventions on fat splitting were all on continuous autoclaving and contained innovations in design of equipment, methods of heating, and control of operations (Ittner—*U.S.* 2,458,170, 2,480,471; Leaders—*U.S.* 2,489,713; Mills—*Brit.* 617,929-30; Brown—*U.S.* 2,486,630; Curletti—*Ital.* 430,821; Böhm & Zucker—*Swiss* 249,126).

The mechanism of hydrolysis was discussed in two communications. Lascaray (*Ind. Eng. Chem.* 41, 786) believed that the reaction mechanism in the autoclave and the Twitchell processes were similar. The hydrolysis was considered homogenous because appreciable water dissolves in the oil in both systems. The purpose of splitting agents was to increase the solubility of water in the oil phase. Mills and McClain (*Ibid.* 1982) believed that autoclave splitting occurred in a two-phase system: (a) an oil phase containing glycerides, fatty acid, glycerol, and water, and (b) a water phase containing glycerol and water. The equilibrium conditions in these were determined on experimental batches with coconut oil and tallow and the results were plotted. The maximum amount of splitting which could occur was determined by the glycerol concentration in the aqueous phase, and this value was affected by changes in temperature.

Many alkyl-diphenyl, -benzene and -naphthalene sulfonic acids and some commercial fat splitting agents were tested for their efficiency in the Twitchell process (Okumura & Tsuchiya—*J. Chem. Soc. Japan* 66, 19; Marroc & Sisley—*Bull. mens. ITERG* 1948, No. 11, 5). The commonly used alkylnaphthalene sulfonic acid gave slightly better results than the other reagents in all tests.

One invention on splitting fats with enzymes showed that one could take advantage of the selectivity of the enzyme process (Sanders—*U.S.* 2,485,779). Preferential liberation of saturated and least unsaturated acids occurred, thus permitting a method of fractionating the oils into a drying oil fraction and acids suitable for soap making.

**FRACTIONATION OF FATTY ACIDS AND FATS.** The patents on fractionation of glyceride oils by crystallization from solvents made use of nonpolar hydrocarbons (James—*U.S.* 2,459,820), simple esters, ethers, or ketones (Stevens—*Brit.* 622,735), and propane (Pasino & Meyers—*U.S.* 2,467,906) as solvents for the

process. Mussett *et al.* (*J. Dairy Sci.* 32, 700) segregated a solid fraction from butter oil by pressing at 70°. This fraction had much superior keeping qualities than the liquid fraction, and as the sole source of fat in dry whole milk and ice cream mixes produced products with improved flavor and storage-life.

A process described for fractionating soybean oil by liquid-liquid extraction made use of furfural and naphtha as solvents (Brekke—*U.S. Dept. Agr., Bur. Agr. Ind. Chem. AIC-194*, 5 pp.). The stripped oil had an iodine value of 144-168 as compared to 134 for the original. The "break" material and phosphatides concentrated in the refined oil phase. The flavor stability of the refined oil was about that of the original oil. Attempts to fractionate sesame oil by washing with methanol, acetone, and mixtures of these with water yielded only small fractions with iodine value only slightly increased over that of the original oil (Paquot & Najand—*Oleagineux* 4, 1). Similar work with linseed oil indicated that the increased drying properties of the first fractions were not sufficient to justify practical application of the process (Salomone—*Olearia* 1948, 834).

The various systems of fractionation of fats were very efficient when applied to the free fatty acid mixtures of the fats. Swern & Ault (*U.S. 2,457,611*) used one of the systems to prepare pure oleic acid. The polyunsaturated acids of fats were selectively hydrogenated to oleic acid and the saturated acids were removed by fractional crystallization and pressing.

Ternary systems of oleic acid-palmitic acid-acetone containing varying amounts of components have been equilibrated at several temperatures between 0 and -40° and the composition isotherms were recorded (Singleton—*J. Am. Oil Chemists' Soc.* 26, 332). These were intended to serve to predict the degree of separation which could be obtained from mixtures of oleic and palmitic acids, and as basic information for design of equipment and methods for segregating unsaturated and saturated acids from mixtures. One plant was designed to fractionate the acids of those oils whose fatty acids comprised principally saturated, oleic and linoleic acids (Towne—*U.S. 2,459,054*). Extraction with acetone gave an extract phase rich in linoleic and a raffinate phase containing mainly oleic acid; these phases were further fractionated by crystallization to separate saturated, oleic, and linoleic acids.

An entirely new method of segregating fatty acids depended on preferential neutralization (Nicholsen & Formo—*J. Am. Oil Chemists' Soc.* 26, 329). Thus when soybean oil fatty acids were neutralized with 40% sodium hydroxide and 60% barium hydroxide about 35% of the soap was soluble, which after separating in the form of free fatty acids had an iodine value of 165. These acids after esterification with glycerol formed a drying oil as good as linseed oil. The process was applied to fish oils with modifications of the mixed alkalies to yield fatty acids of 283 iodine value. Keuzenkamp *et al.* (*J. Am. Oil Chemists' Soc.* 26, 479) suggested that products of increased degree of unsaturation could be separated from cod-liver oils by the various segregation methods if the oil was first submitted to catalytic isomerization with sulfur dioxide.

#### Products (Except Detergents)

HOUSEHOLD PRODUCTS. Two milk fat fractions precipitated from a solvent at -20° and at -53° were

used as shortening in cake baking tests (Morse & Jack—*Food Res.* 14, 320). The -20° fraction was satisfactory when 5% emulsifier was added; the -53° fraction was less satisfactory. Refrigerator cookies were impractical with these fractions, because their physical state did not permit adequate manipulation. An investigation of the effectiveness of 24 emulsifiers on maintaining crumb softness of bread, showed that polyoxyethylene stearate was most effective (Edelmann & Cathcart—*Cereal Chem.* 26, 345). The emulsifier brightened the crumb color and improved the grain and texture of the bread, but did not effect the rate of loss of moisture from the bread. Favor & Johnston (*Ibid.* 25, 424) also found that polyoxyethylene stearate improved dough conditioning and baking, particularly with certain types of flour. A large amount of the literature on the polyoxyethylene fatty acid bread softeners appeared in the trade journals of the bakery and meat packing industry. These were largely news reports of a hearing before the Food and Drug Administration on devising standards for bread. The testimony of technical and medical authorities formed a very comprehensive description of the utility and pharmacology of the bread softeners. No decision was rendered regarding whether they should or should not be used in foods.

Other bakery fats literature dealt with greasing pans. A patented pan greasing process comprised spraying the pans with powdered hardened fat (Hansen—*U.S. 2,463,870*). Coppock & Cookson (*J. Soc. Chem. Ind.* 68, 274), recorded that when mineral oil was used for pan greasing some was absorbed by the baked product. They suggested possible physiological hazards from such oils and recommended that the quantity in the food should not exceed 0.2%, and that only mineral oils of high purity should be permitted.

Frying tests were made on egg and on potato pancakes to determine the caloric value decreases due to fat losses (Rossmann—*Z. Lebensm.-Untersuch. u. Forsch.* 89, 21, 274). When butter, margarine, lard, oil, and synthetic fats were compared using various cake formulas, losses due to pan residue, sputtering, and burning varied from 7 to 70%. The losses were greatest with the moisture-containing fats, and among the pure fats lowest loss occurred with lard. Overman & Li (*Food Res.* 14, 278) studied experimental deep-fat frying of doughnuts; reporting observations on fat adsorption, moisture loss, chemical changes of the frying fat, and chemical changes in the fat extracted from the doughnuts. Their work showed that different portions of the same fat did not behave alike. This and other variables suggested that considerable replications were necessary in comparing different frying fats. The foaming of coconut oil during frying could be inhibited by blending with other oils or by adding certain ethyl esters of coconut oil fatty acids (Hato—*J. Nippon Oil Technol. Soc.* 1, No. 2, 28).

Two patented salad dressing preparations comprised fat and condiments encased in gelatinized flour or gelatin to a dry powder form which could be mixed with aqueous solutions to produce liquid salad dressings (Kimball *et al.*—*U.S. 2,471,434-5*).

A substitute for cacao fat was made from coconut oil by distilling off 30% under vacuum and adding 10% hydrogenated oil to the residue (Nakajima & Kosuge—*J. Nippon Oil Technol. Soc.* 1, No. 4, 7).

Several new fat-vitamin preparations were described. A fortifying product for grain comprised a



coating material containing water-soluble vitamins, a saturated higher acid as a plasticizer, and abietic acid as an adhesive (Furter & Lauter—*U.S.* 2,475,133). A vitamin rich emulsion contained vitamin rich oil, and glycerol and prolamine to emulsify the oil in aqueous solutions (Bernhart—*U.S.* 2,463,738). The vitamin A in fish liver oils was increased about 10% by exposure to radon (Libermann & Grundland—*Compt. rend.* 224, 1033). The addition was probably formed from kitol or carotene.  $\alpha$ -Tocopherol became a more stable vitamin E preparation for dissolving in oil when it was acylated with propionyl chloride (Hoffmann-LaRoche & Co.—*Swiss* 220,956).

**EMULSIFIERS.** The most common emulsifiers now being treated in the literature are partial esters of fatty acids and polyhydric alcohols. New methods of preparing the glycerides were by ester interchange of the glycerol with methyl esters of the fatty acids (Lippincott—*U.S.* 2,476,053, Colbeth—*U.S.* 2,469,371), and a continuous process where fats were passed counter-current with a glycerol-water mixture through a heated zone (Ittner—*U.S.* 2,474,740; Allen & Malkinus—*U.S.* 2,478,354).

Partial fatty acid esters of sugars and polyethylene glycols were made from various raw materials and were patented for many uses. Sorbitan and sorbide partial esters of fatty acids were used as emulsifiers in a hair-waving cream (Mace—*U.S.* 2,479,382) and in wax coating compositions (Habib & Greenlie—*U.S.* 2,466,672), and for de-icing aircraft surfaces (Dissel & Newell—*U.S.* 2,451,814). Some partial ester emulsifiers were made by condensing ethylene glycol, ethylene oxide, and/or polyoxyethylene glycols with lanolin (Griffin—*U.S.* 2,478,820), dimerized fatty alkylol amides (Thurston & Warner—*U.S.* 2,470,081), stearyl stearate (Lerner—*U.S.* 2,476,609), dimerized poly-unsaturated long chain fatty acids (Kienle *et al.*—*U.S.* 2,473,798), and certain specific fatty acids (Ciba Ltd.—*Swiss* 244,048, 248,685-7; Fife & Roberts—*U.S.* 2,480,185). The various methods used and choice of the raw materials differed to obtain products suitable for specific preparations such as cosmetics, foods, and resins, and for inhibiting matting of cellulose fibers. One emulsifier for stabilizing food products contained several compounds such as alkali alginates and partial fatty esters of sugar, glycerol, and polyoxyethylene glycols (Steiner & Rothe—*U.S.* 2,474,019). Other patented emulsifiers were condensation products of alginic acid, epoxystearic acid, and epoxystearyl alcohol (Steiner & McNeely—*U.S.* 2,463,824), and esters of mono- and diglycerides, and lactic acid (Little—*U.S.* 2,480,332). The latter were recommended for ice cream and "high ratio" bakery products.

In investigations on manufacture of partial glycerides, Kawai *et al.* (*J. Soc. Chem. Ind. Japan* 46, 475, 478) obtained similar yields of diglycerides when glycerol was reacted with like moles of lauric, stearic, or oleic acid, and Savary (*Oleagineux* 4, 155; *Bull. soc. chim. France* 1948, 361) recorded that under optimum conditions the reaction attained results close to those calculated from the rule of random distribution. However, without catalyst and at temperatures lower than 180° two phases occurred in some reaction mixtures which caused results to differ from those of random reaction.

Emulsions of hydrocarbon oils and water formed with monoglycerides were studied by interfacial ten-

sion measurements and appearance.  $\alpha$ -Monostearin gave water-in-oil emulsions which would change to oil-in-water on addition of a small amount of soap (Jelinek & Anson—*J. Soc. Chem. Ind.* 68, 108). The combined emulsifiers gave more stable emulsions than equivalent amounts of each emulsifier alone. In another investigation of the same type an oil-in-water emulsion, formed with laurate soap, was reversed and made more stable by the addition of a small amount of monoolein (Dickinson & Iball—*Research (London)* 1, Suppl. 614). Each of the above reports contained a discussion of the phenomena occurring during emulsification and reversal of emulsions. Kremnev (*Kolloid Zhur.* 10, 18) discussed the principles of formation of concentrated hydrocarbon emulsions. His examples indicated that highly stable concentrations of benzene in water could be obtained with thixotropic mixtures of aliphatic alcohols and sodium oleate, and the stability of the emulsion increased with the length of the alcohol chain.

Phosphatide emulsifiers were rendered fluid or softened by additions of esters of lower alcohols and fatty acids (Wittcoff—*U. S.* 2,483,748). Secondary aromatic amines were dispersed by using fatty alcohols as the emulsifiers (Sturgis—*Brit.* 605,918). Aminoethyl ester of difatty acid glycerophosphoric acid was said to be useful as a dispersing compound and as a "nonblushing" agent for chocolates (Rose—*U. S.* 2,447,715). Quaternary ammonium emulsifiers containing hydroxy fatty acid radicals were recommended for casein emulsion paints and in carbon black dispersions (Schaeffer—*U. S.* 2,448,626). The newly patented emulsifiers for asphalt and tar emulsions included the still residues obtained from the distillation of animal greases (Muntzer—*Fr.* 929,805), condensation products of hydroxystearic acid (Jense—*Dutch* 63,008), and fatty acid amines (Fischer—*U. S.* 2,461,971). Fatty mercaptans were suitable for dispersing phenyl- $\beta$ -naphthylamine (Sturgis—*U. S.* 2,467,706). Fatty acid and polyglycol derivatives of silicon trihalides were patented as general purpose emulsifiers (Klein—*U. S.* 2,476,308).

Reviews on surface active agents and emulsifiers covered uses in nonferrous metal technology [Koerner—*Metal Ind. (London)* 73, 452] and the nonionic types (Janistyn—*Seifen-Öle-Fette-Wachse* 75, 26). The possibilities and limitations of using ultrasonic waves for emulsification of vegetable oils were discussed by Audouin & Levavasseur (*Oleagineux* 4, 95). Some frequencies tended to break emulsions, but in general emulsification was favored by progressive ultrasonic waves, low temperature, and presence of an emulsifying agent.

The literature on synthetic rubber and other emulsion polymers was of interest to fat and oil chemists, because most of the emulsifiers used were fat derivatives. The emulsifiers named in some new patents on emulsion polymerization were saturated alkali soaps (Barnes—*U. S.* 2,470,065, Vanderbilt & Hetchler—*U. S.* 2,470,417, Weber—*U. S.* 2,485,682), alkyl amine soaps (Vanderbilt & Bascom—*U. S.* 2,488,149, Van Valkenburgh—*U. S.* 2,483,797), ammonium soaps (Rumbold—*U. S.* 2,467,053-4, Vanderbilt & Bascom—*U. S.* 2,461,358), sodium salt of dioctyl sulfosuccinate (Hayes—*U. S.* 2,473,708), soaps of fatty acid-maleic anhydride adducts (McKennon & Lawrence—*U. S.* 2,465,901), and fatty acid sulfonates (Hendrik & Akkerman—*U. S.* 2,479,241).

The behavior of various commercial emulsifiers in emulsion copolymerization was recorded by Gould & Hulse (*Ind. Eng. Chem.* 41, 1021), and by Fordyce & Ham (*J. Polymer Sci.* 3, 891). Similar work on the methyl, ethyl, and propyl esters of addition products of maleic anhydride and *l*-pimaric acid indicated that best results were obtained with the ethyl adduct ester soap (McKennon *et al.*—*Ind. Eng. Chem.* 41, 1296). An investigation of soaps for the copolymerization in rubber manufacture provided proof that linoleic and linolenic acids cause irregularities in the polymerization (Ault *et al.*—*J. Am. Oil Chemists' Soc.* 26, 700). Similarly a conjugated diolefinic structure in rosin acid soaps retarded or inhibited polymerization. Those without aliphatic unsaturation were most suitable for the reaction; whereas, those with unconjugated unsaturation were somewhat less effective (Azorlosa—*Ind. Eng. Chem.* 41, 1626). In a nonaqueous emulsion polymerization system formamide with sodium lauryl sulfate emulsifier was adapted to polymerize styrene and copolymerize butadiene with styrene (Carr & Johnson—*Ind. Eng. Chem.* 41, 1588). Among the reviews on emulsion polymerization was a comprehensive review of the process (Reynolds—*J. Chem. Ed.* 26, 135), and another that dealt with the role of emulsifying agents in the polymerization (Staudinger—*Chemistry & Industry* 1948, 563).

In an emulsion polymerization system whose mechanism contained an oxidation-reduction cycle involving ferrous iron and benzoyl peroxide, the action of the soap was two-fold; it promoted emulsification, and it rendered the ferrous salt soluble in the oil phase (Wall & Swoboda—*J. Am. Chem. Soc.* 71, 919). Polymerization of methyl methacrylate with sodium peroxydisulfate was considerably higher in 3% potassium palmitate solution, whereas similar polymerization of vinyl cyanide was somewhat inhibited with the presence of the soap (Khomikovskii—*Doklady Akad. Nauk S.S.S.R.* 60, 615).

The fat derived surface active agents used in the petroleum industry for demulsification purposes included condensation products of ethylene oxide or ethylene glycol with castor oil fatty acid amines (DeGroote & Keiser—*U. S.* 2,468,181, 2,472,573) or with dehydrated mixtures of oiticica and castor oils (DeGroote & Keiser—*U. S.* 2,472,574).

PROTECTIVE COATINGS, RESINS, AND PLASTICS. The outstanding reviews on this subject were the papers presented at the twenty-fifth anniversary program of the Division of the Paint, Varnish, and Plastic Chemistry of the American Chemical Society and at the drying oil symposium jointly sponsored by University of Minnesota and the Minnesota Section of the American Chemical Society. These papers reviewed the contribution of the oil chemists (Wheeler—*Ind. Eng. Chem.* 41, 252), contributions of polymer chemistry (Fuller—*Ibid.* 259), paint testing (van Loo—*Ibid.* 267), liquid-liquid fractionation of oils (Passino—*Ibid.* 280), synthetic drying oils (Bolley—*Ibid.* 287), isomerization reactions of drying oils (Cowan—*Ibid.* 294), mechanism of oxidation of drying oil (Powers—*Ibid.* 304), polymerization of esters of drying oil acids (Bradley & Tess—*Ibid.* 310), and deterioration of dried oil films (Elm—*Ibid.* 319). Other reviews were on analysis of coatings (Rochow & Stafford—*Anal. Chem.* 21, 196), progress in drying oils (Nepoux & Bourlot—*Congr. tech. intern. ind. peintures et inds. assoc.* 1947, 428; Chatfield—*Paint*

*Manuf.* 19, 115), glycerol and alkyd resins in coatings (Lesser—*Am. Paint J.* 33, No. 19, 48), comparison of drying oils (Mundy—*Oil Colour Trades J.* 114, 1277; Greaves—*Paint Manuf.* 19, 111), acceleration of drying (Karsten—*Farben, Lacke, Anstrichstoffe* 3, 69), oxidation products of oxidized and polymerized oils (Gillam—*Australian Chem. Inst. J. & Proc.* 16, 19), mechanism of oxidation of linoleic acid by oxygen (Lundberg—*Oleagineux* 4, 86, 165), manufacture of bodied linseed oils (Sussmeyer—*Chim. peintures* 12, 240), mechanism of drying and ageing of linseed oil films (Slansky—*Paint Manuf.* 19, 113), tung oil (Hafeli—*Can. Paint & Varnish Mag.* 22, No. 11, 36), dehydration of castor oil for the paint industry (Prakash *et al.*—*J. Indian Chem. Soc. Ind. & News Ed.* 10, 89; Kappelmeier *et al.*—*Paint, Oil Chem. Rev.* 112, No. 1, 22, Damen—*Verfkhroniek* 20, 92), soybean and rubberseed oils for paint uses (Jordan—*Paint Technol.* 12, 287) and paint application of tall oil (Scheifele—*Farbe u Lack* 55, 105).

Several fatty acids were oxidized and the analyses of the products were discussed in relation to the present hypotheses of the mechanisms of polymerization and autoxidation of drying oils. Lundberg *et al.*'s (*J. Am. Oil Chemists' Soc.* 26, 109) data indicated that the initial products of oxidation of methyl linoleate were monomeric monohydroperoxides most of which were conjugated. Some unconjugated hydroperoxides were also formed. The diperoxides, formed to some extent, seemed to be cyclic. Spectral absorption, iodine values, and hydroxyl values were determined on the oxidized products. Another chemical-spectroscopic method for studying the autoxidation involved determination of hydroperoxides iodometrically, carboxylic acid by acid-base titration, hydroxy groups by acetyl procedures, and total hydroxyl content spectroscopically (Honn *et al.*—*J. Am. Chem. Soc.* 71, 812). The courses of reaction reported for linseed oil were: development of hydroperoxides and formation of carboxylic groups. As the drying oil begins to polymerize the decomposition of peroxide exceeds that of formation while carboxylic acids continue to form.

The steps involved in autoxidation were studied by oxidation and hydrogenation. With oxidation of oleic acid and hydrogenation to ketostearic acid, Ross *et al.* (*J. Am. Chem. Soc.* 71, 282) found that substitution can be at C<sub>8</sub>, C<sub>9</sub>, C<sub>10</sub>, or C<sub>12</sub> and that the double bond was always adjacent to the hydroperoxide group. Allen *et al.* (*J. Am. Oil Chemists' Soc.* 26, 395) data by this technic supported the hypothesis that the  $\alpha$ -methylene groups of double bonds rather than the double bonds themselves were initially attacked during autoxidation of nonconjugated esters. Data showing that linoleic acid esters which had adsorbed 0.2 moles of oxygen required more than two moles of hydrogen for saturation were submitted as proof. Other data suggested that during polymerization the union was by oxygen-carbon rather than by carbon-carbon binding. In contrast to Allen *et al.*, Franke & Mönch (*Ann.* 556, 200) published data indicating that partially oxidized linoleic and linolenic esters do not require more hydrogen than the pure fatty acid esters. They presented this as evidence against the hypothesis that part of the oxidation occurs at the methylene group adjacent to the double bond, for such a mechanism would require hydrogen to saturate the double bonds and additional

hydrogen to reduce CH(OOH) to CHOH groups. They found that with linoleic acid the double bond farthest from the carboxyl group was primarily attacked, and with linolenic acid the next susceptible bond was the middle member. With similar technic Treibs (*Chem. Ber.* 81, 472) recorded that in linolenic acid two oxygen molecules saturated two double bonds with the formation of a peroxide group. On hydrogenation, the third double bond was saturated and one oxygen atom was split from the peroxide group. Changes on further oxidation were explained as the results of rearrangement of peroxide groups with simultaneous cleavage of chains, or some aldehydic fragments formed in oxidation.

Bolland (*Trans. Faraday Soc.* 44, 669) explained oxidation of linoleates as removal of hydrogen from  $\alpha$ -methylenes of double bonds, addition of other compounds at this point and occurrence of chain-propagation and chain-termination steps. Gibson (*J. Chem. Soc.* 1948, 2275) studied the autoxidation reaction by partially oxidizing the  $C_{18}$  acids of palm oil and distilling. He believed that hydroperoxide formation was followed by an activation resulting in bond fission; each broken bond splitting into two centers of activity which may rearrange to form free radicals or new bonds. In the second stage the hydroperoxides attacked  $CH_2$ , *tert*-C, or unsaturated groups within its own or other molecules which thereby might be split into two parts or give mono-, di-, or trimeric products. Paschke & Wheeler (*J. Am. Oil Chemists' Soc.* 26, 278) studied the kinetics of polymerization of methyl linoleate at 290-300° and traced the development of various polymers. They suggested that a conjugated ester first develops, and that it unites with a normal ester to form a dimer. The formation of cyclic monomers and trimers was also discussed. Anderson & Porter (*Ind. Eng. Chem.* 41, 741) plotted the logarithm of viscosity against polymerization time for vacuum-bodied drying oils. Three distinct portions of the curve, two lines of different slopes followed by a curve of increasing slope until gelation when compared with analyses indicated that linoleic polymerizes more rapidly relative to linolenic in the second stage of the reaction than in the first, and that oleic acid played a role in the reaction in the third stage. The polymerization rates of many oils and oil blends were presented.

Gillam (*Australian Chem. Inst. J. & Proc.* 15, 150) discussed the oxidation of drying oils from the standpoint of esterification reactions occurring during the process. He suggested that some large molecules were built up by esterification of hydroxyl and carboxyl groups formed during the oxidation; castor oil which contains original hydroxyl groups develops considerable large molecules of this type. Basu *et al.* [*J. Sci. Ind. Research (India)* 7B, 153] illustrated this type reaction with the trihydroxypalmitic acid, aleuritic acid. On heating to about 150° a dimer forms and at higher temperatures condensates were linear polyesters involving the carboxyl and the end hydroxyl groups.

General treatises on catalytic conjugation of oils were published by Armitage & Cottrell (*Paint Technol.* 13, 353) and by Gordon (*Bull. mens. ITERG* 1948, No. 11, 38). A new process for developing conjugated compounds in soybean oil comprised chlorinating the oil with *tert*-butyl hydrochloride and dehydrochlorinating with steam (Teeter *et al.*—*Ind.*

*Eng. Chem.* 41, 849). The products contained 18-24% conjugates, principally of the diene and triene types. They dried rapidly to colorless films which were frequently wrinkled or frosted. Dehydrochlorination in the above process could be accomplished in the presence of inorganic cobalt compounds as catalyst for the process (Van Atta & Dietrich—*U. S.* 2,466,340). Commercial paint driers increased the rate of diene conjugation during oxidation of unconjugated linoleic acid and in the pure conjugated isomer it mildly promoted destruction of the dienes (Jackson & Kummerow—*J. Am. Oil Chemists' Soc.* 26, 460). However, the principal role of the driers was to accelerate the decomposition of peroxides.

Control testing of oil bodying operations was the subject of several reports. Gillam (*Australian Chem. Inst. J. & Proc.* 15, 126) discussed the changes in iodine value, peroxide value, and viscosity and the types of reactions tending to cause the changes during bodying. The measurement of viscosity in a simple cylindrical bubble viscometer was recommended as a control procedure for the bodying oils by von Mikusch (*Farbe u. Lack* 55, 241). With the use of equations and certain constants for the equations predictions were made for the increase of viscosity during the heating-up and cooling-down periods of the heat bodying of oils. In a study of the conventional analytical procedures, Knight & Swern (*J. Am. Oil Chemists' Soc.* 26, 366) found that determination of acid value, and peroxide and oxirane oxygen were reliable, while the presence of peroxides caused unreliable values for carbonyl oxygen, and iodine and saponification numbers. Booy & Waterman (*Anal. Chim. Acta* 3, 440) reported that the degree of polymerization could be approximated rapidly by molecularly distilling a small sample of the bodied oil. O'Hare *et al.* (*J. Am. Oil Chemists' Soc.* 26, 484) recommended and described three analytical physical technics for bodied oils. These comprise (a) molecular weight determination, (b) determination of increase in dielectric constant which gave an insight to the oxygenated structure of the oil, and (c) power factor determination which increased on both polymerization and oxidation.

A quite comprehensive work on evaluating drying oils was a large record of the compatibilities with resin, bodying, drying, film, cold and hot water resistance, alkali resistance, varnish making, chemical, physical, and other characteristics of the common drying, semidrying, synthetic, and blended oils (Houston *et al.*—*Ibid.* 244). The data were of particular interest, because they not only gave the characteristics of the products, but also showed the behavior on treatment and blending in terms of the quality of the paints and varnishes manufactured. In somewhat similar work Arnold (*Farben, Lacke, Anstrichstoffe* 3, 95) evaluated zinc white enamels made from various bodied oils and fraction thereof. The effects of thinners, flow promoters, driers, anti-skinning agents, and mixing procedures were also discussed.

Factory and test experiences in making coating products from some individual oils were recorded. Tachimori & Ito (*J. Soc. Chem. Ind. Japan* 45, 825, 827; 47, 484, 598) described the gelation of tung oil, and mixtures of tung oil with sardine oil, maleic anhydride, and glycerol giving the relationships of rates of polymerization and gelation. A similar report on isano oil gave its composition, method for and be-

havior in bodying, behavior with linseed, sardine, olive, peanut and dehydrated castor oils, and resins (Fauve—*Peintures, pigments, vernis* 24, No. 5, 147). The experiences of Scheiber (*Farbe u. Lack* 55, 35) on manufacturing of baking varnishes indicated that linseed oil was superior to tung oil for the purpose. The characteristic of various films dried at several temperatures were recorded. According to one patent the darkening of oxidized bodied oils was inhibited during a further heat treatment when it was water extracted prior to the subsequent heating (Novak—*U. S.* 2,488,680).

The drying characteristics of oils were improved by various methods. The addition of small amounts of lime to coatings made from soybean oil reduced the tack and increased the durability (Lewis—*U. S. Dept. Agr. Bur. Agr. Ind. Chem. AIC—199*, 3 pp.; Lewis *et al.*—*J. Am. Oil Chemists' Soc.* 26, 488). The Pittsburgh Paint and Varnish Production Club (*Official Digest Fed. Paint & Varnish Production Club No. 286*, 854) demonstrated that a drying oil which dried at the same rate as linseed oil could be produced by copolymerization of two parts of soybean oil with one part of tung oil. Semidrying and nondrying oils when used with tung oil yielded better drying products when the mixtures were interesterified than when simply blended (Reutenauer—*Bull. mens, ITERG 1948*, No. 8, 28).

Castor oil was converted to a drying oil by dehydroxylation with heat. Newly patented catalyst for the process were boron compounds (Colbeth—*U. S.* 2,469,370) and glycerol-phthalic acid resin (Cova—*Ital.* 420,475). According to an outline of Soviet research, castor oil dehydrated with sodium pyrosulfate as a catalyst yielded a product with properties approximating those of tung oil (Ivanova & Bepalko—*Paint Manuf.* 19, 118). Castor oil could be simultaneously dehydrated and bodied in a continuous operation by passing it through a zone heated at 355–380° (Meyer—*Congr. tech. intern. ind. peintures inds. assoc.* 1, 417). Dooper & Hermann (*Centraal Inst. Materiaal Onderzoek, Afdel. Verf. Circ. No. 51*, 16 pp.) prepared varnishes and putties from dehydrated castor oil and compared the products with those of tung, linseed, and modified phenolic resins. The castor oil varnish was inferior in tackiness, but was equal or better than other varnishes in clearness, drying, stability to water and 5% sodium carbonate solution, skinning, and sanding. The putties made from some samples of the dehydrated castor oil wrinkled.

Oils were modified by several chemical means to improve their coating characteristic. New methods of production and novel products were developed from action of various dicarboxylic acids on oils (Rust—*U. S.* 2,464,202, 2,467,912, 2,482,736; Minter—*U. S.* 2,462,209; Marling—*U. S.* 2,486,665; Moore—*U. S.* 2,459,176; Floyd—*U. S.* 2,483,726; Sauer—*U. S.* 2,454,294; Lilley *et al.*—*Brit.* 572,822-3; Centre national recherche scientifique—*Fr.* 869,132; Cova—*Ital.* 420,477). New drying oil products were made by condensing glycerol with a mixture of fatty acids and mercaptocarboxylic acids (Pratt—*U. S.* 2,461,920; Mortenson—*U. S.* 2,467,891). Other coating oils were made by reacting oils or fatty acid with polyalcohols other than glycerol (Woodruff—*U. S.* 2,486,353; Greenlee—*U. S.* 2,456,408), polymerized allyl alcohol (Am. Cyanamid Co.—*Brit.* 573,757), diallylresor-

cinol (Wittecoff—*U. S.* 2,459,835), and 2,2,6,6-tetra-methylcyclohexanol (Wittecoff—*J. Am. Oil Chemists' Soc.* 26, 157). Fatty acids of weakly drying oils were converted to drying oils by fractional distillation to recover drying constituents and reesterification of these with polyalcohols (Myers & Ritz—*U. S.* 2,479,857).

The journal literature contained some reports on experiences in manufacture of various oil adducts. Petit (*Am. Paint J.* 33, No. 12, 82; *Official Digest Fed. Paint & Varnish Production Clubs No. 287*, 977) discussed the reactions occurring in the preparation of monoglyceride for use in manufacture of alkyd resins. Partial glycerides were found to be compatible with shellac for varnish making (Sankaranarayanan—*J. Sci. Ind. Research India 6B*, 117). Partial fatty acid esters of pentaerythritol and dipentaerythritol (Lundberg & Chipault—*Off. Digest Fed. Paint & Varnish Production Clubs No. 288*, 11) and of several polyhydroxy alcohols (Elmer & Holman—*Ibid.* No. 263, 711) were prepared for film studies and their characteristics were recorded. In similar work Mattiello & Parekh (*J. Sci. Ind. Res. India 8B*, 29) used the fatty acids from cottonseed, fish liver, fish, peanut and tall oils, and six polyhydroxy alcohols; and recorded the course of manufacture and the characteristic of the products. Some of the products were considerably improved by additions of small amounts of tung or oiticica oil fatty acids. In similar work with tall oil one series of tests were made with addition of styrene and data on varnishes, enamels, and barn paints made from the esters were recorded (Northwestern Paint & Varnish Production Club—*Off. Digest Fed. Paint & Varnish Production Clubs No. 286*, 845). Products comparable to oleoresinous varnishes were made from linseed, soybean, and certain oxidized oils by heating styrene (Schroeder & Terrill—*J. Am. Oil Chem. Soc.* 26, 153; Detroit Paint & Varnish Production Club—*Off. Digest Fed. Paint & Varnish Production Club No. 286*, 861). In a study of the reactions of unsaturated dibasic acids with linseed oil, cyclopentadiene and substituted cyclopentadiene, maleic anhydride reacted like fumaric acid and maleic anhydride; whereas tetrahydrophthalic anhydride compounds formed from maleic anhydride reacting with butadiene, isoprene, piperylene, and 2-methylpentadiene did not react with the linseed oils under the same conditions (Cosgrove & Earhart—*Ind. Eng. Chem.* 41, 1492). The explanation offered for the difference in reactivity was based on the former belonging to the terpene series and the latter to the aromatic series.

Influence of the composition and the manufacturing procedures of phenolic resin-tung oil varnishes (Hermann—*Centraal Inst. Materiaal Onderzoek, Afdel. Verf. Circ. No. 55*, 11) and of alkyd resin-oil enamels (West—*Off. Digest Fed. Paint & Varnish Production Clubs 285*, 773) on the properties of the films obtained were determined.

Drying oils were prepared from petroleum constituents. These were reaction products of glycerol  $\alpha$ -allyl ethers with phthalic and succinic acids (Dannenberg *et al.*—*Ind. Eng. Chem.* 41, 1709) and reaction products of olefinic hydrocarbons with hydrogen fluoride (Johnstone—*U. S.* 2,470,894, 2,491,496, Bloch—*U. S.* 2,476,955).

The characteristic of forming wrinkle finishes by drying oils was induced by addition of certain alkyd

type preparations (Wyler—*U. S. 2,462,046*, Luaces—*U. S. 2,465,243*), polyvinyl chloride (Beynon—*U. S. 2,460,485*), polyvinyl acetate (Beynon—*U. S. 2,479,298*), polyvinyl butyral resin (Waldie—*U. S. 2,486,232*), and synthetic elastomers (Luaces—*U. S. 2,468,989*, Beynon—*U. S. 2,468,724*). The wrinkling character of coatings could be inhibited by glycol, solvent naphtha, turpentine, limed rosin, and selection of resins which do not impart the characteristic (Hadert—*Farbe & Lack 55, 2*). A crackle finish was produced by use of two coats of varnish with the first coating containing metallic soap or fatty acid amide (Pritzker—*U. S. 2,467,228-9*). One varnish contained zinc salts of polymeric fatty acids and zinc resinate dissolved in a volatile organic solvent (Cowan & Teeter—*U. S. 2,477,116*). Oil-cellulose ether compositions were suitable as varnishes (Stubblebine—*U. S. 2,457,847*) and for insulation coatings for electrical equipment (Smith & O'Halloran—*U. S. 2,462,912*). Metallic stearates were treated as constituents of coating in regard to plasticizing action (Cincinnati-Dayton-Indianapolis-Columbus Paint and Varnish Club—*Off. Digest Fed. Paint & Varnish Production Club No. 286, 826*), for thickening and flattening paints (Licata—*Ibid. No. 291, 165*), to render gelatinized drying oils soluble (Kronstein—*U. S. 2,476,879*) and as constituents of wire coating compositions (Boak—*U. S. 2,469,150*).

The metal soaps of 16 metals were investigated as drying catalysts for their efficiency as driers, losses on oxidation, and characteristics of films (Pagani—*Congr. tech. intern. ind. peintures inds. assoc. 1, 364, 369*). The drying acceleration by manganese soaps of oiticica, tung, perilla, and grapeseed oils fell in that order. Highest losses in the oxidation process occurred with sodium, cesium, barium, and cadmium soaps. Water permeability was highest with lead soap and lowest with cobalt soaps. With the use of copper driers the films were most elastic. The use of Werner complex coordinated soaps as driers was patented (Brauner—*U. S. 2,466,925*) and one communication contained a record of tests indicating that the coordinated soaps were better drying catalysts than the plain soaps (Worthington & Nicholson—*Paint, Oil, Chem. Rev. 112, No. 11, 20*). Oxy-boron organic compounds (Whiting—*U. S. 2,480,206*) and boron trifluoride (Lange & Folzenlogen—*U. S. 2,480,485*) were also patented as catalysts for bodying oils. Aromatic monocyclic amines were recommended as catalysts to stop bodying reactions before gelation occurs (Berger *et al.*—*U. S. 2,478,451*).

Resinous and plastic products were manufactured by the interpolymerization of fatty oils or their derivatives with styrene or butadiene (Nye—*U. S. 2,461,761*, Griess & Teot—*U. S. 2,468,748*, Young & Hoogsteen—*U. S. 2,468,798*, Robertson & Rust—*U. S. 2,470,953*, Foster—*U. S. 2,484,215*, Ralston & Corley—*U. S. 2,461,349*, Dyer & Maxwell—*J. Am. Oil Chemists' Soc. 26, 649*). Various modifications of alkyd resins were patented (Gehrenbeck—*U. S. 2,456,629*, Fleck—*U. S. 2,458,772*, Eilerman—*U. S. 2,462,618*, Moore—*U. S. 2,461,564*, Ender—*U. S. 2,476,714*, Marling—*U. S. 2,479,951*, Kropa—*U. S. 2,485,294*). Vol'nov & Saffronchik (*Zhur. Priklad. Khim. 21, 744*) recommend determination of the polarization as a control procedure in alkyd manufacture. Adducts of itaconic and citraconic anhydrides with methyl linoleate formed gels much slower when heated with ethylene diamine than did corresponding maleic ad-

ducts (Teeter *et al.*—*J. Am. Oil Chemists' Soc. 26, 660*). Fatty oils or fatty acid derivatives were used to make resins or plastics by condensation, copolymerization, or special treatments with aminotriazine-aldehyde (Widmer & Fisch—*U. S. 2,448,338*), diallyl tetrachlorophthalate (Nordlander—*U. S. 2,450,682*), sulfur (Blume & Spokes—*U. S. 2,453,188*), ethylene polymers (Alderson—*U. S. 2,455,910*), chlorinated rubber (Speyer—*U. S. 2,461,704*), phenol-formaldehyde resin (Ximenez *et al.*—*U. S. 2,460,962*), polyamides (Buechele—*U. S. 2,462,053*), ester gum (Willis—*U. S. 2,467,796*), alkenyl-aromatic compounds (Griess & Teot—*U. S. 2,468,747*), polyamide-pinene resin (Fries—*U. S. 2,469,108*), monovinyl aromatic compounds (Bobalek—*U. S. 2,470,752, 2,470,757, 2,470,759*), vinyl acetate (Swern & Dickel—*U. S. 2,475,557*), sulfur and a cyclopentadiene (Gerhart—*U. S. 2,475,664*), vinyl resin (Rothrock & Wayne—*U. S. 2,479,410*), and urea-phenol or starch-phenol resin (L'Impregnation Soc.—*Fr. 865,407*). The residue from the manufacture of sebacic acid from castor oil was converted to a resin by reaction with polybasic acids (Hanson—*U. S. 2,470,849*), and with alkylene diamines (McKeever—*U. S. 2,471,230*). Vinyl fluoride polymers were stabilized with glyceryl monolaurate (Johnston & Richter—*U. S. 2,476,606*).

Rubberlike products were made from soybean oil fatty acid polymers by condensing with various glycols, alkanolamine and diamines, and vulcanizing with polybasic acids and ethylene glycol (Cowan *et al.*—*Ind. Eng. Chem. 41, 1647*). Some showed tensile strengths and extensibilities comparable to some commercial synthetic elastomers.

The newly patented fat derived plasticizers were epoxidized soybean oil (Niederhauser & Koroly—*U. S. 2,485,160*), lead soap (Fletcher & Taylor—*U. S. 2,467,550*), stearic acid amide of ethylene diamine (Duggan & Stambaugh—*U. S. 2,464,855*), esters of glycols and fatty acids (Strauss—*U. S. 2,469,446*, Stamberger—*U. S. 2,459,298*), sulfolanyl esters of fatty acids (Morris & Shokal—*U. S. 2,451,299*), mixed ester of glycols with a fatty acid and fatty nitriles (Myers & Fitzpatrick—*U. S. 2,474,010*), and oxidized alcohol esters of unsaturated fatty acids (Myers & Webster—*U. S. 2,485,910*). A symposium presented before the Division of Paint and Plastic Chemistry of the 114th American Chemical Society on plasticizers was a comprehensive review on manufacture and use of plasticizers (many authors—*Ind. Eng. Chem. 41, 663 through 740*). Twelve papers were presented.

ANTICORROSIVE COMPOUNDS. Most of the new anticorrosive compounds comprised a major portion of mineral oil and minor portions of other ingredients along with certain fat derivatives. The fat derivatives patented for the purpose were fatty alcohols and lead soaps of wool grease (Schindler & Anderson—*U. S. 2,453,816*), oil soluble wetting agent and blown soybean oil mixture (McCarthy—*U. S. 2,471,638*), a combination of dicarboxylic acid and fatty acid ester of acids of phosphorus (Kluge & Patterson—*U. S. 2,452,321*), fatty acid phosphates (Engle & Fikar—*U. S. 2,472,099*), polyethylene glycol hexaricinoleate (Wasson & Zimmer—*U. S. 2,474,604*), and pentaerythritol monostearate triacetate (Paliwoda & Duncan—*U. S. 2,471,889*). Fatty acid amines were also useful as rust inhibitors, particularly for water conduits (Kahler—*U. S. 2,460,259*).

In an investigation on testing rust inhibitors, the turbine oil rusting test, the static water drop corrosion test, and the fog cabinet corrosion test were applied to 150 different rust inhibitors (Baker *et al.*—*Ind. Eng. Chem.* 41, 137). The significance of the results were discussed from the standpoint of conditions during application and selection of anticorrosive compatible with the intended use. Most of the rust inhibitors tested were fatty acid derivatives.

**PRODUCTION OF ACID, ALCOHOL, ESTER, KETONE, NITROGEN, AND HYDROCARBON DERIVATIVES.** In attempts to convert saturated fatty acids to unsaturated acids Raney catalyst (Moretti—*Bull. soc. chim. France* 1948, 1154) and ethylene and acetylene hydrogen acceptors with active nickel on pumice catalyst (Franke *et al.*—*Ann.* 561, 98) were used. Some unsaturated fatty acids were formed in both investigations but the reaction was accompanied by decarboxylation and other reactions which produced hydrocarbons, ketones, and new mono- and dicarboxylic acids.

Many pure fatty acids containing branched chains were synthesized and their properties recorded (Cason *et al.*—*J. Org. Chem.* 14, 132, 137, 147, 155; Campbell *et al.*—*J. Chem. Soc.* 1948, 1741; David *et al.*—*Ibid.* 1949, 1541). Interest in preparing and studying the pure chemistry of these was no doubt stimulated by recent discoveries of their natural occurrence. Tridecanoic acid containing C<sup>14</sup> in the carboxyl group was prepared from lauryl bromide and carbon dioxide by the Grignard reaction (Hines & Germant—*Science* 110, 19). The compound was made for use in studies on the metabolism of fats.

Glycerides and free fatty acids were oxidized with chemicals for various purposes. Oleic and other mono-unsaturated acids were oxidized with chromic acid (Emery Ind. Inc.—*Brit.* 618,412; Fitzpatrick & Myers—*U. S.* 2,450,858), and with air (Patrick & Emerson—*Ind. Eng. Chem.* 41, 636) for the production of dibasic acids. New monobasic acids and large amounts of high molecular weight by-products were also formed during the processes. High molecular weight dibasic acids were made by polymerizing unsaturated fatty acids to dimers (Goebel—*U. S.* 2,482,761). Rice oil was hydroxylated with a mixture of acetic acid and hydrogen peroxide to produce a castor oil substitute (Kuwayama—*J. Nippon Oil Technol. Soc.* 1, No. 4, 27). Similarly oleic acid was hydroxylated to 9,10-dihydroxystearic acid with hydrogen peroxide and formic acid (Swern *et al.*—*U. S.* 2,492,201). Fatty acids were hydroxylated and ketonized by warming with selenium dioxide (Turk—*U. S.* 2,469,059). Specific hydroxy fatty acids were also produced by fractionating wool fat (Nozoe—*Japan* 153, 628-9). Fatty acids chlorinated at carbons near the carboxyl were converted into slightly lower members of the acid series when fused with alkalis (Ishii—*J. Soc. Chem. Ind. Japan* 46, 885, 889).

The processes described for converting fatty acids into primary alcohols comprised hydrogenation of the zinc and chromium soaps without catalyst (Procter & Gamble Co.—*Brit.* 573,788), hydrogenation of the oils with Raney nickel (Ueno *et al.*—*J. Soc. Chem. Ind. Japan* 48, 78) and iron oxide (Ueno *et al.*—*Ibid.* 46, 483) as catalysts, by reduction with sodium (Kastens & Peddicord—*Ind. Eng. Chem.* 41, 438), and heating under pressure with slaked lime (Miyoshi Chem. Inds. Co.—*Japan* 158,119). Commercially produced fatty alcohols were intended for use as intermediates for

manufacture of detergents, plasticizers and other products. The total synthesis of fatty alcohols and acids with crotonaldehyde as the starting material was of interest from a pure chemistry viewpoint (Grundmann—*Chem. Ber.* 81, 510).

Epoxy derivatives of fats which were suitable plasticizers and intermediates for other compounds were prepared by treating the fats or fatty acids with a reaction product of glacial acetic acid and hydrogen peroxide (Terry & Wheeler—*U. S.* 2,458,484). Methanolysis of ricinoleic acid followed by oxidation produced ketostearic acid (Grummitt & Siedschlag—*J. Am. Oil Chem. Soc.* 24, 690). Ketenes, suitable as ingredients for protective coatings were prepared by heating fatty acids with acetic anhydride (Miller & Sorenson—*U. S.* 2,465,337).

Fatty acid chloride mixtures, suitable as intermediates for manufacture of esters, were prepared by treatment of fats with carbonyl chloride in the presence of tertiary amine hydrochloride (Soc. pour l'ind. chim. a Bale—*Swiss* 222,970-1). In an investigation of the chemistry of chlorination of oils with tertiary butyl hypochlorite, allylic monochloro derivatives, non-allylic monochloro derivatives, and a saturated dichloro derivative were produced from methyl oleate (Teeter & Jackson—*J. Am. Oil Chemists' Soc.* 26, 535).

Fatty acid esters were manufactured for various purposes. A therapeutic vitamin D<sub>2</sub> product in pure crystalline form resulted from esterifying the vitamin with chaulmoogric acid (Penau & Hagemann—*U. S.* 2,484,526). Hydroxy fatty acids were polyesterified to yield waxy or resinous solids (Basu—*Science & Culture* 14, 120, 157, 164). Oily esters of phenols and fatty acids were made by heating phenols with methyl esters of fatty acids in the presence of boron trifluoride (E. I. du Pont de Nemours & Co.—*Brit.* 573,909). Diesters of erythrol and several fatty acids were prepared and their characteristics recorded.

A very novel method of manufacturing fatty acid esters comprised heating fatty acids under pressure in 30% aqueous formaldehyde solution (Paquot & Peron—*Bull. soc. chim. France* 1948, 855). This treatment of palmitic acid at 300° for five hours produced 37% methyl palmitate and 16% ethyl palmitate.

Thermal decomposition of fats served various purposes. Daruwala *et al.* (*J. Indian Chem. Soc. Ind. & News Ed.* 10, 107) heated various vegetable oils at 300 mm. pressure to selectively crack highly unsaturated constituents and to distil off decomposition products in the production of saturated fatty acids or fats. Wool grease was pyrolyzed and the fuel and pitch products obtained were discussed in regard to their economic value (Lower—*Oil & Colour Trades J.* 1949, Jan. 7/14). The thermal decomposition products of a 6-10% methanol extract of sesame oil was useful as a synergist for pyrethrin insecticides (Simanton—*U.S.* 2,463,324). A discussion on the use of vegetable oils as diesel fuel and the modification of engines for these fuels was published by Baker & Sweiger (*Gas Oil Power, Ann. Tech. Rev. No.* 1947, 338).

The electrical conductivity of nitrogen-alkylated fatty ammonium chlorides was determined in a study on their colloidal properties (Ralston *et al.*—*J. Am. Chem. Soc.* 71, 671, 672). The substitution of hydroxyethyl groups for methyl groups in trimethyl-dodecylammonium chloride did not greatly modify

the colloidal properties, whereas the substitution of 2,3 dihydroxypropyl resulted in a tendency to make the compounds act like cationic electrolytes. A similar substitution in trimethylhexadecylammonium chloride was without significant effect. Similar work on dodecylammonium chloride in water solutions containing methanol or acetonitrile indicated the transition of the dodecylammonium chloride from a colloid to an electrolyte was increased with additions of the organic solvents (Ralston & Brake—*Ibid.* 1327).

Quinoloxo-fatty-ammonium compounds were patented as disinfecting and preserving compounds (Hartmann & Bosshard—*U.S.* 2,487,707).

Oleoneitrile, for use as an assistant in rayon manufacture, was made by heating fatty acids and ammonia under pressure (Stegemeyer—*U.S.* 2,460,772). Unsaturated fatty acid nitriles were oxidized with chromic acid to produce shorter chain nitriles and fatty acids (Fitzpatrick & Myers—*U.S.* 2,468,436). A new patent was issued on converting fatty acid nitriles to amines by hydrogenation (Emery Industries, Inc.—*Brit.* 612,712). Linolyl nitrile was dimerized and then hydrogenated to provide a diamino resin compound (Bruson & Niederhauser—*U.S.* 2,460,733).

Methods of preparing oleamide and N-(n-alkyl)oleamides from methyl through hexyl and the even members through octadecyl were studied (Roe *et al.*—*J. Am. Chem. Soc.* 71, 2215). Good yields were obtained and the characteristics were recorded. Similar data was recorded on some of the epoxidation derivatives of the above mentioned preparations (*Ibid.* 2219). The preparation of fatty amides by the reaction of fats with amines and alkali was patented (Meade—*U.S.* 2,464,094).

As pure fundamental information Naudet & Desnuelle (*Bull. soc. chim. France* 1948, 1143) determined the relative yields of amide formed by the reaction of oleyl chloride on six amino acids.

DEFOAMERS AND FLOTATION AGENTS. The newly patented defoamers, for use principally in steam boilers, were condensation products of fatty acids and aliphatic polyamines (Gunderson—*U.S.* 2,461,730), a mixture of fatty acid amines and a dibasic acid (Bird & Jacoby—*U.S.* 2,469,450), fat derivatives which may be designated as substituted-amino-N-substituted alkanamides (Bird & Jacoby—*U.S.* 2,481,899), and mixtures of castor oil and fatty acid amides of a hydroxy alkyl amine (Gunderson—*U.S.* 2,485,378).

Various fat derivatives were patented as flotation agents for ores. The products of treating fatty acids with nitric acid were recommended for nonsulfide and nonsilicate ores (Duke—*U.S.* 2,459,219). Use of fat and tall oil soaps was patented for concentration of vanadium (Weinig—*U.S.* 2,464,313) barite (Gieseke—*U.S.* 2,483,970) and phosphate (Gieseke—*U.S.* 2,466,671) ores. Certain solutions of fatty acid amines and other chemicals were useful as general flotation agents (Hoerr—*U.S.* 2,468,755) and for zinc ores (McKenna *et al.*—*U.S.* 2,482,859). Iron ores were concentrated with use of sulfonated fatty acids as the flotation agent (Booth & Herkenhoff—*U.S.* 2,475,581).

LUBRICANTS, WATER REPELLENTS, AND SOFTENERS FOR TEXTILES AND LEATHER. A surface active agent, made by condensing fatty acid amides with formaldehyde and sulfonating, was added to viscose spinning solution to impart a water resistant coating, increase resistance to swelling, and to decrease the tendency of freshly formed filaments to cohere (Ciba Ltd.

—*Swiss* 241,211). Moisture was removed from wound regenerated cellulose thread by treatment with a 5% solution of polyethylene glycol distearate in Stoddard's solvent (Schlatter & Holmberg—*U.S.* 2,460,400). Polyoxyethylene glycol fatty acid esters were also used with mineral oil to lubricate cellulose ester filaments (Eisen—*U.S.* 2,461,043).

Two new textile waterproofers were made, respectively, by treating fatty acid amidomethylol compounds with tertiary nitrogen bases (E. I. duPont de Nemours & Co.—*Brit.* 605,599), and by condensing stearamide with chloroacetic anhydride and glycolic acid (Ciba Ltd.—*Swiss* 248,208). Cellulose materials were waterproofed by treating with fatty acid peroxides and heating to decompose the peroxide (Warden—*U.S.* 2,460,777). Another waterproofing process comprised forming zirconium soaps in the fabric by treating first with solutions of soluble zirconium salts and then with fatty acids (van Mater—*U.S.* 2,457,853). In a paraffin wax coating for the same purpose the wax was dispersed in hot water using sorbitan monopalmitate and polyalkylene sorbitan monopalmitate as the emulsifiers (Rood—*U.S.* 2,456,595).

Scroop was imparted to rayon and silk by impregnating with a small amount of butoxyethyl stearate by means of water emulsions (Kaplan—*U.S.* 2,482,917). Sodium salts of semiesters of oxyethyl-fatty acid-amides and dicarboxylic acids were recommended as anticreasing agents for fabrics (Ciba Ltd.—*Brit.* 621,324). Sponging fabrics with dilute solutions of commercial wetting agents reduced the undesirable gloss which was caused by wear (McKee—*U.S.* 2,459,236).

A substitute for egg yolk for oiling leather contained rape oil, rape oil lecithin, ethanolamine soap, and polyoxy ethers of fatty alcohols (Thiele & Sisley—*Bull. mens. ITERG* 3, 77). A patented composition for the same purpose contained mineral oil, rosin acids, polyoxyethylene hexitol fatty acid ester, lower fatty acids, and substituted glyoxalidine (Koppenhoefer—*U.S.* 2,456,587).

INCENDIARY FUEL. The heat capacities of the incendiary, "Napalm"-gasoline gels in the range of  $-50^{\circ}$  to  $50^{\circ}$  were recorded (Langstroth—*Can. J. Res.* 27A, 151). An over-all analysis of "Napalm" including x-ray diffraction patterns, moisture, soap, and hydrocarbon indicated that the aluminum, laurate soap present was aluminum dilaurate (Mysels—*Ind. Eng. Chem.* 41, 1435).

LUBRICANTS. A series of reviews on grease manufacture by Boner (*Petroleum Refiner* 28, No. 3, 109; No. 4, 152; No. 5, 164; No. 6, 127; No. 7, 129) contained information on raw materials additives, processing equipment, and methods for manufacturing calcium, sodium, aluminum, barium, and miscellaneous greases. Methods for making lithium greases of low water solubility were published by Rapetti (*Riv. ital. petrol.* 15, No. 176, 14).

Continuous equipment for making aluminum soaps suitable for greases and many other purposes contained a reaction stage for aluminum salts and sodium soap, and washing and drying stages (Gebhart & Ross—*U.S.* 2,447,064). According to a new metallic soap preparation patent, washing and drying could be eliminated by using aluminum alcoholates and fatty acids as the raw material (Jones—*U.S.* 2,469,041). For the final preparation of greases two patents concerned continuously dispersing soap in

mineral oil (Hetherington—*U. S. 2,461,276*; Hain—*U. S. 2,478,917*), and three inventions involved specific cooling means to obtain suitable hardness and textures (Woods *et al.*—*U. S. 2,470,965*, Gurd & Sproule—*U. S. 2,480,647*, Houlton—*U. S. 2,483,382*). Special high temperature greases were made from lithium and aluminum soaps and mineral oils (Morway & Zimmer—*U. S. 2,451,039*; Georgi—*U. S. 2,477,296*). Use of metallic soaps of hydroxy fatty acids in grease produced products of good mechanical stability (Bondi—*U. S. 2,475,589*). Other fatty raw materials recommended for grease making, probably for economy, were oxidized petroleum wax acids (Forney—*U. S. 2,480,564*; Tsyskovskii—*Azerbaidzhanskoe Neftyanoe Khoz. 26*, No. 8, 17) and rosin acids (Stamm—*U. S. 2,463,822*, Weitkamp—*U. S. 2,463,823*).

The literature for lubricant technologists was enriched with new fundamental data on the behavior of metallic soaps in hydrocarbons. Vold *et al.* (*J. Colloid Sci. 4*, 93; *Ind. Eng. Chem. 41*, 2539; *J. Am. Oil Chem. Soc. 26*, 520) compared the phase states and thermal transitions of several of the lubricant soaps by means of x-ray diffraction patterns. Calcium stearate was obtained in three forms by dehydration of calcium stearate monohydrate. The x-ray diffraction patterns of commercial greases at room temperatures indicated that the soaps were principally in finely divided crystalline form, but, could be modified by *in situ* manufacture in the mineral oil. On heating, some soaps seem to undergo polymeric-like transformations while others formed liquid crystalline solutions. Different soaps of the same metal had characteristic patterns; and with mixed fatty acids, mixed crystals were formed. Gray & Alexander (*J. Physical & Colloid Chem. 53*, 9, 23) studied the formation of aluminum soaps and their gelling characteristics. The heat of reaction, measured as a function of the fatty acid added, showed that not more than two fatty acid groups combined with the metal. A polymeric formula for the soap formed was based on six-fold coordination of aluminum and oxygen. It was suggested that soap molecules aggregated to form long fibrous micelles with fatty acid chains extended sideways. McGee's (*J. Am. Chem. Soc. 71*, 278) analyses of aluminum soaps also suggested a polymeric structure in which six carboxyl groups were coordinated with alumina. In a study of the solubility of zinc soaps in organic solvents by Martin & Pink (*J. Chem. Soc. 1948*, 1750), an abrupt increase in solubility at a critical temperature was attributed to the effect of a mesomorphic change in the soap which allowed solvent molecules to penetrate the hydrocarbon lattice of the soap.

The setting time, syneresis, and gel-strength of gels of sodium palmitate, stearate, and oleate in many organic liquids were recorded (Hattiangdi & Adarkar—*J. Am. Oil Chem. Soc. 26*, 364). The gels in any solvent decreased in setting time and extent of syneresis with different soaps in the order, oleate > stearate > palmitate. The gel strength increased in the order, oleate < stearate < palmitate. For solvents belonging to a homologous series the setting time and extent of syneresis of the gels increased and gel-strength decreased as the series was extended. Sodium stearate gels were studied under anhydrous and hydrous conditions for their ability to retain hydrocarbon liquids (Doscher & Vold—*J. Am. Oil Chem.*

*Soc. 26*, 515). Differences in the stability of the gel structures was correlated with changes in phases of anhydrous soaps. With hydrous systems the increased stability was suggested to develop from the ability of water to form complexes or aggregates. Boner (*J. Physical & Colloid Chem. 52*, 1383) studied the soap-hydrocarbon gels with regard to the effect of the metal soap. Soaps of monovalent metals were less thixotropic than those of di- and tri-valent metals, and soaps of the metal of lowest atomic weight in a series were most thixotropic. This information was discussed on the basis of structure and flow of lubricant greases. The softening points of gels of 16 metal stearates in paraffin oil were recorded by Seifer (*Doklady Akad. Nauk. S.S.S.R. 67*, 291).

Moses & Puddington (*Can. J. Res. 27B*, 616) correlated changes in the flow properties of dispersions of calcium soaps in hydrocarbons with the thixotropy of the systems. The coefficient of thixotropy found by this method had a linear relation to the hardness of the dispersion as determined by a falling cone. Wilson & Smith (*Ind. Eng. Chem. 41*, 770) developed an empirical equation which permitted a more accurate calculation of the viscosity of lubricant grease when under pressure than was previously possible.

A symposium on surface chemistry (*Research London Suppl., 1949*) contained several theoretical communications on lubricating films. A symposium on functional tests for ball bearing greases (*Am. Soc. Testing Materials No. 84*) contained papers by several investigators on grease testing and correlations of laboratory performance tests with experiences in use of various greases under different conditions. Other data of basic interest for lubrication concerned determination of the number of fatty molecules adsorbed on ball bearings (Jacques & Brignonnet—*Compt. rend. 228*, 1587), influence of pH and heat on the surface tension of lubricants (Baouman—*Industrie chimique 36*, 113), and the relation between interfacial tension and friction value of the C<sub>4</sub> to C<sub>18</sub> fatty alcohols and C<sub>4</sub> to C<sub>9</sub> fatty acids (Ramsauer & Wolf—*Chem.-Ing.-Tech. 21*, 216). A continuous method for determining the viscosity of grease was patented (Zimmer & Beerbower—*U. S. 2,459,483*).

The heat dehydroxylation of castor oil for lubricant uses with lead compounds as catalysts was patented (Agster—*U. S. 2,484,328*). Fatty ester of polyoxyalkylene diols were patented as low temperature lubricants (Fife & Toussaint—*U. S. 2,457,139*).

The additives used in lubricating oil as pour-point depressants and viscosity index improvers were comprehensively reviewed, primarily from the patent literature (Kalichevsky—*Petroleum Refiner 28*, No. 6, 97; No. 7, 125). Another review on additives treated the theoretical aspects in connection to their mechanism of accelerating or retarding formation of jellies (Smith *et al.*—*J. Am. Oil Chemists' Soc. 26*, 135). Many new greases of the metal soap-mineral oil type contained some polymeric compounds to impart tackiness, high temperature efficiency, or improve viscosity (White & Harman—*U. S. 2,451,895*, Morway—*U. S. 2,487,260*, 2,491,054, Roehner & Morway—*U. S. 2,487,376-9*, Foehr—*U. S. 2,489,281*, Foehr & Leyda—*U. S. 2,489,301*, Leyda—*U. S. 2,489,300*, Beerbower & Murray—*U. S. 2,491,028*). Most of the polymeric additives were resins or gums derived from reaction of fatty acids and other compounds. An oil lubricant was improved by adding a mixture of acrylic



acid polymers and fatty acid esters of a phosphorus acid (Revukas—*U. S. 2,486,493*).

A grease to be used for propellers contained mineral oil, aluminum soap, and polymerized products of a mixture of drying oils and polyalcohols. Mineral oil separation in greases was inhibited with hydroxylated fatty acids (Beerbower & Ricards—*U. S. 2,455,649*). For the same purpose and to improve the dispersion of metal soaps in mineral oil, partial esters of polyhydroxy alcohols and fatty acids were used (Waugh—*U. S. 2,470,537*, van Olphen—*Dutch 63,011*). The melting point of soda soap base grease was increased by heating with a small amount of glycolic or lactic acid (Morway & Daniels—*U. S. 2,468,098-9*).

The fat derivatives used to impart detergent properties to lubricants were a coordinate metal complex containing organic bases of tertiary nitrogen compounds and fatty acids (Giammaria—*U. S. 2,464,497*), metal salts of organic sulfonates (Zimmer *et al.*—*U. S. 2,467,176*), metal salt of naphthenoxystearic acid (Rocchini—*U. S. 2,469,003*), and heated mixtures of fatty acid amines or quaternary compounds and organic sulfonates (Freeman—*U. S. 2,481,585*). The compounds recommended for improving viscosity and depressing pour points of lubricants were condensed products of fatty nitriles and other organic compounds (Lieber & Cashman—*U. S. 2,454,394*), polyvinyl oleyl ether (Rosen & Sparks—*U. S. 2,468,516*), copolymerized products of fatty and aromatic halides (Lieber & Cashman—*U. S. 2,470,504*), sperm oil alcohols (Smith and Cantrell—*U. S. 2,475,727*), phenol and cresol fatty derivatives (Reiff *et al.*—*U. S. 2,475,916*), and tertiary aliphatic amines containing at least one unsaturated fatty acid radical (Bartleson—*U. S. 2,476,271*). The nitrogen compounds among the above additives were also said to have anticorrosive properties. Other rust inhibiting lubricant additives were fatty acid-succinic acid monoamide product (Rocchini—*U. S. 2,458,425*), lauryl pyridinium chloride—benzyl thiocyanate mixture (Rucker—*U. S. 2,459,119*), a mixture of addition products of dicarboxylic and fatty acids and sulfurized oleic acid (Perry—*U. S. 2,459,717*),  $\alpha,\alpha$ -thiofatty acids (Klein—*U. S. 2,450,403*, McNab & Bartlett—*U. S. 2,460,025*, Lincoln & Byrkit—*U. S. 2,468,089*, Sproule & King—

*U. S. 2,468,520*, Musselman—*U. S. 2,484,843*, van Ess—*U. S. 2,487,840*).

Studies on inhibiting foaming in lubricating oils were recorded by McBain *et al.* (*Natl. Advisory Comm. Aeronaut. Tech. Notes No. 1840*, 25 pp.; *No. 1841*, 10 pp.; *No. 1842*, 12 pp.; *No. 1844*, 17 pp.; *No. 1845*, 26 pp.). The surface properties of oils, Holz—*U. S. 2,462,200*), mono-fatty acid esters of sorbitan and pentaerythritol (Sproule & King—*U. S. 2,479,424*),  $\alpha$ -halogenated keto fatty acids (Price & Sprules—*U. S. 2,481,036*), and a mixture of fatty acids, sulfurized unsaturated fatty acids, and/or fatty acid-phosphoric acid products (von Fuchs & Pilz—*U. S. 2,481,372*). Various fats were sulfurized to produce sulfurized additives for lubricants (Wells analyses of properties of foams, effect of many defoaming chemicals, and the effect of processing were determined. The requirements of oil insolubility, low volatility, and low reactivity limited the choice of liquid defoamers to the higher polyhydric alcohols.

An aqueous lubricant comprised an aqueous solution of triethanolamine salt of halogenated stearic acid and free amine (Rodgers—*U. S. 2,474,325*).

The newly patented lubricants and coolants for metal cutting were sulfurized sperm oil containing octyl phenol (Leland—*U. S. 2,467,137*), oils containing partial esters of polyhydric alcohol and tall oil (Meyers & Muckerheide—*U. S. 2,466,645*), mineral oil containing sorbitan—oleic acid partial esters and reaction product of ethylene oxide and palmitic acid (Leland—*U. S. 2,470,405*), and mineral oils containing soaps of unsaturated fatty acids (Soc. pour l'ind. chim. a Bale—*Swiss 222,257*). Work on cutting and machining aluminum indicated that the cutting work could be decreased considerably with polar compounds, particularly cetyl alcohol (Pleteneva *et al.*—*Doklady Akad. Nauk. S.S.S.R. 62*, 501, 653). The polar compounds were used in kerosene solutions. The hardening of the bottom of drill holes was considerably reduced by the polar compounds.

The life of grinding wheels was increased by dressing with mineral oil containing reaction products of castor oil and phosphorus pentoxide (Hughes & Veatch—*U. S. 2,453,710*).

(To be continued)