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. The Bureau of Agricultural Economics of the U. S. Department of Agriculture and the U. S. Department of Commerce through their respective periodicals are the sources for the basic economic information of the fat, oil, and soap industry. Late 1950 and early 1951 issues of these were reviewed for the preparation of the following brief summaries.

World production of fats and oil seeds, in terms of oil equivalent, in 1950 was estimated at 22.9 million short tons, 1% larger than in 1949 and 3% above prewar. Since the population increased about 10% the per capita supplies should be considered below prewar level.

Domestic production in the year which began October 1, 1950, was estimated at slightly greater than the record output of 12 billion pounds produced a year earlier. Output of lard, tallow, and greases should increase moderately; production of vegetable oils may decline slightly, and butter production was expected to decline. For the 1951 crops, the government will encourage soybean production with an average support price of 39 cents higher than for a year earlier; and the production of 34 million pounds of castor oil will be encouraged because it is in demand for military purposes.

Exports of fats and oils throughout the world in 1950 were about 5.9 million tons, 10% larger than 1949 but 10% smaller than prewar. The United States exports of 1950 amounted to 2 billion pounds. The United States furnished 60% of the dollars for this purchase, and since foreign aid might be more limited in 1951 a reduction in export demand should prevail.

The United States imported 1.2 billion pounds of fats and oils in the year ending September, 1950. A further increase is likely in 1951 for there is an incentive for stockpiling strategic fatty materials such as coconut, palm, castor, and sperm-whale oils.

The index number of wholesale prices of 26 major fats and oils, excluding butter, in mid-January of 1951 was about 230 (1935-1939=100) compared to 144 in January, 1950. Future prices should be more stable for on January 26, 1951, general ceiling price regulations were issued and up to March 12 two amendments pertaining to fats and oils have been added to the original regulations.

Several treatises were published on fat and oil economics. Brandt (*J. Am. Oil Chemists' Soc. 27*, 401) comprehensively reviewed the world economic situation since before world war number one. He discussed geographical changes in production and exports and the forces of adjustments. He felt that much progress is being made and will be made in the fat economy, which will mean more production, lower cost, and better quality in the finished products. Other discussions on world fat situation were prepared by Faure (*Fette u. Seifen 52*, 506; *Olearia 3*, 647; *4*, 181) and Rudorf (*Fette u. Seifen 52*, 261). The production, export, and per capita consumption of soap in seven leading countries was also reviewed (anom.—*Ibid.* 508).

An outstanding source of information on the domestic fat and oil situation and outlook is the Senate report on hearings on "Utilization of Farm Crops"—Fats and Oils (*Senate Res. 36*, 463 pp.) or the summary of this report (81st Congress, 2nd Session, Report No. 1374). The post war rise and crash of fat prices was reviewed with producers and consumers. Some of the highlights of these hearings were the present and future influence of synthetic detergents on the soap business, the effect of bread emulsifiers on the amounts of fats being used in the baking industry, the need of exportation, and the need of importing certain fats which cannot be produced in our climate. Retail trade of soaps, oils, fats, and waxes in North America was reviewed by Schmidt-Lamberg (*Seifen-Öle-Fette-Wachse 76*, 75).

Economic treatises for limited geographical regions were also published. In a symposium on the status of the Japanese fat and oil industry, papers by various authors were written on statistics, rice oil, land animal fats, whale oil, uses of marine animal oils, processing vegetable oils, industrial fats and oils, nutritive

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value, and margarine manufacture (*Nogaku 3,* 603, 611, 633, 639, 643, 648, 652, 657, 658). The Canadian vegetable oil industry was reviewed by Grace & Lemon (*Agr. Inst. Rev. 4,* 341, 420). The present situation in respect to the vegetable oil industry was reviewed for Guatemala (Markley—*Agr. Division, Food & Agr. Organization of the United Nations*), Turkey (Yazicioglu & Dean—*Soap, Perfumery & Cosmetics 23,* 921), and Sweden (Andersson—*Fette u. Seifen 52,* 665). The fats used in the leather industry were reviewed by Morrison (*Leather Mfr. 1950,* 3). A review on recent development in fat and oil research was prepared by Harwood & Plambeck (*Fette u. Seifen 52,* 84).

The general treatises on specific oils had the following text: almond oil (Wittka & Muscari-Tomajoli—*Olearia 4,* 10), candlenut oil and its drying properties (Kehren—*Oleagineux 5,* 359), chemistry of castor oil (Paleni—*Olearia 3,* 733), oil from coffee grounds (Gernert—*Seifen-Öle-Fette-Wachse 76,* 181), *cynara carduncuIus* seed oil (Fernandez *et al.*—*Anales asoc. quim. argentina 37,* 139), red-berried elder seed oil (Voituret—*Seifen-Öle-Fette-Wachse 76,* 115), Canadian erucic acid oils (Grace *et al.*—*Can. J. Research 28F,* 401), fruit seed oil (Koblic—*Chem. Obzor 25,* 87, 106), grape seed utilization (Frolov-Bagreev—*Vinodelie i Vinogradarstvo S.S.S.R. 8,* No. 8, 15), marine animal body oils (Minato—*J. Pharm. Soc. Japan 69,* 348), melon seed oil (Alpar & Esin—*Rev. faculte sci. univ. Istanbul 14A,* 328), *Oenothera biennis* seed oil (Dieckmann—*Pharmazie 3,* 275), oiticica oil for lacquer (Garmsen—*Fette u. Seifen 52,* 112), okra seed oil (Haarer—*Paint Oil Colour J. 118,* 576), olive oil from Morocco (Rohr—*Ann. fals. fraudes 42,* 176), palm oil for human use (Loury—*Ann. nutrition et aliment. 3,* 451), purghere oil (Mensier & Loury—*Oleagineux 5,* 167), rapeseed oil (Wittka & Tomajoli—*Olearia 3,* 578), stability and processing of rice-bran oil (Swift *et al.*—*J. Am. Oil Chemists' Soc. 27,* 14), salad oil from rice bran (Lee—*Chem. Eng. 57,* 123), safflower oil: growth, processing, utilization, polymerization, and uses (Christensen—*Am. Paint J. 34,* No. 20, 54), cultivation of safflower (Sag—*Rev. intern. botan. appl. et agr. trop 30,* 216), use of safflower oil in paints (Winter—*J. Am. Oil Chemists' Soc. 27,* 82), extraction, processing characteristics, and chemical and physical characteristics of oil obtained from white sesame seed (Andraos *et al.*—*Ibid.* 31), processing of Chinese tallow tree seed (Bolley & McCormack—*Ibid.* 84), and a review on soybean oil (Harding—*Am. J. Pharm. 121,* 356). Other reports on individual oils are represented in the section of this review on composition and characteristics because the papers contained original analytical data.

SYNTHESIS OF FATS. The process of synthesizing fats by the Fischer-Tropsch method was described by Imhausen (*Z. Ver. deut. Ing. 91,* 463). In brief this comprises blowing air through paraffinic residues of C_{20} to C_{30} chain length at 100° for 15-30 hours, converting the acids formed to soap, removing unsaponified material, regenerating to acids, fractionally distilling and esterifying with glycerol. A manganese catalyst was used. Fractions containing C_5 to C_9, C_{10} to C_{18}, and C_{18} and higher were obtained in 70 to 80% total yield. Similar descriptions and data were published on this process by Wietzel (*Farben, Lacke Anstrichstoffe 3,* 416). He pointed out that the C_5 to C_9 fraction was used in plasticizers, perfumery, flotation, solvents, and detergents, the C_{10} to C_{18} acids in soap, food, Buna rubber, and for the manufacture of fatty alcohols, and the tail cuts in lubricants, and in rubber. Pardum (*Fette u. Seifen 52,* 290) recorded fundamental data for the course of this synthesis. He analyzed the compositions obtained from paraffin fractions boiling between 168 to 233° C. at 13 mm. of Hg pressure, by oxidation at 110°, 120°, 130°, and 140° C. to acid numbers of 10, 20, 40 and 80. The same investigator and Kuchinka (*Erdöl u. Kohle 3,* 109) presented considerable data on the behavior of numerous catalysts in the process. The mechanism of the synthesis was discussed by Kölbel and Engelhardt (*Chem.-Ing.-Tech. 22,* 97). A new patented process for the synthesis involved adding some tallow acids, potassium stearate, and zinc stearate to the paraffins before the oxidation (Cargill Inc. — *Brit 628,457*). A small amount of potassium permanganate aided in initiating the reaction.

In a discussion on the use of the fats synthesized from paraffins in food, the arguments reviewed were against such use (Meyer-Döring—*Klin. Wochschr. 27,* 113; *28,* 233). Some synthetic branched chain acids were both fed and injected into rabbits and the many unnatural decomposition products of these were isolated from the urine of the animals (Asano & Yamakawa—*J. Pharm. Soc. Japan 69,* 388).

Biological synthesis seemed more promising for supplying food fats because the products are similar to natural fats. This process has been developed to a semicommercial stage in which the fermentation was done in 20 liter containers (Diemair & Boresch—*Z. Lebensm.-Untersuch. u. -Forsch 90,* 14). Mycelium of 8 to 12 grams and fat of 3-5 grams per liter of medium were obtained. They recorded data showing the effect of various factors on the yield of mycelium, fat, organic matter, and calories produced per 100 parts of carbohydrate used. Weigner and Weigner (*Chem.-Ing.-Tech. 22,* 129) also described apparatus and methods for such a process. Yield and experiences on production of fat biologically with the microorganisms *Rhodatorula gracilus* (Lundin—*Rept. Proc. 4th Intern. Congr. Microbiol. 1947,* 542) and *Torulopsis lipofera* (Kleinzeller—*Ibid.* 544) were recorded. Similarly Kaibara (*J. Agr. Chem. Soc. Japan 22,* 89) recorded the yields of fats and their properties from culturing *Penicillium javanicum* in juice of sweet potatoes sweetened with malt and containing various other nutrients. The present status of microbiological fat synthesis was reviewed by Bernhauer (*Fette u. Seifen 52,* 203), Lundin (*Suomen Kemistilehti 23A,* 23), and Angermair (*Seifen-Öle-Fette-Wachse 76,* 24, 45, 68).

A biological synthesized oil was extracted from the principal by-product of brewing operation (Brasch *et al.*—*J. Am. Oil Chemists' Soc. 27,* 133). Although the fatty acid composition was similar to that of cottonseed oil, it did not refine well, and the investigators suggested classifying it with vegetable oil foots.

COMPREHENSIVE LITERATURE FOR THE FAT AND OIL FIELD. During the period under review the following books were published:

Industrial Chemistry of Fats and Waxes, Edited by T. P. Hilditch, 3rd Ed. Bailliere, Tindall & Cox, London. 500 pp.

Oils, Fats and Fatty Foods. Their Practical Examination. By K. A. Williams. Blakiston Co., Philadelphia.

Deutsche Einheitsmethoden zur Untersuchung von Fette, Fetteprodukten und verwandten Stoffen, Wissenschaft, Stuttgart. 53 pp.

1949 Book of A.S.T.M. Standards—Part 5 (Includes standards for soap). American Society for Testing Materials, Philadelphia.

Modern Soap and Detergent Industry Vol. 1. Theory and practice of Soap Making. 3rd Ed. Edited by I. Cooke. Technical Press, London, 400 pp.

Soybeans and Soybean Products. Vol. 1. Edited by K. S. Markley. Interscience Publishers Inc., N. Y. 540 pp.

Tecnologia de los aceites vegetales con especial referencia al aceite de oliva. By G. P. Giovanni. Min. Ed. Univ. Nacl. Cuyo, Mendoz Argentina. 1284 pp.

Melting and Solidification of Fats. By Alton E. Bailey. Interscience Publishers Inc. 371 pp.

The lectures given at the American Oil Chemists' Society and Federation of Paint and Varnish Production Clubs sponsored short course on drying oils formed a comprehensive treatise on the subject (*J. Am. Oil Chemists' Society 27,* 433 through 544). Papers were read on economics, chemistry, mechanical extraction, solvent extraction, refining, fractionation, heat bodying, blowing, dehydration of castor oil, copolymerization, isomerization, transesterification, driers, testing, alkyds, vegetable oil paints, oleoresinous varnish, floor coverings, printing inks and miscellaneous uses. In a series of papers reviewing unit-processes the reviews on esterification (Reid—*Ind. Eng. Chem. 42,* 1667), hydrogenation and hydrogenolysis (O'Boyle—*Ibid.* 1705), isomerization (Perry—*Ibid.* 1715), polymerization (Winding—*Ibid.* 1725), and sulfonation (Lisk—*Ibid.* 1746) should contain information of interest to workers in the fat and oil field.

A nomenclature for glycerides was proposed by Kaufmann (*Fette u. Seifen 52,* 208).

Production

ANIMAL AND FISH FATS. The methods and apparatus of new rendering processes varied for different purposes. Pavia (*U. S. 2,516,071*) allowed the cracklings to remain in the product to induce stability to oxidative deterioration. The stock was finely comminuted and rendered to an anhydrous product in a few minutes at temperatures of 180-325° F. In a new steam rendering apparatus the pork fats were cooked, settled into strata of lard, floaters, tankwater and tankage, and the components were withdrawn separately (Koppit and Davis—*U. S. 2,493,459*). In one rendering invention proteolytic enzymes and a reducing activator substance, such as cysteine, methionine, or bisulfites were used to release the fat from the tissue (Halmbacher—*U. S. 2,527,305*). Rendering at about 180° F. in the presence of liquefied propane yielded fats of low color (Leaders—*U. S. 2,503,205*). A solvent extraction method for bones was similar in principle to the extraction process used in the sugar industry (Morandi—*Ital. 435,274*). The solvent was circulated through several extraction columns connected in series. One batch solvent process was suitable for animal or vegetable material (Worsham & Levin—*U. S. 2,503,312*). The stock was refluxed with halogenated hydrocarbons. Water was trapped from the refluxing liquid and the fat was recovered from the solvent. Two Russian articles on the production of lard treated, respectively, the use of a combined cooker and expeller press (Petrovskii & Komarova—*Myasnaya Ind. S.S.S.R. 20,* No. 4, 35) for rendering and the use of the "Votator machine" (Liberman & Mirkin—*Ibid. 21,* No. 2, 27) for cooling lard.

A study was made on rendering of fish livers by enzyme, steam, water, alkali, and acid digestion from the viewpoint of efficient recovery of Vitamin A and oil (Hartman—*J. Am. Oil Chem. Soc. 27,* 409). With shark livers, alkali digestion was most desirable, and the alkali did not affect the stability of the Vitamin A in the oil. With livers of about 10% oil content, such as groper livers, treatment with pepsin enzymes and acid was necessary for efficient extraction. A newly patented fish liver extraction process was based on comminuting and then centrifuging out the oil (Sarland—*U. S. 2,507,614*). A method for rendering fish offal comprised partially drying and pressing out the oil at 60-90° C. (Notevarp—*U. S. 2,497,367*). Details of plant operation and laboratory control methods of the Karitane Products Society fish liver oil plant in New Zealand were published (Cunningham *et al.—New Zealand J. Sci. Technol. 30B,* 214).

Much of the new information on butter production deals with the continuous processes. Reviews on the processes were prepared by Mohr (*Fette. u. Seifen 52,* 96, 161) and Petersen (*Ibid.* 98). The new fundamental data developed for designing the processes and methods were dilatometric curves for milks, butter oil, and creams of 35, 45, 60 and 80% fat content (Mohr & Kaufmann—*Ibid.* 537), the physical structure of the birefringement layers of the fat globules in butter (King—*Netherlands Milk Dairy J. 4,* 30), and weight stability of different butters in storage (Mrozek & Keller—*Milchwissenschaft 5,* 179). Butter globules of birefringement zone of about 0.1 of their diameter and 0.5 of their volume were found in products of continuous processes where pressures were used in the manufactures. Water losses of continuous butters were comparable to those of sour-cream butter, and the oiling-off was 15% for the continuous butters and 11% for the sour cream product. Zheltakov (*Molochnaya Prom. 10,* No. 6, 31) recorded that butter with water dispersed to micron size had 10-20 times lower microflora levels after 30-60 days' storage than butter with poorly dispersed water. A higher degree of solidification of fat in cream increased the time required for churning (Brunner—*J. Dairy Sci. 33,* 267). Thus warm cream cooled to churning temperature just prior to churning churned faster than lots held at low temperatures and warmed to the required temperature. However, one inventor (Toulmin—*U. S. 2,505,654*) preferred to freeze the cream, thaw it to separate serum, and then churn, so that a better flavored product was obtained. A new continuous sour cream butter process deals with neutralizing the cream and centrifuging it in a special centrifuge to a fat content of 80-85% (Staaff—*U. S. 2,526,292*). A new variable speed churn and butter worker was patented (Cornell—*U. S. 2,514,375*).

Butter for use in the army or for making a spread stable enough for use in the tropics was usually rendered, hardened, and re-emulsified. American army, German, and Swiss products of this type were reviewed by Schulz (*Fette u. Seifen 52,* 541). A new improved product which he developed comprised butter oil, salt, and 5-20% spray dried milk powder. The spray dried milk was said to bind the butter oil and render the product less adhesive and gummy than comparable common spreads.

VEGETABLE FATS. In storage of seed, formation of free ammonia indicates break-down of protein and this is paralleled by free fatty acid formation in the oil. According to Jensen, *et al.* (*Oil Mill Gaz. 54,* No. 7, 43) treatment of cottonseed with propylene glycol dipropionate and 1,3-dimethyl-4,6-bischloromethylbenzene eliminated heating (decomposition by mold) during a 73-day storage period and with drying to a low moisture content, development of free fatty acids (lipase action) was inhibited for 52 days.

A method of processing cottonseed to an oil and a meal essentially free of pigment glands and hulls received further development. The scheme of a pilot-plant for this purpose comprised disintegration of the cottonseed flakes into a slurry with solvent, separation by settling or centrifuge into a sediment of coarse meal, hulls and glands, and a suspension of fine meal in miscella (Spadaro, *et al.—J. Am. Oil Chem. Soc. 27,* 336). A fine meal essentially free of pigment was filtered from the suspension. A cost study of commercial application was recorded. Similarly Persell, *et al.* (*Ibid.* 383) recorded the cost of a like plant in combination with expeller extraction. The desirability of such a plant was based on the production of a higher grade oil, a purified high protein meal, and a concentrated pigment gland fraction. A newly patented continuous process for extracting cottonseed oil made use of two solvents in a successive manner; the first removed free fatty acids and color and the second extracted the oil (Trottmann—*U. S. 2,489,599*).

Much fundamental information on methods of extraction and data useful for designing equipment was recorded. Magne *et al.* (*J. Am. Oil Chem. Soc. 27,* 552) determined the complete density-composition-temperature data for binary systems of refined cottonseed oil with methyl pentane, diethyl ether, trichloroethylene, and tetrachloroethylene from incipient phase separation to within 10-15° C. of the boiling point of the solvents. These data should be useful for estimating the composition of crude miscellas from their densities. The vapor pressure data of hexane-soybean oil solutions at low solvent concentration recorded by Smith & Wechter (*Ibid.* 381) should be important for the economical design and efficient operation of oil recovery. In work on effect of seed particle size on extraction rate, data for both flakes and grits were recorded (Coats, *et al—Ibid.* 51, 93). This study was made to establish the magnitude of the effect of changing particle size on the rate of extraction. Types of machinery used for flaking were compared to provide data of importance to hydraulic oil mill economy (Rea & Wamble—*Texas Eng. Expt. Sta. Res. Rept. 16*). Ghose (*Trans. Indian Inst. Chem. Eng. 1,* 72) determined the viscosity, density, and index of refraction of solutions of peanut oil in benzene, toluene, hexane, phenyl chloride, trichloroethylene, ethylene, and carbon tetrachloride. Points of concentration where maximum penetration of solvent into meal was expected and where maximum separation of solution from meal occurred were pointed out. Drying of cottonseed and peanut flakes aided in producing optimum solvent extraction conditions and it did not degrade the color of the oils or quality of the meal (Spadaro—*J. Am. Oil Chem. Soc. 27,* 394). Much information useful for solvent extraction and processing oil was recorded in several papers (*Ind. Eng. Chem. 42,* 1021) presented at an American Chemical Society symposium on absorption and extraction. Theoretical physical, chemical, and physical-chemical consideration in pretreatment and pressing of oil seed was described by Singer (*Seifen-Öle-Fette-Wachse 75,* 49, 67). Other general papers on extraction of oils covered methods used (Schwitzer—*Indian Soap J. 15,* 60; Clark—*Oil Mill Gaz. 55,* No. 1, 28), descriptions of the "Exsolex" process (Moore—*Oil Mill Gaz. 54,* No. 10, 13; *Chem. Eng. 57,* No. 6, 106), description of a complete processing plant (Shearon, *et al—Ind. Eng. Chem. 42,* 1266), and discussion of the solvents used (McInnes—*Am. Paint J. 34,* No. 30, 86; *Paint, Oil & Chem. Rev. 113,* No. 9, 20).

Harris & Hayward (*J. Am. Oil Chem. Soc. 27,* 273) in demonstrating the use and economy of water miscible solvents in cottonseed oil extraction presented solubility diagrams of cottonseed oil and water in isopropanol and acetone and information on equipment, solvent requirements, and quality of the products. A review on extraction of soybeans with ethanol was prepared by Pardun (*Fette u. Seifen 52,* 90). Berti (*Olearia 3,* 629) advised that the carbon disulfide solvent used for extraction of olive cake should be replaced by *n*-hexane because of better operation, safety, and quality of the oil.

Many inventions were concerned with improvement of solvent extraction equipment. Beckel's *et al.* (*U. S. 2,505,749, 2,511,833, 2,524,037*) improvements on an alcohol extraction process concerned a special heating step to release trapped alcohol from semisolid materials that collects at the interface between the alcohol and oily strata. A means of heating oil in thin films in order to strip out residual solvent, and a means for handling the solvent alcohol to inhibit the build-up of alcohol soluble materials on repeated recirculation were disclosed. New forms of equipment containing U-shaped columns through which ground seeds were mechanically passed counter-current with solvent were patented (Sweeney & Arnold—*U. S. 2,497,700, 2,501,880*; Straight—*U. S. 2,517,143*). A system in which the seed was passed counter-currently to the solvent in sieve bottom bucket was improved by vibrating devices for the buckets (Beeson—*U. S. 2,512,710*); another had stirring devices for the same purpose (Harcourt—*U. S. 2,510,221*). One continuous apparatus contained successive stages of mixers and centrifuges (Pascal—*U. S. 2,505,139*). According to Kincaide (*U. S. 2,491,115*) discoloration and decomposition in continuous extraction was reduced by short solvent contact with the solid, efficient clarification and chemical treatment of the raffinate and by flash evaporation.

Bibby's (*U. S. 2,484,445*) equipment for recovering solvent used in the extraction of oils comprised rotary drum evaporators within concentric evaporating chambers. Saunders (*U. S. 2,502,484*) and Saunders & Larson (*U. S. 2,502,485*) processed solvent wetted extraction residues by adding water or aqueous alkali, distilling the solvent, and by means of precipitation, settling, and skimming or evaporating, produced adhesives, coatings, or food materials from the protein.

A quite novel method for extracting seed oils comprised extracting the seeds with hot oil and completing the extraction by boiling in a weak sodium carbonate solution (Chaudary—*Indian 39,493*). A small plant for extraction of palm oil by dry centrifuging was found to be practical and gave good yields (Wilbaux—*Olearia 3,* 374). The production of both palm and olive oil from pulp by pressing was improved by the addition of alkaline phosphate or silicate salts to reduce the surface tension (Soc. ind. d'equipments—*Fr. 938,350*).

BY-PRODUCT FATS—TALL OIL FATTY ACIDS, LANOLIN, WASTE FATS. Tall oil fatty acid production information concerned the refining of the tall oil and separation of the rosin and fatty acids. A review of the Industry was prepared by Last (*Seifen-Öle-Fette-Wachse 76,* 177). The color of the oil was improved by heating the crude product with 0.1-2.5% metallic zinc (Sherwood & Barlow—*U. S. 2,515,739*).

Dunlap, *et al.* (*J. Am. Oil Chem. Soc. 27,* 361) in investigating the segregation of fatty acids from tall oil for use as a drying oil, selectively esterified the fatty acids with glycerol and pentaerythritol and washed out the rosin acids with aqueous alkali solution. When heated at 180° for six hours, the rosin acids were not appreciably esterified while the esterification of the fatty acids was complete. Drying oils prepared in this manner had an iodine value greater than that of soybean oil. In similar work Mueller, *et al.* (*Ind. Eng. Chem. 42,* 1532) recorded the rates of complete esterification of tall oil fatty acids at several temperatures (437 to 585° F.) with several polyalcohols. Both of the above cited reports contain considerable data useful for converting tall oil to raw material products useful in protective coating. In two newly patented methods of segregating the fatty from the rosin acids, the former were selectively esterified with alcohol and the latter in one case was removed by precipitation with cyclohexylamine (Rosher—*U. S. 2,509,884*) and in the other by adsorption on some preferential adsorbent (Koonce & Perry—*U. S. 2,485,744*). A review of patents on the subject was prepared by Jakobson (*Svensk Papperstidn. 52,* 193, 290, 379, 451, 481).

Wool fat, lanolin, was recovered from wool wash water by adsorption on a solid ion exchange material comprising an insoluble infusible sulfonated phenolic resin in its acid form (Shawcross—*U. S. 2,522,140*).

Stearic acid and other fatty acids recovered from ball mill processing metallic powders were recovered by converting to fatty acids, washing, and skimming (Akers—*U. S. 2,501,806*).

REFINING, BLEACHING, AND DEODORIZATION. The aspects of the reviews on refining varied. Under the title "Refining of Vegetable Oils," Steinbock (*Can. Chem. Process Inds. 34,* 28) briefly discussed production and treatment methods given to oils in conditioning for their various uses. Refining reviews by Kaufmann (*Olearia 4,* 5, 101) and Kaufmann *et al.* (*Fette u. Seifen 52,* 35) concerned the losses of accessory food substances, vitamin A, phosphatides, etc. Bigoni (*Olearia 3,* 172) made suggestions in regard to preparation of an edible oil product from the carbon disulfide extract of olive pressing residues. The continuous refining methods were reviewed by Lude (*Fette u. Seifen 52,* 326).

Some of the inventions on refining of oils concerned principally degumming of oils such as soybean oil. Umschuld (*U. S. 2,516,733*) degummed the oil by passing electrical current of 500-10,000 volts and 300-500 milliamperes through it at 160° C. and cooling to 0 to 54° C. The treatment was said to precipitate phosphatides and fatty acids so that they could be removed by filtration. A simple degumming process for producing "break-free" oil comprised neutralizing the free fatty acids with alkali and then treating with an acid in amount equivalent to the alkali used (Christenson—*U. S. 2,510,379*). In a process for improving the flavor stability of soybean oil, it was degummed with water and centrifuged, and free fatty acids were then removed by distillation (Jakobsen—*U. S. 2,508,919*).

In an investigation on refining of oils containing vitamin A, it was found that the alkali method was the simplest and most economical way of removing the free fatty acids (Hartman—*J. Soc. Chem. Ind. 69,* 55). An increase in the vitamin A of some oils on careful refining as recorded by other investigators, was attributed to the effect of reduced volume due to removal of free fatty acids and impurities. According to two patents, losses in alkali refining were reduced by the presence of certain inorganic compounds. Thus, Fash (*U. S. 2,512,245*) mist-mixed oil and refining agent containing sodium silicate and caustic soda, heated to 200° F., and centrifuged out the soap stock; and Rini (*U. S. 2,507,184*) alkali refined the oils in the presence of small amounts of aqueous inorganic phosphates.

The use of a liquid propane refining system has attracted interest because of efficient removal of color. A Lever Brothers Company plant operating with this system on tallow was described (Moore—*J. Am. Oil Chem. Soc. 27,* 75). Mattikow (*Ibid.* 11) recorded the behavior of cottonseed and soybean oils, tallow, and greases in the propane solvent at various temperatures as basic data for the process. In general gums were precipitated at about 70° C. and 350 lb. pressure; color bodies, some free fatty acids, and part of the minor constituents precipitated with the gums and phosphatides. Palmer (*U. S. 2,505,338*) in applying precipitation in propane technic separated fish oils continuously into four fractions: a small color fraction, an intermediate drying-oil fraction, an intermediate edible-oil fraction, and a vitamin fraction. Passino (*U. S. 2,523,630*) used the technic for refining special oil products. Thus, vitamin concentrates could be further concentrated by fractionation with propane; the same was true of lecithin concentrates, and neutral fat could be recovered from refining residues. Similarly Leaders & Argue (*U. S. 2,509,509*) used liquid propane to recover neutral oil and other materials from spent bleaching clays and agents. Liquid propane and its close homologues were also recommended for refining free fatty acids (Synergic Foundation, Inc.—*Brit. 639,941*).

Fundamental data and a flow sheet of a plant for deacidifying palm oil by washing out the acids with alcohol were published (Martinenghi — *Olearia 3,* 239).

Some fat refining literature was limited to bleaching. Jespersen (*U. S. 2,524,056*) underlaid the batch of fat with water and hydrogen peroxide solution and boiled until sufficient bleaching took place. The use of hydrogen peroxide in combination with an acid clay was recommended for decolorizing rice oil (Kawai—*J. Nippon Oil Technol. Soc. 2,* No. 5, 16). The objections to the use of benzoyl peroxide for bleaching linseed oil in that it may cause yellowing of the films produced was investigated and denied by Colomb (*Ind. vernice 3,* 220).

Mathur (*J. Indian Chem. Soc., Ind. & News Ed. 12,* 133) added 0.1% Fuller's earth and 0.02% activated charcoal to oils undergoing hydrogenation to produce a decolorized product. Taufel & Nazli (*Deut. Lebensm.-Rundschau 44,* 157) recommend that aluminum and magnesium silicate decolorizing agent be used in place of activated carbon on crude olive oils, because they do not reduce the stability of the oils as much as was the case with carbon.

The latest inventions in steam deodorization were the use of a cyclone separator to return fat entrained in vapors (Gunther—*U. S. 2,484,788*) and a new deodorizer comprising a stripping column in which fats could be dropped in stages down the column and the steam ran countercurrently (Dean—*U. S. 2,500,934*). Chrysalis oil was deodorized by heating with bamboo leaves (Oyama—*Japan 175,685*). Lips (*J. Am. Oil Chem. Soc. 27, 422*) designed a small glass deodorizer which was found convenient for laboratory investigation of steam and vacuum deodorization.

FRACTIONATION, WINTERIZING, AND RECOVERY OF NON-GLYCERIDES. The literature suggested that most interest was turning to solvent methods. The phase relations pertaining to solvent winterization of cottonseed and peanut oils in acetone were recorded (Skau *et al.*—*J. Am. Oil Chem. Soc. 27,* 556). These were intended to serve as a basis for selecting the conditions for the effective solvent winterization of the oils in acetone. Muckerheide (*U. S. 2,514,608*) crystallized animal fats from ether in order to produce high yields of liquid animal oils.

Propane fractionation was used in several inventions. A concentrate of sterols and a nonreverting oil was fractionated from soybean oil (Leaders & Norris—*U. S. 2,521,234*). Lanolin was fractionated into fatty material and sterols (Young & Christopher —*U. S. 2,528,482*). Propane fractionation was used to concentrate tocopherols from crude sterol mixtures (Hixson & Miller—*U. S. 2,508,387*).

Fractionation of unsaponifiable matter from fats by saponification followed by extraction was also improved by innovations. In such a process for concentrating fat soluble vitamins, Freiman (*U. S. 2,516,112*) mixed the saponified crude product with inert material before extracting with hydrocarbons. Where moisture was present in such a process Buxton (*U. S. 2,508,220*) preferred to use ethylene dichloride as the solvent. The process of Porter (*U. S. 2,499,877*) was quite similar in principle.

Several other means of segregating by-product material were described. Gloyer (*U. S. 2,524,103*) extracted sterols from soybean oil with furfural. Vitamins were segregated from oil and concentrated by distillation methods (Hickman & Weisler—*U. S. 2,486,540;* Omote—*J. Chem. Soc. Japan Ind. Chem. Sect. 51,* 115, 116). Chromatographic adsorption was useful for concentrating carotene from palm oil (Boldingh — *Dutch 66,316,* Blaizot — *Ann. nutrition et aliment 3,* 455).

For the production of lecithin, Molines & Desnuelle (*Oleagineux 5,* 17) prepared operational data for the hydration method of separation. Larger amounts of water were required and the phosphorus content diminished as the acidity of the crude oils increased. Singer & Deobold (*U. S. 2,508,624*) concentrated lecithin from foots by emulsification and allowing to stand until the lecithin settled to the bottom layer.

HARDENING OF OILS. One review on hardening oils was published (Arneil—*Chemistry & Industry 1950,* 3). Other general papers were on the kinetics of the hydrogenation reaction. Zinov'ev (*Zhur. Priklad. Khim. 22,* 1253; *23,* 99) followed the hydrogenation of glycerides of oleic, linoleic, and linolenic acids recording hydrogen uptake and changes in iodine value and composition. Constants for the various reactions were calculated. Curves for the iodine value and index of refraction of hydrogenation of peanut oil with 0.03% Raney nickel at 60, 90, and 120° were recorded by Gordon (*Bull. mens. ITERG 3,* 410). Benedict & Daubert (*J. Am. Chem. Soc. 72,* 4356) partially hydrogenated triolein and isolated *trans*-8-octadecenoic and elaidic acids from the reaction products. In a comparison of hydrogenation rates of oleic acid and its esters, the fatty acid hydrogenated 2.28-2.82 times faster than the methyl ester. This figure for other esters was: ethyl—3.09, propyl—3.58, isopropyl—3.50, butyl—3.82, and isoamyl—3.09 (Tsuchuiya—*Repts. Tokyo Ind. Res. Inst. Lab. 44,* 111, 116).

The new inventions on hydrogenation of oils pertained principally to development of continuous processes. The patents assigned to Procter and Gamble Company (*U. S. 2,520,422-5, 2,520,440, Brit. 642,012*) describe the apparatus and method in which the oil was dissolved in ethanol, and continuously supplied with catalyst and hydrogen in proper amount to give the desired reduction. Selective hydrogenation of polyethylenes to monoethylene was claimed by the technic. In a new continuous system by Potts & Morris (*U. S. 2,521,602*) the heat developed in the hydrogenation operation was later utilized in the deodorizing steps. Hershberg, *et al.* (*Ind. Eng. Chem. 42,* 2336) designed a low pressure rotary laboratory hydrogenator and recorded some operational data with the equipment.

Other hydrogenation literature concerned the catalyst used. Miyake (*J. Pharm. Soc. Japan 68,* 1, 6, 8, 12, 14, 18, 22, 26, 29, 32, 33, 38) compared nickel, copper, and copper-chromium (Adkin's catalyst) catalyst on various oils. The Adkin's catalyst gave good hydrogenation and selectivity, and was further investigated to determine the effect of manufacturing technic, time, temperature, etc. on its efficiency. Adkins, *et al.* (*J. Am. Chem. Soc. 72,* 2626) discussed the preparation and use of his copper-chromium catalyst, but the examples given were on synthesis of certain compounds rather than hardening of oils. A kiln for manufacture of nickel catalyst for hydrogenation of oils was patented (Martignoni—*Ital. 436,583*). Nickel catalyst was stabilized by condensing steam on it and evaporating the film with air (Ahlberg & Hiskey—*U. S. 2,495,497*). Zinc was active for the hydrogenation of perilla oil at a temperature range of 200-320° (Sato & Maruyama—*Science Repts. Res. Inst. Tohoku Univ. Ser. A, 1,* No. 1, 51).

Fats can also be hardened by elaidinization. A new process using this principle comprised heating the oil with sulfur dioxide while in ether solution and then separating the solid fraction by cooling to —48° (Sijpesteijn—*Brit. 627,742*). A similar process was investigated for the production of solid and highly unsaturated liquid fats from sunflower and grapeseed oils (Vandone—*Ind. vernice 4,* 42). The liquid products of the process dried (as a drying oil) more poorly than the original oils.

The mechanism of elaidinization was reviewed by Blekkingh (*Bull. soc. chim. France 17,* 278). He suggested that elaidinization and reversed transmission was based on the presence of some atom in the catalyst which can have more than one kind of valency. He theorized that there was a *trans*- addition of the catalyst to a double bond, a shifting of hydrogen atoms originally bound to them to the catalyst, an elimination of the latter, and a turning through 180° of one carbon atom so that the double bond was reconstituted in the opposite form. He indicated by diagrams that each double bond in unsaturated fatty acids could occur in five different transitional forms.

Splitting of Fats and Segregation of Fatty Acids. Corrosion is a problem in splitting of fats and distillation segregation of fatty acids. Plant corrosion tests for these operations and for soap making were recorded by Paul (*Corrosion 5,* 439) and Friend & Mason (*Ibid.* 355). The behavior of many commercial metals and alloys, and their welds as equipment material for each of the processes was evaluated.

Most of the new literature on splitting was on continuous autoclaving in water. Operational data of the system according to German Patent 677,957 were recorded by Konstandt (*Seifen-Öle-Fette-Wachse 76,* 461). A continuous splitting plant patented by Mills (*U. S. 2,495,071*) was designed so that the water and fatty acids produced were immediately subjected to distillation, thus taking advantage of the heat in the liberated fatty acids. Drew (*U. S. 2,471,942*) scrubbed the waste vapors of splitting operations on coconut oil with caustic to recover volatile fatty acids. These acids were desirable intermediates for the manufacture of plasticizers. To improve the efficiency of continuous systems, Paquot & Richet (*Bull. mens. ITERG 4,* 332) recommended hydrolysis in two stages, first with 15% by weight of water to obtain a concentrated glycerol phase and then with 30-40% water to complete the splitting.

Yanase (*J. Nippon Oil Technol. Soc. 2,* No. 5, 23, 32; No. 6, 7; *3,* No. ½, 15, 24) developed some fundamental data pertinent to splitting technic. In aqueous autoclaving at 200°C. the relative rates of splitting with oil:water ratios at 1:0.7, 1:1, 1:1.3, 1:2.0 were 1, 1.05, 1.09, 1.10, and 1.14. Analyses during the course of the process indicated that glycerides of lower fatty acids hydrolyzed faster than those of higher fatty acids. In a comparison of hydrolysis in iron and in stainless steel vessels, the process was much more rapid in iron because the product picked-up 1.87% iron which acted as a catalyst. The author also rated the accelerating effect of various amounts of calcium, oxide, magnesia, zinc powder, and zinc oxide for the reaction. The addition of emulsifying agents, such as triethanolamine or lecithin, gave no particular benefit.

A new invention on combined splitting and fractionation of fatty acids was based on hydrolysis with pancreatin at pH 8.2, removal of saturated acids by crystallization, and concentrating the triunsaturated acid by bromine-derivative crystallization (Grün & Schweizer—*Swiss 261,214*).

Three patents on segregation of fatty acid mixtures pertained to crystallization from solvents (Spannuth—*U. S. 2,505,012;* Feldpush—*U. S. 2,510,015;* Gee—*U. S. 2,520,801*). The novelty in these was concerned with the solvent used and method of operation.

A new system of segregating polyunsaturated fatty acids from oils comprised reaction with urea and crystallization removal of stearic and oleic acids (Schlank & Holman—*Science 112,* 19; *J. Am. Chem. Soc. 72,* 5001; Newey, *et al—Ind. Eng. Chem. 42,* 2538). In a test on soybean oil of iodine value of 141, fractions having values of 86, 148, 181, and 200 were separated. The preparation of methyl oleate by this method was outlined. The method was not confined to the fatty acids or their esters but was effective with fatty alcohols and nitriles. The unaturated fractions were very stable to autoxidation.

Alkyl Esters of Fatty Acids. The conversion of fats to alkyl esters of their fatty acids was used as a primary treatment for fats for various purposes. It is an efficient method of refining soap stock and preparing the stock for certain soap making processes; fatty acids are often segregated by distillation while in the form of their alkyl esters; the alkyl esters could be used as substitutes for the glycerides for many uses, etc. The British Pharmacopeia has approved the use of ethyl oleate for preparation of certain intramuscular injections and as a substitute solvent oil for vitamin A (Macpherson—*Pharm. J. 163,* 196; Basu & Bhattacharya—*Ibid.* 196). Kawai & Kinoshita (*J. Nippon Oil Technol. Soc. 2,* No. 6, 33) recommended that rice oil could be utilized as a substitute for cacao fat when converted to ethyl esters and hydrogenated. The commercial production of fatty acid ethyl esters was reviewed by Pardun (*Seifen-Öle-Fette-Wachse 76,* 397).

Several patented methods of preparing alkyl esters were described. Low grade fat stock, *i.e.* 5-30% free fatty acids was treated with alcohol vapors in such a manner that the alkyl esters formed distilled off (Lever Bros. & Unilever, Ltd.—*Brit. 634,411*). In another process ethyl esterification of the free fatty acids was at 150°C. in the presence of oxides of metals of groups seven and eight of the periodic table, and then alkali catalyst was used for alcoholysis of the neutral fat (Patterson—*U. S. 2,521,742*). Sprules & Price (*U. S. 2,494,366*) transesterified with alkaline catalyst and then added an acid catalyst to release fatty acid from soap and the transesterification was continued to completion. The above inventions pertained principally to preparing a stock suitable for light soap from household waste greases, dark fats, etc. Smith (*U. S. 2,486,444*) prepared methylated fatty acids from castor oil with use of alkaline catalyst and an alcohol:oil ratio of 6:1. The products were suitable plasticizers.

Only a small amount of laboratory work was reported on alkylation of fatty acids. The effect of temperature and various proportions of butanol and sulfuric acid catalyst for the preparation of butyl oleate were graphically recorded (Othmer & Rao—*Ind. Eng. Chem. 42,* 1912). Reaction rate was proportional to catalyst concentrations from 0.5 to 1.2%, to the molecular ratio of butanol to oleic acid, and to the negative reciprocal of temperature from 100 to 150°C. Loury & Piquard's (*Oleagineux 4,* 505) work on the kinetics of esterification of oleic acid pertained to the speed at which sufficient reaction takes place to yield a single phase solution. The C_1 to C_5 alcohols were investigated at room temperature and with sulfuric acid as the catalyst. The extent of the esterifications were also recorded. A laboratory method for obtaining 99% methanolysis of fatty acids comprised use of 1:3 fatty acid:methanol ratio, and 2% sulfuric acid, and boiling gently to remove excess methanol (Willis—*Chemist-Analyst 39,* 62).

Products (except detergents)

Edible Fat Products. According to a new margarine patent (Turgasen—*U. S. 2,526,302*) a fat and milk mixture could be treated with steam in a pressure zone, passed through a reduced pressure zone, and churned to yield a product with fat in the discontinuous phase. Such products had a desirable waxy texture. White (*Food Ind. 22,* 1538) published a flow sheet and description of a modern margarine plant. Two new margarine packaging wrappers were designed so that the buyer could color the product by kneading while still in the container (Brown—*U. S. 2,502,920;* Peters—*U. S. 2,532,513*). A natural pigment extracted from ripened persimmons was said to be suitable for coloring margarine or butter (Hayashi —*Japan 175,416*).

A review on cooking fats contained information on the characteristics most suitable for frying, baking, and other culinary uses (Arenson—*Food Industries 22, 1015*). A new shortening in dried powdered form contained fat, milk solids, and dried egg material (North *et al.*—*U. S. 2,520,954*). Shortening was also incorporated into prepared baking mixtures by means of volatile solvent solutions and the solvent was removed by evaporation (Musher—*U. S. 2,493,080*). A shortening patented by Holman & Quimby (*U. S. 2,521,219*) was a mixture of liquid oil with high melting fat in beta-crystalline form. This preparation was fluid enough at room temperature to permit pumping through conduits. Other information on shortening pertained to emulsifiers and will be reviewed further along in this section.

The texture of peanut butter was improved and the "oiling-out" properties inhibited by converting a portion of the solid fat in the product to the beta-crystalline form (Mitchell, Jr.—*U. S. 2,521,242-3*). The separation of oil, that is "oiling-off" of peanut butters was also inhibited by finely grinding the nuts and suspending them in a nut oil-water emulsion (Mitchell—*U. S. 2,511,119*) and by adding alkaline salts and hard fat (Vincent—*U. S. 2,511,136*). The expansibility, specific volume (Singleton & Freeman —*Food Res. 15, 297*) and the heat capacity (Ward *et al.*—*Ibid.* 146) of peanut butter have been recorded for large ranges of temperature and should serve as fundamental information for design of processing and packaging equipment.

The tendency of solid glycerides to appear in salad oil at low temperatures was inhibited by the presence of alkylated naphthalenes and hydroxyaromatic compounds (Mattil—*U. S. 2,524,732; 2,518,917*).

Other developments concerning fat in food and drugs pertained to a variety of products. Hoffman (*U. S. 2,524,291*) patented the use of fat-water emulsions containing water-soluble dyes as coatings for ice cream bars. Schotte (*U. S. 2,516,923*) improved the quality of beef from grass-fed cattle by flushing the blood from the circulatory system of the carcasses and injecting melted fats derived from corn-fed cattle in the circulatory system. A fat-soluble vitamin supplement for fortifying feeds comprised enzyme-inactivated ground soybean meal coated with a hard fat containing the vitamin (Melnick—*U. S. 2,496,634*). Buu-Hoi & Cagniant (*Ber. 77B,* 761) prepared various aniline, sulfonamide, amine, and toludine derivatives of the acids of chaulmoogra oil and found that some retained the bactericidal activity of the original oil.

EMULSIFIERS AND DEMULSIFIERS. The reviews on emulsifiers were on the preparation and properties of partial fatty acid esters of poly hydroxy alcohols (Neu—*Fette u. Seifen 52,* 558), on types and trade names of emulsifiers (Ruemele—*Seifen-Öle-Fette-Wachse 75,* 416), on water-in-oil and oil-in-water emulsions and their inversion (Russ—*Ibid. 76,* 305), on size distribution of particles of emulsions (Jellinek —*J. Soc. Chem. Ind. 69,* 225) and on phase relationships in salves (Schmalfuss & Schmalfuss—*Fette u. Seifen 52,* 26, 100).

Most literature and invention activity on emulsifiers concerned the partial esters of fatty acids and polyhydroxy compounds. Kuhrt *et al.* (*J. Am. Oil Chem. Soc. 27,* 310, 344) purified monoglycerides by molecular distillation and recorded some of their properties. The interfacial tension lowering produced by these products was essentially proportional to the monoester content. In water absorption tests, the unsaturated fatty acid monoglycerides were considerably more active than those of the saturated fatty acids. In cake baking tests the distilled monoesters improved volume and texture considerably more than expected; and such greater activity was shown to be due to absence of diesters in the monoester products. Fundamental information on α-monostearin and sodium stearate with regard to emulsification was recorded by Jellinek & Anson (*J. Soc. Chem. Ind. 69,* 229, 235). Stability of the emulsions was dependent on the concentration of the emulsifier and initial homogeneity of the emulsion. Mathematical and graphical presentations were recorded on distribution and specific surface areas of globules and stability of emulsions. In tests on the effects of several inorganic salts on water-oil emulsions made with 1% α-monostearin and 0.5% sodium stearate, the equi-valent salts gave similar phase separation curves, the emulsions were oil-in-water type, oil separation was very rapid at certain salt concentrations, and the emulsions were most stable at the higher pH values.

Manufacture of partial glyceride esters was also investigated. When prepared from fatty acid soaps and monochlorohydrins, the yield of monoester increased with time of the reaction and decreased with high reaction temperatures (Savary—*Bull. soc. chim. France 1950, 218*). Technical monoglycerides were purified by disproportionation between hexane and alcohols, and then fractionally crystallized from the alcohol (Feuge & Gros—*J. Am. Oil Chem. Soc. 27,* 117). A product of high monoglyceride content was prepared by using a glycerol:fatty acid ratio of 5:1 (Bell & Alsop—*U. S. 2,496,328*). Equipment was designed for manufacture of partial esters by autoclaving fat and glycerol in the presence of water (Allen *et al.*—*U. S. 2,478,354*). Heating fats with boric acid and allowing free fatty acids formed to distill off was a new method of manufacturing the partial glycerides (Barsky—*U. S. 2,484,979; 2,509,413*). The lower fatty acids were preferentially removed with this method. Emulsifier type shortening ingredients were also made by esterifying mono- and di-glycerides with lactic acid (Barsky—*U. S. 2,509,414*; Little—*U. S. 2,480,332*). The new application of mono- and di-glycerides were as ingredients for liquid cake shortening (Trempel & Frink—*U. S. 2,532,523*), as an emulsifier for DDT insecticide (Kemp & Barragat—*Rev. brasil. malariol. 2,* 66), and in combination with titanium soaps as a water repellent for textiles (Signaigo—*U. S. 2,505,259*).

Polyoxyethylene monofatty acid esters, another partial ester-type emulsifier, were demonstrated to be a good shortening for bread (Carson *et al.*—*Cereal Chem. 27,* 438; Bekkering & Hintzer—*Chem. Week-*

blad 45, 605; Lord—*J. Colloid Sci. 5,* 360; Johnston—*U. S. 2,509,926-7*). In general they improved volume and preserved softness of the breads. However, food and drug officials have rejected the use of these in food because: intravenous injection of small amounts produced histamine-like shock in dogs; fat absorption was modified by the compounds; they enhanced the absorption of certain poisons; some on ingestion led to the production of bladder stones; some disturbed bile secretion; some caused gastrointestinal irritation; and continued ingestion could change intestinal flora (Lehman—*Assoc. Food & Drug Off. U.S.A. 14,* 82). Some of the above pathology and necrosis of the liver, decrease of spermatogenetic activity of the testis, and tubular degeneration of the kidney were observed in hamsters fed basal rations containing 5 to 15% polyoxyethylene monostearate by Schweigert *et al.* (*Proc. Soc. Exptl. Biol. & Med. 73,* 427) and Wang *et al.* (*Ibid. 75,* 342). Polyoxyethylene and sugar partial esters of fatty esters were also suggested for emulsifying essential oils or resins in foods (Tribble—*U. S. 2,508,978*), for improving the whipping ability of ice-cream mixes (Steiner & Miller—*U. S. 2,493,324*), and as hydrophilic suppository bases (Ward—*J. Am. Pharm. Assoc. 39, 265*). Mannitan emulsifiers of this type were prepared by esterification of the sugar and fatty acid in the presence of sulfur dioxide, lead oxide, or sodium acetate as the catalyst (Muralti—*Boll. chim. farm. 88,* 413). A mixture of monomethylated polyethylene glycol and free fatty acids was also recommended as an emulsifier (Goldstein & Waldman—*U. S. 2,528,136*). The information on use of these emulsifiers in lubricants will be found in a lubricant division of this section of the review.

Fat derived emulsifiers, usually soap, are being used in the rubber industry. In generalizing on the theory of emulsion polymerization Harkins (*J. Polymer Sci. 5,* 217) suggested that soap stabilized monomer and polymer-monomer particles by forming a monolayer of soap around each globule, and it also solubilized a small portion of monomer inside a micelle to provide a large target for free radical monomer to contact. As fundamental data for emulsion polymerization Corrin *et al.* (*J. Colloid Sci. 4,* 485) compared the adsorption of soaps on graphite of known area with that on polystyrenes in order to approximate the surface areas of the latter. These data applied to emulsion polymerization of styrene showed that micellas disappeared at 20% polymer yields and the number of polymer particles as a function of the yield was estimated from the average particle diameters derived from the adsorption data (Corrin—*J. Phys. & Colloid Chem. 54,* 265). The rate of emulsion polymerization of butadiene-styrene was measured as a function of the emulsifier used by Carr *et al.* (*J. Polymer Sci. 5,* 191, 201). Linoleic and linolenic acid in commercial soaps retarded polymerization while tocopherols and lecithin did not. There was no significant differences in soaps of chain length C_{10} to C_{18} or in disproportionated rosin soap, but all synthetic detergents retarded the rate of polymerization. In studying the emulsion behavior of natural rubber latex, Gardiner (*Ind. Eng. Chem. 41,* 2644) found stearate soap was a good stabilizer. The data recorded in this work was of interest in regard to blending GR-S synthetic rubber with natural latices. The newly patented emulsion polymerization processes made use of fat derivatives for emulsification (Mast *et al.*—*U. S. 2,492,169*; de Nie—*U. S. 2,496,384;* Frolich *et al.*—*U. S. 2,500,983*).

The new demulsifiers for separation of petroleum oils from emulsion were prepared by reaction of fatty acids (principally those of castor oil), polymerized ethylene glycol, and resin forming material as phenol and polycarboxylic acids (DeGroote & Keiser—*U. S. 2,498,656-8; 2,505,824-5; 2,507,560; 2,507,910; 2,510,-335*).

PROTECTIVE COATINGS, RESINS AND PLASTICS. The historical, review, and general information papers on the above subjects treated apparatus for varnish and resin making (Hadert—*Fette u. Seifen 52,* 283), application of ultra-sonics in the lacquer industry (Tröger—*Ibid.* 115), polyester resins in the paint field (Hamann—*Angew. Chem. 62A,* 325; Baltes—*Fette u. Seifen 52,* 19) maleic anhydride treated oils (Kappelmeier *et al.*—*Paint, Oil & Chem. Rev. 113,* No. 18, 11), isomerization of drying oils (de Wilde—*Ind. chim. belge 15,* 72), modified drying oils (Boekenoogen—*Verfkroniek 23,* 77), tall-oil paint (Emerson—*Paint, Oil, Chem. Rev. 112,* No. 24, 13), oxidation reactions during drying of oils (Franke—*Farben, Lacke, Anstrichstoffe 4,* 301), formation, properties, and deterioration of films (Long—*J. Oil & Colour Chemists' Assoc. 32,* 377) and industrial oil and fat chromatography (Weil—*Paint Technol. 14,* 391).

The theoretical aspects of drying of oils were discussed by several investigators. Kern (*Farben, Lacke, Anstrichstoffe 4,* 242) suggested that peroxides first form, with suitable reducing agents these yield free oxide radicals, and these become part of a polymer chain. The chain propagation involved the reaction of the oxide radical with one or more monomer molecules, leaving a chain radical, or terminating a chain and forming a new radical. The mechanisms proposed by Kaufmann *et al.* (*Fette u. Seifen 52,* 140, 276), Moseback & Shauenstein (*Paint, Oil & Chem. Rev. 113,* No. 15, 9), and Maschka & Mendl (*J. Polymer Sci. 5,* 429) included a preliminary isomerization of unsaturated acids followed by Diels-Alder type reactions. The latter two groups of authors published ultraviolet spectroscopic observations which support their views. Kronstein (*N. Y. Univ. Coll. Eng. Symposium on Varnish and Paint Chem. 1948,* 13) recorded infrared spectrum observations on several bodied oils and on solid polystyrene which showed similar shifting of infrared patterns. This suggested that similar changes occur in the structures of bodied oils and styrene resins. Treibs (*Fette u. Seifen 52,* 549) suggested that during bodying the conjugated structures formed, activated the near methylene group to release hydrogen. This arrangement caused the formation of hydroperoxide which was stabilized by cyclization with another double bond, etc. Waterman *et al.* (*Research, London, 2,* 483) in investigations to confirm cyclization during polymerization isolated a cyclic product from bodied oils which had an average of three rings per molecule.

Data recorded on the changes in characteristics of oils during bodying should be of interest in designing equipment and developing methods for the process. Hess & O'Hare (*Ind. Eng. Chem. 42,* 1424) plotted the effect of temperature of oxidation of linseed oil between 84 and 200°C. on the rate of increase of viscosity. Bernstein's (*J. Oil & Colour Chem. Assoc. 32,* 447) data on linseed and soybean oils showed the relation between time of heating at 307° to changes in refractive index and pointed out the stages at which gelation and dimerization occurred. Data on molecular weight, viscosity, and spectra measurements on cooking linseed oil by Schauenstein & Schober (*Österr. Chem.-Ztg. 50,* 2) was interpreted to indicate that initial polymerization was predominately between doubly conjugated unsaturated acid chains of the same glyceride and that intermolecular polymerization to dimers follows. Kronstein *et al.* (*N. Y. Univ. Coll. Eng. Symposium on Varnish and Paint Chem. 1948,* 77; *Paint & Varnish Production 29,* No. 10, 14) studied the progress of gelling of oils by means of x-ray diffraction spectra. The technic could reveal approaching gelation. The information was correlated with spectroscopic and analytical data. A report by Petit (*N. Y. Univ. Coll. Eng. Symposium on Varnish and Paint Chem. 1948,* 71) on alcohol fractionation of bodied linseed oil demonstrated the chemical heterogeneity of the oils. Analyses of the products from polymerization of methyl oleate in the presence of boron fluoride and phosphoric acid catalyst indicated that the dimer was formed (Topchiev & Vishnyakova—*Doklady Akad. Nauk S.S.S.R. 71,* 685). The absorption of oxygen by linseed oil films was correlated with bleaching, iodine value changes, active oxygen value, and skin formation (Schlick—*Farben, Lacke, Anstrichstoffe 3,* 303).

Many means of improving the drying characteristic of oils by increasing the conjugated double bonds were investigated. Crowder & Elm (*Ind. Eng. Chem. 41,* 1771) converted monounsaturated fatty acids to conjugated double bond products by converting to the epoxide derivatives, reacting these with a suitable acid or anhydride, and pyrolyzing to the conjugated diene. According to Sutton & Dutta (*J. Chem. Soc. 1949,* 939) reaction of oils with *N*-bromosuccinimide followed by debromination aids in the development of conjugated polyunsaturation. The method of conjugating oils by reaction with tertiary butyl hypochlorite and dechlorination has now been developed to a pilot plant stage (Bell & Teeter—*J. Am. Oil Chemists' Soc. 27,* 102). According to new patents nickel-silicates (Stejskal—*U. S. 2,513,529*), nickel-carbon (Radlove—*U. S. 2,501,851;* Lewis & Cowan—*U. S. 2,494,565*), and iodine compounds (Lever Bros. & Unilever Ltd.—*Brit. 630,634;* Ralston & Van Akkeren—*U. S. 2,498,133*) were suitable catalyst for thermal conjugation of oils. In work on soybean oil with nickel-kiesselguhr or nickel-carbon catalyst at 180-200° for 5-8 hours the diene and triene increased from 9 to 24% (Masuno—*J. Nippon Oil Technol. Soc. 3,* No. 1/2, 113). Atomic hydrogen or nitrogen obtained by passing the gases over tungsten wire heated to 1800-2000°C. increase the conjugation of linseed oil (Boelhouwer *et al.*—*Rec. trav. chim. 69,* 769).

Since the alkali method of isomerization was the process used commercially, most interest in applied conjugation work was on this method. The effect of the alkali concentration and the temperature on the rate of this reaction for castor oil was graphically recorded by von Mikusch (*Farben, Lacke, Anstrichstoffe 4,* 149) who also reviewed the literature on the process. In similar work on pure fatty acids, Holman & Burr (*Arch. Biochem. 19,* 474) obtained maximum triene conjugation with ethylene glycol containing 25 grams of potassium hydroxide per 100 cc. as the fatty acid solvent; at a concentration 10 grams of the lye per 100 cc. maximum diene concentration occurred. This work, however, was in connection with analysis of fatty acid mixtures rather than with preparation of improved drying oils. The kinetics of alkali isomerization of linoleic, linolenic, and arachidonic acids was discussed by Nichols Jr. *et al.* (*J. Am. Oil Chemists' Soc. 27, 329*), and equations for the rates of the various reactions were developed from recent experimental findings and the general mechanisms of the changes. Baltes (*Fette u. Seifen 52,* 462) in reviewing isomerization suggested that the alkali method was most used, because it was most fully developed for commercial practice, but catalytic and chlorination processes gave higher degrees of conjugation. In the development of conjugation during oxidation of oils, Burger & Weidmann (*Fette u. Seifen 52,* 459) found that both air and light were required.

Radlove (*U. S. 2,497,689*) in preparing varnish oils from perilla, linseed, and other oils which contain triene structures, selectively hydrogenated all but two of the double bonds in each fat radical having three, and then isomerized to conjugated systems. The treatment was said to inhibit after-yellowing of films. Frosting and gas-checking of conjugated drying oil films was accelerated by atmospheric dust (Dannenberg—*Ind. Eng. Chem. 42,* 1594). These defects were controlled by reduction of dust during drying or by addition of surface active agents to the oils. Practical tests on using various isomerized oils in paints were recorded by Talen (*Verfkroniek 23,* 80). The data tabulated included amount of conjugation, clarity, color, and drying, chalking and scorching tests.

Castor oil intended for the paint and varnish industry must be dehydrated to remove the hydroxyl groups. Radlove (*U. S. 2,515,797*) continuously dehydrated castor oil under vacuum using sulfuric acid as a catalyst. He pointed out that an outstanding feature of the method was production of at least 29% conjugation in the product. According to Kane & Kuloor (*J. Sci. Ind. Research, India 7B,* No. 11, 184) the outstanding feature of such a method was that the product was pale in color and low in acid value. Sulfur dioxide as the catalyst for the dehydroxylation of castor oil was said to act as a dehydrating, deoxidizing, and bleaching agent (Etablissements Robbe Freres—*Brit. 625,123*). Castor oil, intended to become a paint ingredient, could be dehydrated with litharge, basic carbonates, white lead pigment or lead linoleate as the catalyst (Agster & Terrill—*U. S. 2,484,328*). In a comparison of catalytic dehydration of castor oil with natural active earths and activated earths the former failed to catalyze the reaction (van Duuren—*Landbouw. 21,* 115). A continuous process using activated clay comprised flowing the oil through an electrically heated aluminum tube containing the clay (Plisov & Tomson—*Zhur. Praklad. Khim. 23,* 200). Dooper's (*Centraal Inst. Materiaal Ondersoek, Afdel. Verf, Circ. No. 61,* 9 pp.) application tests with bodied dehydrated castor oil showed that replacing some tung and linseed oils with it in varnishes had only little effect on gloss retention and cracking but it increased after-tack.

Several investigations were on the manufacture of bodied oils. In experimental work on menhaden oil it was found that the process should be carried out at temperatures below 120°C. to obtain a light product. Cobalt driers accelerated the process, while organic peroxides had only a slight accelerating effect on the process (Bittenbender—*Com. Fisheries Rev. 12,* No.

5, 17). Chinese perilla oil was bodied with air at 150-280°C. to produce a suitable linseed oil substitute for use in printing ink (Chow & Li—*J. Chem. Eng. China 16,* 7). Improvements in bodied oils were obtained by performing the operation in the presence of a small amount of 3,4-epoxy-1-butene (Moffett—*U. S. 2,471,577*) or resin prepared by the reaction of sulfur dioxide on organic compounds containing double bonds (Pratt—*U. S. 2,516,590*). In polymerizing polyester resins, *tert*-butyl hydroperoxide and dodecyl mercaptan were very effective curing agents (French—*Paint, Oil, Chem. Rev. 112,* No. 20, 15). The presence of moisture during polymerization inhibited decomposition of unsaturated fatty acids (Goebel—*U. S. 2,482,761*). Over-heating during bodying of oils could be controlled when the heat was supplied by infrared rays (Reavell—*Brit. 590,218*). The polymerization action of silent electric discharge could only be applied to oil as a preliminary to thermal treatment, for the electrical treatment alone induced a tendency toward resinification (Yzu & Vian—*Combustibles, Zaragoza, 8,* 201).

The drying rate of oils was hastened by refluxing with acetic anhydride (Kass & Nichols—*U. S. 2,497,890;* Nichols—*U. S. 2,497,904*). Other means of increasing the drying rate of oils pertained to the use of metallic soap driers (Unkefer—*U. S. 2,528,803*). The efficiency of various driers and the characteristic they impart were recorded for the drying or oxidation of castor oil (Oil & Chem.-Werk A.-G.—*Congr. tech. intern. ind. peintures inds. assoc. 1,* 451), tobacco and sunflower seed oils (Castorina—*Olearia 3,* 801), safflower oil (Packer & Christensen—*Am. Paint J. 34,* No. 42, 60), and for monounsaturated fatty acids (Skellon—*J. Soc. Chem. Ind. 67,* 116). One investigation on driers pertained to material that would cause the least yellowing of linseed oil. Calcium naphthenate and certain combinations of driers did not favor yellowing (Colomb—*Ind. vernice 4,* 64). Observation on the effect of oil treatment, drier used, pigments present, and many other factors on aging linseed oil films were recorded by Pamfilov *et al.* (*Zhur. Priklad. Khim. 22,* 87). Generally, polymerization or oxidation increased the tensile strength of the films, titanium oxide increased tendency to crumble, films pigmented with zinc oxide aged faster than those with lead oxide.

The drying of coatings to wrinkle finishes was induced by addition of dextran ethers (Luaces—*U. S. 2,490,070; 2,503,622-4*) or polyvinyl chloride latex (Beynon—*U. S. 2,508,092*) to the drying oil ingredient.

Historical and mechanism discussions on modifying oils with dicarboxylic acids were published by Kappelmeier *et al.* (*Kunstoffe 40,* 81) and Petit (*Peintures, pigments, vernes 25,* 300). In studying this reaction at 180-220°C., Plimmer (*J. Oil & Colour Chemists' Assoc. 32,* No. 345, 99) recorded that 1 molecule of methyl linoleate condensed with 1.2-1.6 molecules of maleic anhydride with the saturation of one double bond; with methyl oleate 0.7 moles of the anhydride condensed without the saturation of the double bond. Data on making bodied oils containing phthalic anhydride condensates with oiticica, linseed, and tung oil monoglycerides were recorded by Pollini (*Ind. vernice, Milan, 3,* 193). The adducts of methyl linoleate with itaconic and citraconic anhydrides were separated into monomeric and polymeric components by Teeter *et al.* (*J. Am. Oil Chemists' Soc. 26,* 660). The polymeric adducts gave gel products on heating with ethylenediamine, and the distillates of the adducts gave tough, tacky resins which did not gel on heating for 20 hours at 170-180°C. Novel uses of the reaction products of dicarboxylic acid with oils to improve the coating properties of the oils or preparation of resins were patented (Ullmann—*U. S. 2,502,606;* Ross & Gebhart—*U. S. 2,527,081; 2,496,358;* Greenlee—*U. S. 2,493,486;* Rust—*U. S. 2,503,772*). Some such products were hydrogenated to reduce the yellowing of the coatings made therefrom (Spurling—*U. S. 2,510,915;* Morgan—*U. S. 2,519,492*).

Powers (*Ind. Eng. Chem. 42,* 146) discussed the possible interreactions of resins and drying oils and the effect of these reactions on the characteristics of the coating product. Experience on making varnishes with alkyl phenolic thermosetting resins and tung oil were recorded by van Lerberghe (*Chim. peintures 13,* 284). His data on blending, effect of baking, cooking, and driers on the final films should be useful for manufacturing such products. New synthetic resins for coatings were made from drying oils and, respectively, rosin and resinous epioxides (Montague—*U. S. 2,500,765*), phenol and epioxides of bisphenol and epichlorohydrin (Greenlee—*U. S. 2,502,145*), and phenol-aldehyde petroleum pitch (Snow—*U. S. 2,485,327*). A linoleum composition contained drying oil, hydrolyzed vinyl chloride compounds, rosin, and filler (Heckles—*U. S. 2,502,457*).

Fatty acids and fats were also reacted with the polymerizable materials used in the synthetic rubber industry. Refluxing oleic, dehydrated castor oil, and linseed oil acids with styrene yielded a series of fatty acids containing 1-25 styrene segments per molecule (Powers—*Ind. Eng. Chem. 42,* 2096). The properties of 23 styrenated castor oil samples were tabulated and plotted by Hoogsteen *et al.* (*Ibid. 1587*), giving rate of styrene reaction, relation between viscosity and degree of dehydration of the oil, and film properties of the products. The most desirable products were obtained by styrenating castor oil that has been dehydrated to a minimum hydroxyl content and boiled to a viscosity of 15 poises. A review on production procedures for styrenated oils and alkyds was prepared by Young (*Off. Digest Federation Paint & Varnish Production Clubs No. 296,* 610). In exposure tests on tall-oil varnishes, styrenated tall oil-soybean oil combinations showed up best (Northwestern Federation Paint & Varnish Production Club—*Ibid. No. 298,* 841).

New synthetic drying oils were also prepared by reaction of fatty acids with various alcohols. The alcohols used in the processes were inositol, a hexahydroxycyclohexane (Gibbons & Gordon—*Ind. Eng. Chem. 42,* 1591), polymeric polyether derivative of 4,4′-dehydroxy-2,2-diphenylpropane and epichlorohydrin (Greenlee—*U. S. 2,504,518*), a condensate of glycerol dichlorohydrin with glycerol or pentaerythritol (Wittcoff & Roach—*U. S. 2,527,870*), and a mixture of thermoplastic resin and pentaerythritol (Gutkin—*U. S. 2,497,449*). The polymerization of 3-butene-1,2 diol dipalmitate yielded dimers (Dyer *et al.*—*J. Am. Chem. Soc. 71,* 2728). The drying properties of hempseed oil were improved by halogenation and reaction with 1-sodium-1,2-propene (Williams—*U. S. 2,529,528*).

Reaction of fatty acids with alkyl diamines yield compounds which polymerize to macromolecular poly-amides with good drying properties (Fournier—*Compt. rend. 230,* 2186). Further polymerization of such compounds was also effected with maleic anhydride and paraformaldehyde (Jordan *et al.—U. S. 2,518,148*).

PLASTICIZERS. In an investigation on the suitability of derivatives of 9,10-dihydroxystearic acid and 9,10-dihydroxyoctadecanol as plasticizers for commercial polymers, the most promising materials were 9,10-methoxyhydroxystearate, esters of 9,10-dihydroxystearic acid with ethylene glycol monobutyl ether and ethylene glycol monobenzyl ether, and the polymeric plasticizers (Knight *et al—J. Am. Oil Chemists' Soc. 27,* 281). Preliminary tests indicated that the alkyl α-acyloxyacetates and propionates derived from fatty acids were compatible with ethyl cellulose as plasticizers (Weil *et al.—Ibid.* 187). Many laurates of lactic acid esters were synthesized for evaluation as plasticizers for vinyl chloride resins (Fein & Fisher—*J. Org. Chem. 15,* 530). The newly patented plasticizers were cellulose acetate laurate (Seymour *et al.—U. S. 2,484,124*), styrene glycol difatty acid esters (Thomas & Hochwalt—*U. S. 2,476,252*), cyanoether esters of an aliphatic dihydric alcohol and a fatty acid (Crews —*U. S. 2,495,214*), acylated ricinoleic acid and its derivatives (Reuter & Syverson—*U. S. 2,500,918*), and di- and tri-alkyl silane derivatives of ricinoleic acid esters (Christ—*U. S. 2,496,335;* Earhart—*U. S. 2,496,340*).

LUBRICANTS. Fatty material was used for lubricants in many forms. In a review of fats for lubricant the applications and characteristics desired for use in greases were presented (Graziani *et al.—Inst. Spokesman 14,* No. 5, 10). Use of polymerized fatty oils for lubrication was also reviewed (Singer—*Seifensieder-Ztg. 73,* 133). Lubricant oils were prepared from tall-oil by decarboxylation (Enkvist—*Finnish Paper Timber J. 30,* 446). Fatty alkylated naphthalenes were satisfactory lubricants provided the alkyl side chain was sufficiently long (Kölbel—*Brennstoff-Chem. 30,* 73). Fish and soybean oils were converted to lubricant products by heating at 300°C. with lead salts (Kobayashi—*Japan 174,648-9*). Grape seed oil, polymerized by silent electric discharges, was used as an additive for lubricant oils (Empresa Nacional "Calvo Sotelo"—*Fr. 941,858*). An investigation on lubricants prepared by glow discharges in fatty materials showed that polymerization, hydrogenation and dehydrogenation occurred and excellent aviation oils resulted from blending these with selected mineral oils (Whiteley *et al.—Ind. Eng. Chem. 42,* 2471). Blending polyoxyalkylene esters of fatty acids with minerals yield lubricants with a reduced change in viscosity with temperature change (Fife & Roberts—*U. S. 2,480,185*). Polyalkyleneamines condensed with fatty acids and phosphated could be used as lubricants alone or admixed with other material (Barber & Eaton—*U. S. 2,484,146*).

Many fat derivatives were used in lubricant oils in small amounts to induce particular properties. Special fat derived detergents were added to mineral oil lubricants for removal of resinous deposits from parts of internal-combustion engines (Mertes—*U. S. 2,501,731-2*; Clayton & Etzler—*U. S. 2,516,616*; Reiff & Andress — *U. S. 2,518,372*; Eby — *U. S. 2,523,100*). Calcium petroleum sulfate and partial esters of fatty acids and sugars mixtures (von Fuchs & Pilz—*U. S. 2,481,372*), and α-halogenated keto fatty compounds (Price & Sprules—*U. S. 2,481,036*) improved the rust inhibiting properties of lubricants. Corrosion of internal combustion engines while idle was inhibited by a mixture of partial fatty acid esters of polyhydroxide compounds and organic phosphites (Wasson & Hand —*U. S. 2,485,341*). Polydimethyl siloxane compounds (Wallace—*U. S. 2,533,700*) and fluorinated hydrocarbons (Davis & Zimmer—*U. S. 2,515,115*) inhibited foaming in lubricants containing fatty acids and fatty acid derivatives. Several patents were issued on the manufacture and use of sulfured fat derivatives in lubricants to improve viscosity, antisticking properties, pour point, to inhibit corrosion, to decrease sludge formation, etc. (Musselman—*U. S. 2,480,873;* Stucker *et al.—U. S. 2,483,600;* Jolly—*U. S. 2,490,271;* Fawcett—*U. S. 2,492,562;* Watson & Mixon—*U. S. 2,496,508;* Bartleson—*U. S. 2,506,572;* Hughes & Bartleson—*U. S. 2,506,597;* Smith *et al.—U. S. 2,506,900-2, 2,513,060;* Rogers & McNab—*U. S. 2,518,379;* Wasson—*U. S. 2,522,476;* N. V. Bataafsche Petroleum Maatschappij—*Dutch 63,961*).

Methods for making greases with metal soaps appeared in journals and patents (Baouman — *Ind. chim. 37,* No. 391, 29; Bloomsberg & Beerbower—*Petroleum, London, 13,* 115; Leyda—*U. S. 2,504,672;* Houlton—*U. S. 2,483,282;* Morita—*Japan 175,367;* N. V. Bataafsche Petroleum Maatschappij—*Dutch 65,126;* assigned to Shell Development Co.—*U. S. 2,491,641, 2,524,563;* Showa Petroleum Oil Co. — *Japan 175,446;* Socony-Vacuum Oil Co., Inc.—*U. S. 2,491,441, 2,513,680;* Standard Oil Development Co.—*U. S. 2,491,028, 2,491,054-5, 2,497,133, 2,503,969, 2,504,717, 2,505,222, 2,514,286, 2,514,296, 2,514,311, 2,514,330-1, 2,515,133, 2,516,136-8, 2,521,395, Brit. 590,994, 578,011;* Texas Co.—*U. S. 2,503,749, 2,508,741*).

Some fundamental research work on lubricants pertained to the fat derived ingredients. Davey (*Ind. Eng. Chem. 42,* 1837) believed that fatty acid blends with mineral oil reduced wear and friction by formation of soap films of low shear strength with the metals. Tingle (*Trans. Faraday Soc. 46,* 93, 97) indicated that freshly cut metal surfaces oxidized readily and oxides react with fatty acids to form a lubricant soap film, or fatty acids themselves may form tough compact skins on metal surfaces. Browning (*Inst. Spokesman 14,* No. 1, 10) recorded that metal soaps formed grease-like structures with mineral oil, silicone oils, or glycerol thus indicating that the oil-retaining properties of a grease might be due to the attracting influence of the soap and not the swelling of the fiber. Phase behavior of Li soaps, and x-ray and thermal analysis of many metal soaps were recorded by Vold *et al.* (*J. Colloid Sci. 5,* 1; *Ind. Eng. Chem. 41,* 2311, 2320). Some of the data could be associated with phenomena occurring with commercial grease manufacture and the properties of the greases.

Some analytical reports contained information on the properties of heavy metal soaps and greases. The determination of the acidity of metal soaps may indicate the structure because the degree of association of the soaps in solvents diminishes rapidly in the presence of polar molecules (Wolff — *Oleagineux 5,* 20). The Karl Fischer method for determining moisture in commercial aluminum soaps was complicated by the reactions between hydroxy groups and reactions between basic soaps and free acid to yield further free water (Parry & Taylor—*Nature 164,* 449, *Trans, Faraday Soc. 46,* 305). Weak metal soap dispersions in liquid dielectrics formed ribbons which connected the electrodes and increased the conductance of the liquid (Putilova *et al.—Doklady Akad. Nauk S.S.S.R. 71,* 81). A new consistency test for greases depended on the pressure required to force samples through standard nozzles (Kesternich — *Z. Ver. deut. Ing. 91,* 93). Wheel bearing grease tests with the American Society for Testing Materials tester correlated well with actual service in motor cars and trucks (Georgi—*Inst. Spokesman 14,* No. 4, 19). In tests on ingredients for extreme pressure lubricants, phosphites were superior to phosphates as additives and fatty esters were superior to aryl esters (Davey—*Ind. Eng. Chem. 42,* 1841).

Martin (*Am. Dyestuff Reptr. 39,* No. 7, P223) described conventional laboratory tests and semi-plant trials for evaluation of woolen-fiber lubricants. A new metal cutting lubricant contained mineral oil and partial esters of fatty acids and a polyhydric alcohol (Blake—*U. S. 2,531,801*). A mixture of cottonseed oils and butyl methacrylate resin was patented as a lubricant for extrudable cork composition (Navikas—*U. S. 2,495,277*).

WAX EMULSIONS, RUST-PREVENTIVES, PIPE JOINT COMPOUNDS, WATER PROOFERS. A review of fats and waxes in the shoe and leather industry was prepared by Hadert (*Fette u. Seifen 52,* 470). Polymerized products of castor oil were recommended for dressing and sizing leather by Prakash *et al.* (*J. Sci. Ind. Research, India, 8B,* 180).

One patented polishing composition comprised a mixture of hydrocarbon oil and rat-fish liver oil (Briton—*U. S. 2,476,281*). Wax-like materials were prepared by esterifying fusible phenolic resins with fatty acids (Smith & Cantrell — *U. S. 2,506,903-4*). A major component of a new wax emulsion was stearic acid monohydrate (Aelony — *U. S. 2,505,931*). Stearic acid was also a major component of a wax suitable for making asbestos-cement building boards water-repellent (Buckman & Rendall—*U. S. 2,504,920*). Mineral wool was waterproofed with heavy metal soaps (Crandell & Burnett—*U. S. 2,501,316*).

Water insoluble fatty acid resin dissolved in a suitable solvent was patented as an antirust protective coating for application by spraying (Beretvás—*U. S. 2,518,438*). The tendency of corrosive brines to attack oil well casings was reduced by mixing a small amount of bone oil with the brines (Menaul—*U. S. 2,493,462*).

A compound for lubricating pipe joints and for preventing "freezing" of threads contained sodium and calcium stearates, clay and other materials (Lorenzo —*U. S. 2,490,949*).

PREPARATION OF ACIDS, ALCOHOLS, ESTERS, KETONES, NITROGEN-CONTAINING AND HYDROCARBON DERIVATIVES. Some pure fatty acids were prepared to study their chemical, physical and/or physiological properties or to develop new methods of synthesis. Electrolyzing mixture of half esters of dicarboxylic acids yielded hydrocarbons, diesters, and monoesters (Greaves *et al.—J. Chem. Soc. 1950,* 3326, 3331, 3333). This proved to be a new method for synthesis of stearic, myristic, and other acids. The Arndt-Eistert reaction was applied for the preparation of C_{19}, C_{20}, and C_{21} fatty acids from stearic acid (Vandenheuvel & Yates—*Can. J. Res. 28B,* 556). Three optical isomers of 15-methyloctadecanoic acid were prepared by the use of keto ester synthesis (Cason & Coad — *J. Am. Chem. Soc. 72, 4695*). The synthesis, properties and infrared absorption spectra of branched chain monobasic fatty acids with even numbers of carbon atoms from 16 to 24 were recorded (Sobotka & Stynler —*Ibid.* 5139). Several fatty acids between C_{14} and C_{23} were synthesized from corresponding keto acid by ketone synthesis (Ames *et al.—J. Chem. Soc. 1950,* 174). The *cis*-linoleic acid was made by reduction of monoacetylenic to linoleic acid (Raphael & Sondheimer — *Nature 165,* 235). Seven monounsaturated straight chain fatty acids were prepared from the corresponding 1-chloroacetylenic hydrocarbon by conversion to the nitrile and partial hydrogenation (Taylor & Strong — *J. Am. Chem. Soc. 72,* 4263). *Trans*-11,12-octadecenoic acid, vaccenic acid, was isolated from the products of hydrogenation of methyl β-eleostearate and its structure and configuration were confirmed (Woltemate & Daubert—*Ibid.* 1233).

Other literature on fatty acid production concerned commercially applied processes. The chemistry equipment, and manufacturing processes for fatty acids, and their nitrile and amine derivatives were described (Potts & McBride—*Chem. Eng. 57,* 124, 172; Kenyon *et al.—Ind. Eng. Chem. 42,* 202). Methods for commercially concentrating oleic acid without the use of distillation were reviewed (Preobrajenski—*Bull. mens ITERG 4,* 215). The oleic acid obtained from rice oil could be used for textile oiling providing 0.5% α-naphthol was added as an antioxidant (Naito & Tsuchiya—*J. Nippon Oil Technol. Soc. 2,* No. 6, 13). Lauric acid of high purity was concentrated from the ethyl esters of palm oil fatty acids by distillation, saponification, and recrystallization (Ragon & Bolle—*Mem. services chim. état, Paris, 34,* 337). Ricinoleic acid of very high purity was concentrated from castor oil fatty acids by fractional crystallization from acetone (Hawke—*J. S. African Chem. Inst., N.S. 2,* 1). Some new substitutes for the palm oil used for hot-dip tin plating were 100% free fatty acids (Johnson *et al.—Yearbook Am. Iron Steel Inst. 1949,* 495), dimer acid mixtures, and modified tallow (Ference *et al.—J. Am. Oil Chem. Soc. 27,* 122). A dienic acid concentrate was prepared from horse fat by hydrolysis with pancreatin and fatty acid fractionation by crystallization Grün—*Swiss 266,511*).

Oxidation processes were used on fats for the production of various products. A process for making short chain mono- and di-acids from fatty acids by oxidation with chromate-sulfuric acid solution was patented (Emery Industries, Inc. — *Brit. 604,281*). The by-products of the manufacture of sebacic acid from castor oil were refined by selective solvent action to yield material suitable for manufacture of synthetic resins and plasticizing agents (Hanson—*U. S. 2,470,849*). Oleic acid, methyl oleate, and oleyl alcohol were converted to epoxy compounds by cooxidation in which benzaldehyde, acetaldehyde and butyraldehyde were employed as the source of the intermediate peracid (Swern & Findley—*J. Am. Chem. Soc. 72,* 4315). Oleates and linoleates epoxidized by formic acid and hydrogen peroxide were useful as plasticizers and for hydrochloric acid "scavengers" in film-forming materials (Niederhauser & Koroly—*U. S. 2,485,160*). The *cis*-11-ketoheptadec-8-ene-1-carboxylic acid and its *trans*-isomer were prepared by chromic acid oxidation of ricinoleic acid in some work connected with the study of oxidation of monounsaturated fatty acids. (Ellis — *J. Chem. Soc. 1950,* 9). Enanthaldehyde and methyl hendecenoate were produced in maximum yields from methyl ricinoleate by heating in presence of sodium borate or phosphate at 550-600°C. (Jacini —*Olearia 3,* 521). The methyl hendecenoate could be oxidized to sebacic acid.

Fatty acids were chlorinated by dissolving in lower fatty acids and bubbling chlorine through the solution (Frilette — *U. S. 2,492,417*). Isoparaffin hydrocarbons were reacted with fatty acids in the presence of anhydrous hydrogen fluoride as a catalyst to hydrogenate the fatty acid and/or to increase the chain length (Frey—*U. S. 2,525,889*). A method for manufacture of higher fatty acid esters of polychlorinated phenols comprised reacting chlorine with phenol in solution with the theoretical quantity of the corresponding higher fatty acid and adding phosphorous oxychloride to the reaction mass (Higgins—*U. S. 2,506,361*). The hexaester of mannitol laurate could be prepared in 86% yield by reaction of lauroyl chloride with mannitol in pyridine solution (Nicoud—*J. recherches centre natl. recherches sci. No. 9,* 286). A nondrying adhesive comprised a mixture of cyclized rubber and polyester of a dihydric alcohol with dimer polymers of fatty acids (Carson — *U. S. 2,496,934*). The properties and uses of metallic soaps were reviewed by Bossert (*J. Chem. Ed. 27,* 10).

Oleic acid was hydroxylated by treatment with inorganic persulfate and acids, in the preparation of intermediates for plasticizers, detergents and resins (Raczynski—*U. S. 2,510,905*). Hydroxylated soybean oil had less swelling effect on rubber than oils of a lower acetyl number (Imata—*J. Nippon Oil Technol. Soc. 2,* No. 4, 1). Stearic acid was prepared from castor oil acids in three steps, hydrogenation to saturated esters, dehydrogenation to isooleic compounds, and rehydrogenation (Abril Corp.—*Brit. 627,531*).

Conversion of fats to hydrocarbons is of interest in those countries poor in mineral oil resources. Hsu *et al.* (*Ind. Eng. Chem. 42,* 2141) investigations on cracking calcium salts of fatty acids showed that highly unsaturated acids such as those of tung oil yield much coke and tars, and less distillate than calcium salts of saturated fatty acids. Tokunaga's (*J. Nippon Oil Technol. Soc. 3,* No. 1/2, 37, 49, 69, 79, 89; *Japan 174,688*) work on pyrolysis of fats dealt with the evaluation of various clays as catalyst for the process on those oils and fats which were available in Japan. Hydrocarbons were also made from fats by hydrogenation under 200 atmospheres pressure at 250-395° in the presence of much catalyst (Hosman *et al.* —*Rec. trav. chim. 68,* 939).

The manufacture of fatty alcohols from fats by both the alkali metal and the hydrogenation methods of reduction was investigated. Jacini's (*Chimica e industria, Milan, 30,* 199) best yield in reduction with sodium in butyl alcohol was 88% from methyl linoleate; other materials gave alcohol yields as follows: castor oil 41.2, linseed oil 67.5, peanut oil 81.2, sunflower oil 58, almond oil 69, babassu oil 85.7, methyl ricinoleate 61, and methyl oleate 84.7%. The unsaturated products were suitable for use as siccative oils. Adkins & Gillespie (*Org. Syntheses 29,* 80) obtained 49-51% yields of oleyl alcohol by reducing ethyl oleate with sodium in ethanol. In preparation of sebacic acid and octyl alcohol by heating castor oil with alkalies, the highest yield of the alcohol was obtained when the castor oil soap was heated with 30% sodium carbonate (Verma & Aggarwal—*J. Sci. Ind. Research, India, 8B,* 183). Excellent yields of alcohols were obtained from fatty acids when lithium aluminum hydride was used as the reducing agent (Ligthelm *et al.*—*J. Chem. Soc. 1950,* 3187). For reduction of fats to alcohols by hydrogenation Sueta & Tasaka (Japan—*174,725*) patented the use of special mixtures of copper and chromium oxides as catalysts. Tests on hydrogenation of methyl esters of rice oils with zinc and chromium oxide catalysts gave alcohol yields of 38 to 68% (Takahashi—*J. Nippon Oil Technol. Soc. 2,* No. 5, 19). Similar work with iron and zinc oxide catalyst gave 90.5% with the methyl esters and 72.8% yield with the rice oil (Iwai—*Ibid.,* No. 6, 19). The use of certain oxides of bivalent metals with a hydrogen overvoltage between 0.3 and 0.6 volts as catalyst in the hydrogenation-manufacture of alcohols from fats was patented by Natta (*Ital. 420,794, 430,809*).

Many nitrogen-containing derivatives were prepared from fats for various purposes. Such compounds as 2-nitro-2-methyl-1-propyl palmitate and 2-nitro-1-butyl stearate (Tindall — *U. S. 2,488,650*), certain quaternary ammonium fat derivatives (Zerner & Pollack—*U. S. 2,489,473, 2,510,007*), reaction products of hydroxy-methylamine and stearate soap (Cathers & Fluck — *U. S. 2,491,249*), condensation products of fatty acid amides and hexaethoxymethylamine or dibutoxymethylurea (Rust—*U. S. 2,510,522*), *N*-ricinoleyl amine (Jacoby—*U. S. 2,511,163;* Imperial Chemical Industries Ltd.—*Brit. 632,242*), and condensation products of melamine and fatty acid anhydrides (Emerson & Patrick—*U. S. 2,507,700*) were particularly patented as waterproofers especially for textiles, but, the usefulness of some as polishing waxes, defoamers, intermediates for other compounds, and other sundry uses were suggested. Acylamino-*N*-substituted amides derived from fatty acids were useful wax-like solids (*Bird—U. S. 2,486,249*). 3-Buten-2-ol fat acid amines (Long—*U. S. 2,497,553*), gamma-fatty acid amidopropydimethyl-*β*-hydroxy ammonium chloride (Dixon & Morgan—*U. S. 2,500,122*), and ether fatty acid esters of alcohol amines (Katzman & Epstein—*U. S. 2,496,875*) were patented as emulsifiers. The use of quaternary ammonium salts for flotation was reviewed (Neunhoeffer — *Z. Erzbergebau u. Metallhüttenw. 2,* 334).

The *cis-* and *trans*-diacido-tetramine-cobalt complexes with fatty acids were synthesized and their properties recorded (Linhard & Weigel — *Z. anorg. Chem. 260,* 65). Equipment for continuous manufacture of fatty acid nitriles from liquid ammonia and fatty acids was designed by Potts (*U. S. 2,524,831*). The use of phosphorus as a catalyst for such a process was suggested by Ralston (*U. S. 2,526,044*).

The solubilities of dodecyl-, *N* methyldodecyl-, *N,N,-dimethyldodecyl-* and *N,N,N,*trimethyldodecyl-ammonium chlorides in hexane, benzene, and 95% ethanol have been recorded (Broome & Harwood — *J. Am. Chem. Soc. 72,* 3257).

Deterioration

REVIEWS. The comprehensive reviews on spoilage of fats contained information on the mechanism of deterioration, methods of testing for susceptibility to oxidation, and prevention with antioxidants and synergists (Dubouloz—*Ann. nutrition et aliment. 3,* 413; Sisley—*Rev. fermentations et inds. aliment. 5,* 126; Fiedler—*Seifen-Öle-Fette-Wachse 75,* 89). Other review papers treated hydrolysis and oxidation (Petrovskii—*Myasnaya Ind. 20,* No. 6, 36), the autoxidation of the saturated fatty acids (Paquot & de Goursac—*Oleagineux 5,* 349); materials and methods used in margarine manufacture with respect to stability of the product (Becker—*Fette u. Seifen 52,* 546); deterioration of dairy products (Greenbank—*Proc. 12th Internat'l Dairy Congr. 2,* 248), antioxidants (Benk—*Seifen-Öle-Fette-Wachse 75,* 536; Anon.—*Ann. Meat Packers Guide 1950,* 75), and stabilization with Nordihydroguaiaretic acid (Blaizot & Cuvier—*Oleagineux 5,* 164).

METHODS OF TESTING. Some modifications of the common methods of measuring spoilage of fats have been suggested. The apparatus used to volumetrically determine the oxygen consumed during oxidation of a fat was supplied with electrolytic cell equipment to automatically compensate and measure the oxygen being consumed (Mellier—*Ann. nutrition et aliment 3,* 447). Better extraction, i.e., without decomposition of peroxidized fat was obtained from rancid sausage with a Waring Blendor than with boiling ethylene chloride (Watt—*Food Technol. 3,* 206). For dairy fats there was a linear relationship between specific absorption at 2300 Å of the peroxides absorbed and then eluted from alumina, and the oxidation (Holm & Wode—*Proc. 12th Internat'l Dairy Congr. 2,* 325). This relation did not exist in the products when the dairy cattle were on rations containing linseed oil.

A new sensitive method for determining the peroxides of fats depended on color reaction of peroxides with 3,5-dichloro-4,4'-dihydroxyphenylenediamine as spectrophotometrically measured at 520 mμ (Hartmann & Glavind—*Acta Chem. Scand. 3,* 954). The results from the method were higher than those by the methods commonly used. The oxidation reaction of such compounds as benzidine, guaiac resin leuco malachite green, and leuco 2,6-dichlorophenolindolphenol by peroxides of fats, some of which can be used for measuring oxidation of fat, could be accelerated by heme (Glavind & Hartmann—*Ibid.,* 914). The color developed by a fat on saponification was suitable criterion for the degree of oxidation (Pallauf—*Seifen-Öle-Fette-Wachse 75,* 51). This reaction depended principally on the hydroxy acid content. The state of rancidity of olive oils was differentiated on the basis of the amount of heat evolved on addition of bromine (Ruiz *et al.*—*Anales real soc. espan. fis. y quim. 45B,* 873). A microchemical method for evaluation of spoilage was based on measuring aldehydes and ketones with *p*-nitrophenylhydrazine (Opfer-Schaum—*Angew. chem. 62,* 144). One characterization of the anti- and proöxidant constituents of fat consisted of redox electrometric measurements (Wachs—*Fette u. Seifen 52,* 466).

Stale, fermented, and oxidized flavors of dairy products were associated with decomposed lipids, and methods for objective evaluation of these defects were applied to the fatty constituents. Torgards (*Proc. 12th Internat'l Dairy Congr. 2,* 797) passed the volatile constituents of butterfat through standardized solutions of dichromate in dilute sulfuric acid and determined the change iodometrically to obtain a "reduction number" (RN no.). If the RN no. was low, the fishy flavor was attributed to oxidation; if high, the cause was microbiological decomposition. Work on the stale flavor component of whole-milk powder showed that it was concentrated with the segregated liquid lipids (Musset *et al.*—*J. Dairy Sci. 33,* 299), or could be concentrated by steam distillation of the butter oil (Whitney *et al.*—*J. Dairy Sci. 33,* 50, 281). A method of reporting the decomposition state of eggs depended on the volatile acid content of the lipids (Hillig—*J. Assoc. Off. Agr. Chemists' Soc. 33,* 723).

MECHANISM OF OXIDATIVE DETERIORATION. In a study of the mechanism of oxidation, Skellon (*J. Chem. Soc. 1950,* 2020) determined the factors influencing hydroperoxide formation and transition into catalytic autoxidation. With air and moisture peroxidation was slow; ultraviolet light with air promoted formation of hyperoxide; and heat accelerated hydroperoxide transition. Some metal soap proöxidants were most active in the initial phases of oxidation while others exerted their maximum effect at the hydroperoxide transition stage. Bergstrom *et al.* (*Acta Chem. Scand. 4,* 245) in studying the oxidation of linoleic acid by means of ultraviolet absorption measurements found that an absorption maximum occurred on addition of one mole of oxygen, which then dropped to zero at about an uptake of two moles of oxygen. Five to six aldehydes, enals, and dienals were isolated from rancid corn and avocado oils by Brekke & Mackinney (*J. Am. Oil Chemists' Soc. 27,* 238).

Skellon & Thruston (*J. Chem. Soc. 1949,* 1626) oxidized elaidic acid and some of its alkyl esters at 55, 85, and 120°C. Induction periods were less evident but did occur at the higher temperatures. The course of the oxidation reactions as evidenced by peroxide value, iodine value, evolution of carbon dioxide, etc., was recorded and was, in general, similar to data obtained with oleic acid. Ellis (*Biochem. J. 46,* 129) studied the same compounds and recorded the proportions of epoxy acid and scission products formed. At all temperatures β-ketonic acids developed and carbon dioxide and water vapor evolved. In similar work Loury & Mellier (*Oleagineux 4,* 665) postulated the coexistence of at least two forms of peroxide, one explosively decomposed with heat while the other was thermostable.

An accelerated oxidation technic was applied to saturated fatty acids to study the products of the decomposition. The principal product on oxidation at 100-120°C. was oxalic acid (Paquot & deGoursac—*Bull. soc. chim. France 1950,* 172). In the oxidation products of stearic acid all the "even carbon" acids lower than stearic were found. This and the isolation of small amounts of methyl ketones of uneven number of carbon atoms was interpreted to indicate that autoxidation of saturated fatty acid was effected through β-oxidation. Lauryl peroxide in organic solvents decomposed to carbon dioxide, hendecane, and *l*-ethoxyethyl laurate (Cass—*J. Am. Chem. Soc. 72,* 4915). The oxidation was eight times faster in diethyl ether than in benzene as the solvent.

FACTORS AFFECTING STABILITY. Chang & Watts (*Food Res. 15,* 313) found that common salt solutions in high concentration behaved as proöxidants in fat oxidation and they discussed their finding with regard to rancidity in cured meats. In work on butter, Hill (*Proc. 12th Internat'l Dairy Congr. 2,* 302) attributed the proöxidant effect of salt to the presence of magnesium chloride as an impurity. According to Scarborough & Watts (*Food

Technol. 3, 152) ascorbic acid and cysteine in the presence of moisture and absence of phenolic inhibitors accelerated rancidification of lard, and this rancidification was much greater in the presence of hemoglobin preparations. Reinart (*Proc. 12th Internat'l Dairy Congr. 2,* 392) related the ease of oxidation of butterfat to the concentration of highly unsaturated acids of the C_{20}-C_{22} series. In the manufacture of ghee, the heating to 110-150°C. induced stability to this butter oil product (Persai & Barnicoat—*J. Dairy Res. 16,* 356). The addition of biacetyl to butter and margarine as is done to improve flavor reduced the stability of the product and had a deleterious effect on the carotene and bixin present (Reinart—*Proc. 12th Internat'l Dairy Congr. 2,* 382). In work on the oxidation of vitamin A acetate in methyl linoleate, the former was destroyed before 10% of the solvent was oxidized (Holman — *Arch. Biochem. 26,* 85). In this work it was observed that the products of oxidation of the vitamin A and the linoleate were spectrally similar.

The proöxidant influence of several copper-amine complexes were measured (Bunyatyan & Kamalyan—*Brokhimiya 15,* 283). A copper-colamine crystalline complex was very proöxidant; as such, it was more effective than equivalent mixtures of copper and colamine and other copper-amines such as of dimethyl amine, trimethyl amine, hydroxyl amine, choline, sarcosine and glycine. Colamine and methyl amine without copper possessed antioxidant properties.

In general papers on stability of fat products, Tsichiya & Kmomura (*J. Nippon Oil Technol. Soc. 2,* No. 4, 30), recorded the course of decomposition of the oil in rice polishing during a 17-month storage period, Liberman & Mirkin (*Myasnaya Ind. 20,* No. 5, 26) tabulated similar data obtained on storing raw and rendered packinghouse fats, and Bose & Subrahmanyan (*Indian J. Med. Research 37,* 11) determined the effect of acidity, moisture, and sunlight on the protection of vitamin A in shark-liver oil containing antioxidants. The above investigators particularly used their data to show that fats must be stored at low temperatures and protected from direct sunlight.

ANTIOXIDANTS. Several investigators determined the protective effect of antioxidants on dairy products. Lea & Smith (*Proc. 12th Internat'l Dairy Congr. 2,* 341) inhibited deterioration flavors in dried milk best by adding ethyl gallate before a heating step in processing or by packing in inert gas. In investigations on the effectiveness of various alkyl gallates for the same purpose, Tollenaar (*Ibid.,* 357) found that antioxygenic activities were inversely proportional to their molecular weights; while the fungistatic activities and the retardation of development of ketonic rancidity were most efficient with the highest molecular weight ester, lauryl, investigated. The astringent bitter taste of the antioxidant esters increased with the molecular weight. Swartling (*Ibid.* 375) rated the protective effect of various aromatic hydroxy compounds for butter stored at room temperature. Gallic acid esters, hydrocaffeate esters, and nordihydroguaiaretic acid were most effective; *p*-methoxyphenol and conidendrin were much less efficient; while tocopherols showed a proöxidant effect and a tendency to promote development of a fishy flavor. Reinart (*Ibid.* 405) also reported that α-tocopherol or its acetate ester were not effective as antioxidants for butterfat. However, Krukovsky *et al.* (*J. Dairy Sci. 33,* 791) reported that there was a correlation between the natural tocopherol content of milk fats and their stability to oxidized flavors. According to Willstaedt & Reinart (*Arkiv. Kemi 1,* 319) lactarviolin, a pigment synthesized by certain molds, was a highly effective antioxidant for butterfat. This compound was an unsaturated aldehyde of the azulene series. Vanillas and vanilla compounds served as flavor and antioxidants in powdered ice cream mixes (Pyenson & Tracy—*J. Dairy Sci. 33,* 815).

The protective effects of several antioxidants for lard were determined. Sandell & Spross (*Svensk Farm. Tid 54,* 61) recorded that 0.003% hydroquinone or nordihydroguaiaretic acid, or 0.006% propyl gallate could stabilize lard for one year. Benzoin and gum guaiac were required in a concentration of 0.3% for the same purpose. α-Tocopherol showed feeble protection in accelerated tests, but acted proöxidant in storage tests. In similar work by Blaizot & Cuvier (*Oleagineux 5,* 96) nordihydroguaiaretic acid was superior to hydroquinone and α-tocopherol when ascorbic acid was used as a synergist. Lips (*Can. J. Research 27F,* 373) reported that citric acid, lecithin and α-tocopherol have a stabilizing action on dry lard, while gum guaiac was effective either in the presence or absence of moisture. His work (*Ibid. 28F,* 451) on the antioxidant properties for lard of ethylene dichloride extract of cottonseed meal indicated that the effect could be attributed to the relatively high concentration of phosphatides in the extract. Morris *et al.* (*J. Am. Oil Chemists' Soc. 27,* 105) evaluated the known antioxidant synergists as proöxidant deactivators for iron, copper, nickel, and tin in lard. Ascorbyl esters, and ascorbic, tartaric, citric, and phosphoric acids were most effective. The synergistic effects of these compounds with phenolic antioxidants was said to be due, in part, to their metal deactivation properties. In tests on the effectiveness of phosphates as synergistic antioxidants by Watts (*Ibid.* 48), the activity increased from pyrophosphate through tri- and heptaphosphate to the most active hexametaphosphate and Maddrell's salt; while the orthophosphates were ineffective.

Many gallic acid esters were synthesized from gallic acid and partial esters of fatty acids and polyhydroxy compounds and their antioxidant effectiveness for fish oils determined (Bittenbender—*Com. Fisheries Rev. 12,* No. 2, 1). The gallic acid esters, glycerol dipalmatate monogallate, and glycerol monogallate mono-coconut oil or mono-cottonseed oil fatty acids were the most effective products tested. In tests on protection of fat in dried herring, smoking had a greater antioxygenic effect than use of antioxidants (Banks—*J. Sci. Food Agr. 1,* 28). The fat of frozen fish flesh stored at —10 or —20°C. was protected a little better with reductic acid than with *l*-ascorbic acid; and other carbonyl enediol type compounds tested were ineffective.

Some antioxidant information pertained to stabilizing fat soluble vitamins. Basu & Bhattacharya (*J. Indian Chem. Soc. 26,* 459) suggested that vitamin A in ethyl oleate should be protected by phenolic antioxidants containing one or more free phenolic hydroxyls. Emulsions of vitamin A alcohol were most stable therapeutically between pHs five to nine, but stability could be enhanced at pH 3 and 4 with tocopherols (Kern & Antoskikiw—*Ind. & Eng. Chem. 42,* 709). The tocopherols were proöxidants at pHs 7 and

9. A prevention of appearance of deficiency symptoms in chicks on a vitamin E-deficient basal diet by oral supplements of crude xanthophyll was believed to be due to the antioxidant properties of the xanthophyll (Goldhaber *et al.*—*J. Nutr. 42,* 453).

The stability of sesame oils was found to be related to the amount of sesamol present (Budowski *et al.*—*J. Am. Oil Chemists' Soc. 27,* 264, 307, 377). A procedure for determination of the sesamol was devised, and the isolated compound was found to possess marked antioxidant activity for lard in the same series of investigations.

In other laboratory work on antioxidants, citric acid was found to have both metal deactivator and synergistic properties in peanut oil (Lemon *et al.*—*Can. J. Res. 28F,* 453), two years toxicity studies with gallate ester antioxidants indicated that they were innoxious (Nilson *et al.*—*Com. Fisheries Rev. 12,* No. 9, 19), and a method for determination of propyl gallate in edible fats was developed (Terrier & Deshusses—*Mitt. Lebensm. Hyg. 40,* 221). The antioxidant properties of butylated hydroxyanisole were reviewed (Dugan *et al.* — *Food Tech. 4,* 457). The oxidation of systems containing bixin, carotene, tocopherol, and methyl linoleate were observed spectroscopically (Kunkel & Nelson—*J. Biol. Chem. 183,* 149). Bixin in methyl linoleate was completely decolorized before 10% of the ester oxidized. The presence of α-tocopherol inhibited the decolorization of both bixin and carotene. In photoxidation of the tocopherol-linoleate system, carotene produced an increased rate of oxygen uptake during the induction period.

Some of the newly patented antioxidants were: combinations of nordihydroguaiaretic acid, citric acid, and lecithin (Black—*U. S. 2,494,114*), materials extracted with water miscible organic solvents from vegetable oils or meals after treatment with ammonium hydroxide (Buxton—*U. S. 2,515,858-60*), materials extracted from fats after treatment with phosphatide and ammonia, and removing the ammonia (Buxton & Dryden—*U. S. 2,511,427-8*), 1,3,8,10-tetra-phenyl-4,7-dithiadecanedione-1,10 (Chenicek & Thompson—*U. S. 2,492,335*), a gas mixture containing carbon dioxide, acetylene, oxygen, carbon monoxide, methane, and nitrogen (Dunkley — *U. S. 2,504,507*), monoisopropyl citrate or monostearyl citrate (Gooding *et al.*—*U. S. 2,518,678*), a combination of tocopherols and a crude preparation of vitamin B complex (Gyorgy—*U. S. 2,526,865*), mixing alkyl esters, lecithin, and tocopherol with the fat and heating (Hall—*U. S. 2,493,288*), mixture of gallic acid esters and benzoic, fumaric, tartaric, and citric acids (Hall —*U. S. 2,511,802-4*), mixture of the preceding with amino acids (Hall—*U. S. 2,518,233*), the squalene fraction from the unsaponifiable substance of shark liver oil (Hosoda—*Japan 174,330*), amine or amide derivatives of gallic acid (Korner—*U. S. 2,486,177*), mixtures of tertiary butylated hydroquinone monoalkyl ether, hydroquinone and citric acid, ascorbic acid, phosphoric acid, ethyl acid phosphate or triethyl phosphate (Kraybill & Beadle—*U. S. 2,521,856*), mixtures of aconitic acid, aconitic anhydride, and itaconic anhydride (Lindsey & Maxwell—*U. S. 2,513,948*), a combination of tocopherols, hydroquinone or nordihydroguaiaretic acid, and an amino acid (Lundberg—*U. S. 2,523,127*), alkylated gallic and other polyhydroxybenzoic acids (Morris & Riemenschneider—*U. S. 2,483,099*), 3-mercaptopropionic acid (O'Leary—*U. S. 2,497,320*), sinapic acid methyl ester, ferulic acid methyl ester, hydroferulic acid, *o*-coumaric acid methyl ester, sinapic acid, or other similar compounds (Schicht — *Brit. 633,084,*) certain β-alkylthioalkanones (Thompson—*U. S. 2,492,334*), tetra alkylthiuran disulfides (Tollenaar — *U. S. 2,502,109*), and *N*-(hydroxyaryl) pyrroles (Valentine—*U. S. 2,489,000*). To prevent color formation in baked goods when the shortening contains gum guaiac as the antioxidant, the gum guaiac should be treated with hydrogen peroxide while dissolved in acetic acid (Black —*U. S. 2,529,446*). Doolin (*U. S. 2,514,479*) recommended storing deep-fat frying fats for reuse by hermetically sealing in containers at 330°F. The proöxidant effect produced when calcium carbonate was mixed with fodder for animals was obviated by admixing sodium thiosulfate with the calcium carbonate (McHan—*U. S. 2,479,583*).

FLAVOR REVERSION. In a survey of research work on flavor stability of soybean oil done at the Northern Regional Research Laboratory, Cowan (*Soybean Digest 9,* 48) related the flavor stability to the logarithm of the peroxide value of the oils. Soybean oils refined by furfural fractionation did not develop off-flavors (reversion) as easily as the extracts or original oil samples (Schwab—*J. Am. Oil Chem. Soc. 27,* 314). In work on isolating the off-flavor constituents of reverted soybean oil, Daubert *et al.* (*J. Am. Oil Chemists' Soc. 27,* 367, 374) isolated 2-heptanol, di-*n*-propyl ketone, 2,4-decadienal and acetaldehyde each of which could contribute to the flavor reversion odor.

In work on the origin of fishy flavors in butter, Storgards & Hietaranta (*Proc. 12th Internat'l Dairy Congr. 2,* 389) associated the defect with the presence of linoleic acid. They could not confirm reports that it may be due to decomposition of lecithin for butterfat freed of lecithin became fishy, and trimethylamine, a decomposition product of lecithin was sometimes found in greater amounts in nonfishy butters than in fishy tasting products. Holm (*Ibid.* 336) related the development of tallowiness in butter to the peroxide value at various temperatures.

MICROBIOLOGICAL DECOMPOSITION OF FAT. Hietaranta (*Suomen Kemistelehti 22B,* 33) isolated organisms from butter and recorded their ability to hydrolyze fats, to form methyl ketones and peroxides, and to form oxidase. All oxidase positive bacteria produced methyl ketones in connection with growth but some of them formed no lipase. Some bacteria which produced catalase slowed the rate of formation of peroxides. Since β-methyl ketones were formed in all cases, both β-oxidation and peroxidation were connected with oxidase positive bacteria. Thaler *et al.* (*Biochem. Z. 320,* 84, 87) identified the methyl ketones produced by *Penicillium glaucum* on various fatty compounds in a study on the mechanism of ketone rancidity. The attack was only by β-oxidation, and since β-methyl-β-hydroxy fatty acids did not give rise to ketones it was suggested that the ketones were formed by dehydrogenation of the acid on α- and β-carbon followed by decarboxylation. In general, the process progressed as follows: saturated fatty acid, α- β-unsaturated fatty acid, β-hydroxy fatty acid, β-keto fatty acid, and methyl ketone. Considerable methyl ketones have been isolated from blue cheese, however, in this case these decomposition materials were part of the distinct flavor of this type cheese

(Patton—*J. Dairy Sci. 33,* 680). In one series of tests by Zollikofer & Fuchs (*Proc. 12th Internat'l. Dairy Congr. 2,* 634) on the butter fat hydrolyzing action of nine microorganisms the hydrolysis varied from 0.4 to 8.7%. Various organisms liberated various mixtures of fatty acids from the butter fat.

Burgoyne & Thomas (*J. Soc. Chem. Ind. 68,* 300), as part of a study on decomposition of palm kernel oil by mold, determined the hygroscopic equilibra between methyl bromide gas and palm kernels, jute sacking contaminated with palm kernel fat, and uncontaminated sacking of the same type. The methyl bromide gas was used as a sterilizing agent. Only jute bags absorbed moisture more readily above 71% humidity and were more prone to microorganism attack than uncontaminated bags.

A method of preservation of suet comprised immersion in a solution of acetic acid and sodium acetate in respective concentrations of 10.5 ml. and 12.3 g. per liter (Francois & Sergent—*Ann. nutrition et aliment. 3,* 441). The preservation was further improved by adding 5 g. of potassium dichromate to the solution (Francois & Sergent—*Bull. mens. ITERG 4,* 151).

DECOMPOSITION BY ELECTRICAL DISCHARGE. Menzel *et al.* (*Chem. Ber. 82,* 418) recorded the reaction taking place on exposure of fatty materials to electric discharges. Stearic acid was converted to an unsaturated acid, and some moisture was split off and this corresponded to a decrease in the acid number. Methyl oleate subjected to electric-glow discharges in hydrogen atmosphere was hydrogenated, and some acidity developed. In nitrogen atmosphere the change in iodine value was less but more acidity developed. Splitting, condensation, and polymerization were also evident in the processes.

Estimation of Monocarbonyl Compounds in Rancid Foods[1]

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A METHOD has been developed for the determination of monocarbonyl compounds in the benzene-soluble fraction of rancid foods. The determination involves the formation of the 2,4-dinitrophenylhydrazones of monocarbonyl compounds in benzene solution, removal of unreacted 2,4-dinitrophenylhydrazine reagent and any hydrazones of dicarbonyl compounds with alumina, and colorimetric measurement of the remaining hydrazones in alkaline solution.

Since monocarbonyl compounds (aldehydes) follow as secondary reaction products of the hydroperoxides initially formed in fat oxidative deterioration and contribute greatly to the off odors and flavors in rancid food (11, 17), there is, of course, a definite need for a convenient and reliable method for the estimation of these compounds. At the low levels of aldehydes found in rancid fats, previously available methods, such as differential titrations with sodium bisulfite (5) or hydroxylamine (6), or quantitative modifications of the Schiff test (2, 8, 13, 18), have failed to yield consistent results and occasionally have given high results with fresh foods.

2,4-Dinitrophenylhydrazine has been used in aqueous solution for the gravimetric determination of aldehydes and ketones (3) and in the colorimetric determination of dicarbonyl compounds (9, 10). Chromatographic separations of various aldehydes and ketones as their 2,4-dinitrophenylhydrazones have been reported (1, 7, 12, 14, 16, 19). No account of the use of this compound as a colorimetric reagent for simple aldehydes and ketones has been noted in the literature. The method as described below is applicable to many aldehydes, and particularly to the aliphatic, saturated or unsaturated, aldehydes which arise in fat deterioration.

Reagents and Apparatus.[3] a) Dissolve 500 mg. of 2,4-dinitrophenylhydrazine in 1 liter of benzene by heating gently and shaking occasionally. b) Dissolve 60 g. of potassium hydroxide in 1 liter of 99% aldehyde-free ethyl alcohol (15) and filter through a fritted-glass funnel or glass wool. The alcohol may be used without purification if the reagent is made up fresh daily. c) Activated alumina, F-20 grade, 80-200 mesh supplied by the Aluminum Ore Company, East St. Louis, Ill., was used throughout this work. It is too active as received and must be modified by mixing with 15% of fully hydrated material prepared by exposing the alumina in a thin layer to water vapor in a vacuum desiccator. Allow the mixed alumina to stand in a closed container several hours before using. If kept in an air-tight container, this mixed alumina is stable indefinitely. d) Chromatograph tubes, 7 mm. inside diameter, 110 mm. long, with a short piece of 1-mm. capillary tubing sealed to the lower end and a 110-mm. length of 10-mm. tubing to the upper end. Insert a small loose plug of glass wool in the upper end of the capillary section to retain the alumina column. e) Twenty-five-ml. glass-stoppered graduated cylinders. f) Photoelectric colorimeter for measurements at 435 mμ. A Coleman photoelectric colorimeter was used in these studies.

Method of Analysis. Prepare the chromatograph column by pouring in alumina to a depth of 3 cm. Pipette in 10 ml. of the dinitrophenylhydrazine reagent and immediately sprinkle in sufficient additional alumina to make the total depth 10 to 11 cm. After all of the reagent solution has entered the top of the alumina column, add 5 ml. of fresh benzene. When all of this has entered the column, add the sample (containing the equivalent of 0.05-0.50 micromole of aldehyde) dissolved in 3-4 ml. of benzene and begin collection of the solution issuing from the column in

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[3] Use of commercial names does not imply recommendation by the Department of Agriculture over other products of similar nature not mentioned.