

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

## REPORT OF THE LITERATURE REVIEW COMMITTEE\*

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### Introduction

**STATISTICS AND OUTLOOK.** The immediately following information is compiled from 1952 issues and the first 1953 issue of the publication "Fats and Oils Situation" which is issued by the Bureau of Agricultural Economics of the United States Department of Agriculture. In these the data are generally recorded in crop years; thus the records of the 1951-52 year represent oil processed the 12 months beginning October 1.

The latest data available on production has the following figures characterized as data for year 1950-1, preliminary estimate for 1951-2, and a forecast for 1952-3 based on crop estimates as made on Dec. 1, 1952:

	Year beginning		
	Oct. 1, 1950	Oct. 1, 1951	Oct. 1, 1952
Animal fats (includes butter in actual weight).....	4,441	4,513	4,280
Edible vegetable oils (includes oil equivalent of seeds exported).....	4,408	4,682	4,770
Inedible fats (or soap fats and oils).....	2,505	2,389	2,375
Drying oils.....	899	631	620
Others (neats-foot oil, wool grease, fish liver oils, etc.).....	27	24	25
Grand Total.....	12,281	12,240	12,070

Although the forecast for 1952-3 is lower than the production of the previous two years, supplies will be larger because stocks at the beginning of the year were up.

The 1952-3 domestic disappearance of fats for food uses is expected to total about the same as the 43.5 lbs. per person in the last year. People eat about as much more as natural components of food.

The index number of wholesale prices of fats and oils except butter in January, 1953, has risen five percent since October 1, 1952, and is slightly less than a year ago. In the 1951-2 crop year, prices declined sharply from September, 1951, through April, 1952. Since then prices were rather stable, except that lard declined. Without this program prices of edible oils would now be much lower. Butter prices declined to governmental support levels and the government purchased 41 million pounds to maintain a price of 67.75 cents per pound. Prices of lard and inedible tallow are now at very low levels because fat supplies are high and there are no governmental direct supports of prices for these fats. An increase in tallow production and decrease in lard production is anticipated in 1952-3.

The statistics and outlook on soaps involve their status with respect to competition from synthetic detergents (syndets) which are principally non-fat derivatives. The situation in this field is well analyzed by Snell (*Chem. Eng. News* 31, 38). The data that he records show that production of solid soap and syndets for 1951 were, respectively, 2444 and 1434 million pounds (total 3878) and the comparable figures estimated for 1952 from reports for the first nine months are 2295 and 1717 (total 4012). He believes advance of syndets continues because of improvements through research; whereas correspondingly relatively little is done to improve soaps. The status of soap versus syndet business is depicted with an unfavorable future for soap in an editorial report on markets (Anon.—*Chem. Week* 71, No. 24, 62). A review of government controls which affect soap and syndet prices is prepared by Carey (*Soap Sanit. Chemicals* 28, No. 3, 37). Information on production, sales, and household types of syndets is recorded by Neidig and Hersberger (*Chem. Eng. News* 30, 3610).

Some foreign communications containing economic information are of general interest in the fat and oil business. An annual review for 1951 on oilseeds, oils, oilcakes, and related commodities published by Frank Fehr & Co., London, England, contains information on world production, consumption, interchange, export balances, competition, etc., according to individual geographical and national areas. The effects of financial conditions, tariffs, etc., on international trade are discussed. Gehrke (*Fette u. Seifen* 54, 28) and a German Study Commission (*Ibid.* 406) compare the economy and processing meth-

ods of the American and German industries. The fat and oil supplies of France for the year 1950 are reviewed by Ferrara (*Olearia* 5, 293). Jordan (*Chem. & Ind.* 1952, 92, 1208) in lecturing on drying oils discusses interchangeability, substitution of materials of resinous character, and value of substitutes in indicating that the era of need of specific oils for drying purposes may end.

General papers of economic interest are on olive oil culture in Spain (Rudorf—*Fette u. Seifen* 54, 1), china wood oil in the French Union (Worms—*Oleagineux* 6, 495), stillingia oil (Takeshita—*J. Chem. Soc. Japan., Ind. Chem. Sect.* 53, 367), fish oils of Cambodia (Lafont—*Oleagineux* 6, 286), and the soybeans produced in the Miyagi Prefecture of Japan (Shibasaki *et al.*—*North-Eastern Agr. Japan* 4, No. 5-6, 2 pp.; *J. Soc. Brewing, Japan* 47K, 15, 16). A series of pamphlets by Markley (*Ministerio Agr. Granaderia, Nos. 102 through 110*) describe several common oils and discuss their possible culture in Paraguay. An investigation on the suitability of safflower oil for edible purposes indicates that it is not as suitable for this purpose as many other domestically produced edible oils (Soltoft & Dollear—*Oil Mill Gaz.* 57, No. 4, 13).

Communications fostering use of new sources of oils are on rice bran oil (Sumiki *et al.*—*J. Agr. Chem. Soc. Japan* 22, 9, 10, 39; Kawai & Hayakawa—*J. Nippon Oil Technol. Soc.* 4, 6, 11, 37; Takesita *et al.*—*Ibid.* 17; Tsuchiya & Kaneko—*Repts. Govt. Chem. Ind. Res. Inst. Tokyo* 45, 252, 307; Lee—*Food Eng.* 27, No. 12, 98; anon.—*Chem. Eng.* 59, No. 10, 222), silk-worm chrysalis (Nuruzhan—*Kimya ve Sanayi* 26-27, 339), *Herrania* seed of West Africa (MacLean—*Nature* 169, 589), jojoba oil (Mirov—*Econ. Botany* 6, 41), palm fruits of Surinam

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(Spoon & Sessler—*Olien Vetten en Oliezaden* 34, No. 3, 25; No. 4, 41), pisa fat as a coconut substitute (Kane—*Indian Soap J. 17*, 72), industrial utilization of tobacco seed oil (Martinez et al.—*Inform. quim. anal. Madrid* 6, 5), fats from fruits and trees of German forests (Wienhaus—*Forschungen u. Fortschr.* 24, 4), oils of the livers of fresh water fish (Cardoso—*Mem. inst. Oswaldo Cruz* 47, 557), vitamin A content of the liver of whales of Antarctic (Mrochkov—*Rybnoe Khoz* 27, No. 3, 54), liver oils of commercially useful fish in the Murmansk region (Sobolev—*Ibid.* No. 4, 54), viscera oil of the sperm whale (Takaoka et al.—*J. Agr. Chem. Soc. Japan* 20, 235) and head oil of dolphin (*Ibid.* 21, 27).

General communications giving progress of the technology are on trends in processing oils in United States (Goss—*J. Am. Oil Chemists' Soc.* 29, 253), processing fats and oils in the United Kingdom (Williams—*Chemistry & Industry* 39, 948), solvent extraction of vegetable oils in India (Ramaswamy et al.—*Indian Soap J. 17*, 24), methods used for extracting oils in Belgian Congo, Portuguese Angola, and French Equatorial Africa (Lelogeais—*Oleagineux* 6, 597), recent development in the fish oil industry (Lovern—*Chemistry & Industry* 1952, 38), fish oil industry in Norway (Domart—*Oleagineux* 6, 351), fat processing industry of Nordrhein Westfalen (Anon.—*Fette u. Seifen* 54, 566), processing oiticica oils for the paint field (Bush—*Paint, Oil & Chem. Rev.* 114, No. 22, 14), castor oil processing (Sfiras—*Oleagineux* 7, 135, 221).

General information is presented on the organization of research in the fat and oil field together with some new results of research in France (Philippart—*Bull. mens ITERG* 5, 531), in Australia (Winter—*Fette u. Seifen* 53, 516), in New Zealand (Shorland—*Ibid.* 54, 521), in Spain (Kaufmann—*Ibid.* 592), and in the United States (Baldwin—*Ibid.* 53, 509).

**FAT SUBSTITUTES AND MICROBIOLOGICAL FATS AND OILS.** A small number of communications are on fatty acid synthesis by paraffin oxidation. The subject is reviewed by Prückner (*Chem. Technik* 4, 193). New processes for such oxidation deal with oxidation with potassium permanganate (Anders—*Fette u. Seifen* 54, 77) and with air in the presence of tin oxide (Eguchi et al.—*Japan 172,994* [46]). Methods of converting the products to detergents are discussed by Trinchieri (*Tincoria* 48, 339).

General known substitutions in the fat field are the use of tall oil acids, petroleum and coal by-products in the detergent industry, and petroleum oils for metal cutting and textile lubrication. These uses are treated in other sections of this review. The production of drying oil substitutes from petroleum products seems to be advancing at a considerable rate. This is evident from the number of patents on the subject that appear during the period under review (Diamond Alkali Co.—*U. S.* 2,587,588; Pan Am. Refining Co.—*U. S.* 2,569,595, 2,575,718, 2,588,639; Phillips Petroleum Co.—*U. S.* 2,588,826; Standard Oil Development Co.—*U. S.* 2,548,503, 2,569,383; Universal Oil Products Co.—*U. S.* 2,565, 654, 2,578,214, 2,579,007, 2,580,184, 2,582,434, 2,590,923, 2,602,820, 2,622,108-9). Petroleum products suitable for fat liquoring leather are described by Liggett et al. (*J. Am. Leather Chemists' Assoc.* 47, 765), and Arbutov & Veretennikov (*Legkaya Prom.* 11, No. 5, 38).

A drying oil is prepared from pine root oil by a polymerization process (Yagi & Inamura—*Japan 181,249* [49], Sakura & Muromoto—*Japan 181,123* [49]). Fatty acids extracted from cork are suitable for manufacture of lubricants, detergents, and wax substitutes (Dupont & Guillemonat—*U. S.* 2,571,221).

The investigations on biosynthesis of fats are on yields obtained with *Rhodotorula gracilis* (Kleinzeller et al.—*Chem. Listy* 46, 470), with fungus *Mucor mucedo* (Blinc—*Slovenska Akad. Znanosti Umetnosti, Mat., Fiz., Tehn., Vede, Class III, Ser. A, Razprave III*, 41, 57), and fungus of the *Styansus* species (*Ibid.* 43). Barker (*Harvey Lectures Ser. 45*, 242) reports that *Clostridium kluyveri* can convert fatty acids up to C<sub>6</sub> to longer acids by adding C<sub>2</sub> units to the chain.

**NEW COMPREHENSIVE LITERATURE.** During the period under review the following books of the fat and oil field have come to the reviewer's attention:

Marine Oils. Those of Canada. By B. E. Bailey, N. M. Carter, and L. A. Swain. Fisheries Res. Board Can. Bull. No. 89, 413 pp.

Properties of Principal Fats, Fatty Oils, Waxes, Fatty Acids, and Their Salts. By M. P. Doss. Texas Co., New York, 244 pp.

Hydrogenation of Fatty Oils. By H. I. Waterman. Elsevier Pub. Co., Houston, Texas, 254 pp.

Die Ole und Fette in Wirtschaft und Technik. By P. F. Rickmers. Verlag H. Ziolkowsky, Aurburg, Germany. 272 pp.

Die Fette und Ole. By Karl Braun. Walter De Gruyter & Co., Berlin. 145 pp.

Maleic Anhydride Derivatives. Reactions of the Double Bond. By L. H. Flett and H. W. Gardner. John Wiley & Sons. New York City. 269 pp.

Die Fettstoffe des Gerbers. By H. Gnam. Wissenschaftliche Verlag, Stuttgart, Germany. 248 pp.

Abstract Bibliography on Chemistry and Technology of Tung Products. By R. W. Planck, F. C. Pack, and D. B. Skau. U. S. Dept. Agr., Bur. Agr. and Ind. Chem. AIC 317. Vol. I 235 pp. Vol. II 236-466.

Detergents. What They Are and What They Do. By D. Price. Chemical Pub. Co. Brooklyn, N. Y. 159 pp.

Organische und anorganische Wash-, Bleich-, und Reinigungsmittel. By C. Lüttgen. Chemie & Tech., Heidelberg, Ger. 365 pp.

Encyclopedia of surface Active Agents. By J. P. Sisley and P. J. Wood. Chem. Publ. Co., New York. 540 pp.

Les detergifs. By W. Kopaczewski. Masson & Cie, Paris, France. 210 pp.

Die Seife und ihre Herstellung. By T. Hempel. Verlag Chem. Ind., Aurburg, Ger. 706 pp.

Seifen-Industrie Kalender. By H. Heller. Klasing & Co., Berlin, Ger. 252 pp.

Die Technologie der Seifenpulver und pulverförmigen Waschmittel. By T. Klug. Verlag Herbert Cram, Berlin, Ger. 58 pp.

Modern Textile Auxiliaries. Edited by A. J. Hall. Thomas Skinner & Co., London.

The two following communications appear as journal articles but are available as separates in booklet form:

Lectures of the 1952 Short Course on Soap and Synthetic Detergents. Various authors—*J. Am. Oil Chemists' Soc.* 29, 481-590. (These lectures taken together comprehensively describe the American soap and detergent industry.)

Synthetic Detergents Up-to-Date II. By John W. McCutcheon—*Soap Sanit. Chemicals* 28, No. 7, 40; No. 8, 52; No. 9, 52; No. 10, 50. (Contains a table of 1,005 trade name detergents, their manufacture, class, formula, etc.)

A new journal entitled "Journal of Detergents" is published by L. Zakarias, Bristol, England.

The previous review of this series is published in the *J. Am. Oil Chemists' Soc.* of last year, pages beginning 136 and 180. Other general reviews are on recent advances in the chemistry and technology of fats (Child—*Soap [India]* 2, No. 3, '9), recent advances in the vegetable oil industry (Paleni—*Riv. ingegneria* 1, 885, 1003), review on fats, fatty oils, and detergents (Williams & Cocks—*Repts. Progress of Applied Chem.* 36, 407), future for the fat industry (Sisley—*Bull. mens. ITERG* 6, 165), animal fats as raw materials (Stingley—*Inst. Spokesman* 16, 8), animal fats (Lawler—*Food Eng.* 24, No. 9, 134), fifty years of fat hardening (Hefe—*Chem.-Ztg.* 76, 769), fats as a source of chemicals (Harwood—*Chem. Eng. News* 30, 1282), chemistry of fatty acids (Mehta—*Indian Soap J.* 17, 201), and chemistry of lipids (Deuel Jr. & Alfin-Slater—*Ann. Rev. Biochem.* 21, 109).

## Production Processing

**ANIMAL AND FISH FATS.** A new extraction system for fats developed by Chayen of British Glues and Chemicals Limited is the subject of widest publicity among new processes in the fat and oil industry (*Chem. Eng. News* 30, 5266; *Chem. & Process Eng.* 33, 659; *Chem. Processing* 16, No. 1, 38; *Chem. Week* 71, No. 25, 42; *Food Manuf.* 27, 487; *Nature* 170, 881). In this, the raw material, including bones, is crushed, ground, subjected to impulses in the presence of water so as to separate fat in floatable state, and separations of solids, aqueous phase, and fat phase are made from cold and hot water successively. The complete equipment permits continuous operation and includes separators, centrifuges, driers, etc. Four such plants for degreasing bones for glue manufacture are already established. Low temperature rendering to produce better grades of animal fats is also the aim in other processes in which the tissues are

ground to fluid masses, warmed, screened, and separated by centrifuge or other means (Anon.—*Meat* 37, No. 1, 26; Morse *et al.*—*Food Eng.* 24, No. 11, 72; Swift & Hankens—*Food Tech.* 6, 161; *Food Eng.* 24, No. 7, 178). A system by Pavia (*U. S.* 2,616,910) is similar except that the comminuted tissue is dried before separation of the fat. Gutman (*Myasnaya Ind. S.S.S.R.* 23, No. 1, 23) recommends vacuum methods to obtain better lard. Fundamental data such as speed of rendering as related to particle size, temperature, and physical properties of fat are recorded by Lapshin (*Ibid.* No. 3, 70). A rendering process for general slaughterhouse waste comprises treatment with ammonia and ammonium diacid phosphate under pressure for peptonization and separation into aqueous and fat phases (Haneschka & Helinger—*Austrian* 159,739). The aim in this case is to produce an edible fat and proteins suitable as cattle food.

Other rendering information deals with production of fish and marine animal oils. Expellers, vibratory screens, vacuum driers, coagulating chambers, tube driers, and solvent extractors as found on new whale factory ships are reviewed (Anon.—*Internat. Chem. Eng.* 33, 28). New improvements on a continuous closed system by Fladmark (*U. S.* 2,565,173; 2,590,303) pertain to separation of the oil and economy of steam used in drying the protein solids. Most convenient use of centrifuges is important in a new system by Davis (*U. S.* 2,614,110). The comminuted cooked material is first centrifugally separated into relatively dry solids and liquid, and a second set of centrifuges separates liquid into oily and aqueous portions.

With fish liver oil, the dominant aim is to produce an oil of high vitamin A potency. In two descriptions (Suzuji—*Japan* 37 [51]; Shimizu & Yamada, *Bull. Research Inst. Food Sci. Kyoto Univ.* No. 5, 29) new livers are immediately treated with alkali. In transit and during storage the alkali acts as both a preservative and as a digesting agent which releases the oil. For the same purpose, Rübénberg (*Pharm. Zentralhalle* 91, 111) immediately freezes the livers to  $-15$  to  $-18^{\circ}$  in containers filled with carbon dioxide. These livers when minced and thawed in water can be centrifuged to produce good quality vitamin oil. Koike (*Japan* 1117 [51]) claims that comminuted liver when heated with high-frequency current releases vitamin A fractions of different potency depending on the current being used. The method is patented as a simple method for obtaining fractions of high vitamin A content.

In dairy literature some items on butter seem pertinent to this review. In an assessment of the Fritz continuous butter-making machine for Canadian use, the process is considered unsuitable because it is not designed for making salted butter which is demanded in the Canadian market; and it is extremely difficult to control moisture content at or below the 16% legal requirement (Pearce *et al.*—*Can. J. Tech.* 30, 167). King (*Meddelande* No. 30) observes the structural changes of alpha butter and discusses these with regard to influence on consistency. He shows that phase inversion is not complete in this product and some air bubbles may be present. A survey of copper content, based on fat, in butter produced by continuous processes indicates the butter contains less than the original cream, and much less than butter from batch systems (Miller & Tracy—*J. Dairy Sci.* 35, 292).

A batch churn invented by Thorstenson—Rydberg (*U. S.* 2,617,732) comprises a rotating tilting container equipped with jacket for a heating or cooling agent. The cream is cultured to develop acidity at warm temperature; the drum is then cooled, tilted, and rotated in order to churn the butter. In a discussion on chemical acidification and flavoring of butter, Petersen (*Fette u. Seifen* 54, 280) emphasizes that natural butter is to be preferred both as to flavor and nutritive value. He (*Ibid.* 471) also points out that in unsalted butters of pH less than 5.0, the souring is caused by acetic acid bacteria. In a procedure for manufacturing butter from whey, by Thomsen (*Can. Dairy and Ice Cream J.* 30, No. 10, 36), methods for handling and skimming whey, handling whey cream, and churning are discussed. The keeping quality of the butter is poorer than that of natural butter.

In two new reports on preparation of butter oil, the oil is prepared directly from cream with the aid of de-emulsification agents to release the fat from the emulsion (Stine & Patton—*J. Dairy Sci.* 35, 655; *U. S.* 2,617,731).

**VEGETABLE FATS.** Some seed storage work is based on fat deterioration as a criterion of storage damage. Working with corn, Bottomley *et al.* (*Cereal Chem.* 29, 53) note that at high moisture content certain molds may reduce oxygen to zero and induce over 30% carbon dioxide concentration in the bins, whereas free fatty acidity of the oil may remain constant. The work indicates that hermetic sealing does not completely

prevent deterioration of the seeds nor can the amount of damage to all constituents of seeds be based on fat decomposition alone. Work on rice bran by Loeb and Mayne (*Ibid.* 163) shows that heating (autoclaving) and drying stabilize the bran against deterioration of the oil therein during storage. Hasko's (*Mészgazdasag es Ipar* 3, No. 11/12, 6) work on deterioration of oil in grape seed shows that the process is quite rapid even when the seeds are separated from the fermented or distilled mare before storage. Patents issued to Altshul *et al.* (*U. S.* 2,571,095, 2,584,972) on preventing deterioration of oil in stored seeds pertain to spraying the seed with a solution of propylene glycol dipropionate and with 1,3-dimethyl-4,6-bis (chloromethyl) benzene or solutions of liquid halohydrin such as ethylene chlorohydrin, propylene chlorohydrin, and related compounds.

Most of the vegetable oil extraction literature pertains to solvent systems. A laboratory apparatus for determination of the rate of extraction of oil is modified by Clark & Wamble (*J. Am. Oil Chemists' Soc.* 29, 56) to render it applicable to many varieties of seeds. Two communications are on evaluations of extraction rate measurements. Smith (*Ibid.* 421) uses published data on extraction of six commercial oil seeds for development of empirical equations that correlate temperature and viscosities with diffusivity of oil and solvent. Schoenemann & Voeste's (*Fette u. Seifen* 54, 385) determinations are on extraction rates as related to thickness of soybean flakes and other factors, and are graphically presented. Hexane solutions containing five percent of a lower alcohol are more rapid and complete oil extractants than *n*-hexane alone (Ayers & Scott—*J. Am. Oil Chemists' Soc.* 29, 213). In this work refining loss is not affected by extraction solvent containing a lower alcohol. Graphs showing density, gravity, viscosity, and composition relationships in English units for hexane miscellas of cottonseed and peanut oils are recorded by Decossas *et al.* (*U. S. Dept. Agr. AIC* 292 and *Ibid.* AIC 304). A quick control method for determining fines in miscella is based on centrifuging a sample and measuring the volume of sediment (Graei, Jr. *et al.*—*J. Am. Oil Chemists' Soc.* 29, 71). The information reviewed in this paragraph is pertinent to the development of the engineering aspects of extraction.

Other fundamental work on vegetable oil extraction pertains to the effect of processing on the quality of the products. In investigating the effect of various stages in the solvent extraction of soybean oil, Burnet, Jr. & Arnold (*Ibid.* 619) find that the moist heating step reduces the enzyme systems of the meals to a point compatible with satisfactory livestock feed, prior to attaining maximum glutelin protein. Water dispersibility of protein, glutelin, and residual protein are used as criteria because other work has shown that interpretations from these agree with poultry feeding tests. In similar work, Belter & Smith (*Ibid.* 170) show that major denaturation of protein occurs in the final meal treating steps; that is in deodorization and toasting, or "Schneekens" desolventizing. These data are pertinent to production of proteins for industrial uses. Similarly, Dangoumau *et al.* (*Bull. mens. ITERG* 5, 306) from work on soybeans and rapeseed show that damage as measured by solubility of nitrogen substances, glutelins, is greater with moist heating than with dry heating of the meals. Work of the same type by Dunning *et al.* (*J. Am. Oil Chemists' Soc.* 29, 153, 627) is for the purpose of ascertaining the maximum amount of precooking compatible with production of good quality cottonseed meal. The effect of this heating is insignificant compared to the effect of the final stages; expelling and desolventization. These data are used for modifying the seed cooking and speed of revolution of expeller shaft in order to increase output within practice compatible with production of good quality oil and meal. Process heating affects the spectral properties of cottonseed oils produced (O'Connor *et al.*—*Ibid.* 220). Cold press oils show maximum bands at 368 and 374  $\mu$  due to gossypol, and bands at 432, 455, and 480  $\mu$  due to carotenoids. In hot pressed oils, bands at 232 and 268  $\mu$  are greater than those of cold pressed oils, and bands at 383 and 400  $\mu$  arise from gossypol-like pigments. A patented treatment for cottonseed to reduce the toxicity of the ultimate meal comprises treatment with water-soluble organic solvents to liberate gossypol from the glands and heating sufficiently to remove the solvent and convert the gossypol to a non-toxic form (Rice—*U. S.* 2,615,808). For improving the extraction of phospholipides with the oil, the seeds are steamed and extracted at about 10% moisture content (Desnuelle *et al.*—*Oleagineux* 6, 264).

Several new seed treatment methods are for the purpose of gaining certain advantages during subsequent extraction. Singer & Deobald (*U. S.* 2,609,299) crack soybeans to form grits, separate hulls, sort and re-crack the larger grits and then adjust the moisture content in preparation for flaking. The

resulting flakes have high tensile strength and resistance to breakage during extraction. Williamson (*U. S. 2,595,825*) pre-wets flakes with a mixture of hydrocarbon and alcohol solvents. The flakes swell and permit further reduction of thickness with retention of percolation rate and acceleration of oil reduction. Treatment of the comminuted vegetable matter with cation-exchange resin is said to weaken cells and make extraction easier and more complete (Erikson—*U. S. 2,589,238*). Clark & Wamble—*Texas Expt. Sta. Bull. No. 125, 77* test the feasibility of extraction of whole comminuted cottonseed and separating the residue meal into linters, hulls, and protein. The process is feasible with seeds from which first cut linters are removed. Pominski *et al.* (*J. Am. Oil Chemists' Soc. 29, 48*) show that skins can be removed from good grade peanuts by treatment with water, drying at 120-150°F. to 4.5% moisture, and blanching in a standard split-nut peanut blancher. Proteins prepared in the processing of such peanuts are light in color. An extraction plant for production of peanut oil and a meal suitable for manufacture of "Ardil" fiber provides means for skinning and the processing is adjusted to inhibit denaturation of the proteins (Anon.—*Oil Mill Gaz. 56, No. 12, 13*). Treatment of decorticated castor beans at 130°F. in the presence of added moisture converts the carbohydrate-protein part of the meats to a tough, tenacious, rubbery mass from which oil may be readily removed (Dunning—*U. S. 2,618,643*).

In a comparison of solvents for extraction of cottonseed, commercial grade hexane is considered with more favor than benzene, ether, acetone, or butanone (Eaves *et al.*—*J. Am. Oil Chemists' Soc. 29, 88*). In general, however, oil yields are about the same, and improved quality of oil is obtained by choice of solvent at the expense of meal quality. Removal of gossypol from cottonseed during solvent extraction procedures is best with butanone containing 10% water and is least with chlorinated hydrocarbon solvents among many solvents tested (Dechary *et al.*—*Ibid.* 339). An investigation of solvents by Mayolle (*Bull. mens. ITERG 6, 96*) indicates alcohol is suitable for extraction of peanut oil, but with rapeseed the extracted oil has a bad odor. Rates of extraction determinations in this work place the solvents in the following order of decreasing efficiency: trichloroethylene, carbon disulfide, hexane, and methyl ethyl ketone. Francois & Khangy (*Bull. mens. ITERG 6, 331*) describe equipment and methods for most efficient extraction of linseed with alcohol but finds that alcohol is not as exhaustive an extractant as hexane or trichloroethylene. Likewise Harris & Hayward (*Bull. Agr. Mech. Coll. Texas 6, No. 9*) tell how to extract cottonseed oil with isopropanol. These authors find the alcohol more efficient than hexane. Continuous extraction with alcohol is described in a new patent (Beckel—*U. S. 2,584,108*). In another patent (Crawford—*U. S. 2,596,010*) it is claimed that  $C_6$  isoparaffin solvents extract more oil, with better quality of both oil and vegetable meal, than is obtainable with  $n$ -hexane. Another extraction patent (Weizmann—*Austrian 164,021*) pertains to use of mixtures of chlorinated hydrocarbons as the solvent. A new extraction process designed by Hunn *et al.* (*U. S. 2,605,271-2*) comprises first wetting the vegetable material with a polar organic solvent and then extracting with a nonpolar solvent. The polar solvent, on becoming immiscible with the miscella separates in a layer containing both the fines and the solid particles. The new patents on extraction of castor oil deal with use of aliphatic hydrocarbon solvent extraction and with cooling the miscella to separate the oil from the major portion of the solvent (Colbeth—*U. S. 2,616,907*; Colbeth & Carter—*U. S. 2,616,998-9*).

Improved equipment for solvent extraction is described. Mechanical improvements are described for the Kennedy apparatus in which the charge is swept through extraction stages countercurrent to solvent (Kennedy—*U. S. 2,585,473*). In a system invented by Iguchi (*Japan 172,096* [1946]) better extraction is induced by grinding the charge with the solvent. A like claim is made for treatment with high frequency sound waves during contact of solvent and charge (Kamibayashi—*Japan 1175* [1950]). The Bottaro extractor which is based on counterflow in pipes of comparatively small diameter is described by Paleni (*Fette u. Seifen 53, 385*). The new improvements in the Bonotto system (Bonotto—*U. S. 2,567,179, 2,594,117, 2,582,675, 2,594,117*) are upon flaking only the meats of cottonseed and reintroducing whole hulls to aid the percolation of solvent; on addition of settling tanks for collection of miscella-free fines; and on removing solvent from meal in a dust-free manner by heating first with superheated solvent vapors and then with steam. On several new extraction systems the reviewer has the references but no details (Koyama—*Japan 857* [1950], Umi *et al.*—*Japan 856* [1950] Koyanagi—*Japan 1310* [1950], Tataru—*Japan 1538* [1950], Takemoto &

Igarashi—*Japan 3728* [1950], Bregman—*Brit. 667,262*, Jojot—*Fr. 963,658*).

Some communications treat a limited part of the solvent extraction process. A lecture by Greenfield (*Proc. 6th Ind. Waste Conf. Purdue Univ. Eng. Bull. Ext. Ser. 76, 141*) is on safe handling of hexane in soybean processing. Stripping of solvent from soybean oil is said to be economical in a new stripping column packed with spaced spiral-weave metallic cloth (Arnold & Ingebo—*J. Am. Oil Chemists' Soc. 29, 23*). Reducing the flow rate of miscella in special channels after leaving the extraction zone permits the suspended fines and flakes to settle out (Smith & Weigel—*U. S. 2,567,450*). Bonotto (*U. S. 2,608,565*), in a novel manner, makes use of prepared oil-bearing material for removal of suspended particles by filtration from the miscella. Desolventizing meals according to a patent issued to Leslie (*U. S. 2,571,143*) is accomplished by heating with superheated solvent vapors followed by steaming. For the unusually fine meal of the fractional method of processing cottonseed a special four-stage continuous drier is designed (Graci Jr. *et al.*—*J. Am. Oil Chemists' Soc. 29, 41*). Other newly designed parts of solvent equipment are a scrubber for separating solvent from the vapors leaving the meal driers (Anderson—*U. S. 2,609,186*), an absorption tower for recovering fatty acids from waste gases issuing from an oil extractor (Drew—*U. S. 2,585,638*), and mechanical details for recirculation of both fresh and partially saturated solvent during extraction (Manning—*Brit. 670,958*).

The seven lectures (*Oil Mill Gaz. 57, No. 1*) given at the Tri-State Oil Mill Superintendents' Assoc. Meeting form a comprehensive monograph on our present cottonseed processing industry. The report of the Cottonseed Products Research Laboratory (Wamble—*Ibid.* 57, No. 2, 15) contains operating and plant cost data for hydraulic, screwpress, prepress, and direct solvent extraction plants for cottonseed. Similar information is developed for oil recovery from okra seed (Holbrook & Wamble—*Texas Eng. Expt. Sta. Research Rept. No. 29, 11 pp.*).

Some unconventional processes are suggested. Sodergreen (*U. S. 2,583,022*) extracts coconut oil by steaming the material to sterilize and to loosen meats from shell. The meats are dried and triturated to a slurry with five percent water and the oil is separated by means of presses. Abadal-Duran & Pares-Canals (*Span. 193,622*) process palm fruits by boiling, screening out the kernels, and expressing the palm oil from the pulp. A new process for various vegetable materials comprises emulsifying the oil in aqueous solution of ammonium hydroxide, ammonium carbonate, or ethanalamines, separating the emulsion, and breaking this emulsion to liberate the oil (Darling & Yelland—*U. S. 2,606,916*).

**BY-PRODUCT OILS: TALL OIL, WOOL OIL, ETC.** Tall oil processing involves extraction of waste sulfite lye skimmings, purification of these to tall oil, and separation of this into resin and fatty constituents. Khudovekov & Kartseva (*Bumazh. Prom. 25, No. 2, 30*) show that recovery from the pulp waste by an air flotation process is more efficient than by settling or by heat treatment processes.

Distillation processes for segregating constituents of tall oil are described by Tähtinen (*Suomen Kemistilehti 24, 13*) and by Sandermann (*Holz Roh- u. Werkstoff 9, 378*). An entirely new method of fractionation of the oil depends on differences in the density produced by a temperature gradient (Jones & Foreman—*Ind. Eng. Chem. 44, 2249*). Thus, the fatty acids of tall oil between parallel vertical surfaces, one hot and the other cool, tend to concentrate at the top and rosin acids, sterols, and alcohols concentrate at the bottom.

A continuous machine for extraction of wool grease is based on drawing a uniform thickness of wool through solvents, rollers, and heating units (Drum & Hopkins—*U. S. 2,593,422*). The use of a special nitrated kerosene for extraction of the wool grease is patented (Fiala—*Brit. 675,660*). Treatment of the chlorinated hydrocarbon miscella of wool extraction with anhydrous triethanolamine coagulates dirt and fatty acids so that they are easily separated before evaporation of the solvent (Derby—*U. S. 2,607,786*).

Fats and oils are also recovered from various other wastes. Ground silk-worm chrysalises are soaked over night in aqueous electrolyte solutions, heated to coagulate proteins, and centrifuged to separate solids, aqueous liquor, and oil (Koide—*Japan 1800* [1950]). In fat recovery from sewage skimmings, the skimmings are mixed with cracklings and rendered with heat (Fazenbaker—*U. S. 2,584,795*). Hempen pressing bags used in olive oil extraction are soaked in dilute sodium carbonate solution, and the solution is evaporated to recover the waste oil (Munoz—*Span. 193,720*). Vegetable oil tank settlings

containing meal, phosphatides, and other impurities are heated with water and settled for some days to permit recovery of an oil layer by siphoning (Durkee—*U. S.* 2,601,375). Further fatty material is recovered from the residual sludge by saponification followed by acidification to release the fatty acids. Alkali digestion followed by acidification is used also to recover fatty material from palm oil pressing waste (Morcardo-Garcia—*Span.* 19,303).

REFINING, BLEACHING, AND DEODORIZATION. Soccart (*Oleagineux* 7, 65) in a general paper on refining discusses the subject with regard to reducing the alkali refining loss due to saponification of neutral oil. Choice of alkali, reaction conditions, and phase relation are related mathematically to a "loss coefficient." Similarly Pinto (*Bol. tech. inst. agron. norte* [Belem, Brazil] No. 21, 3) relates refining cost to the acidity of the oils by means of mathematical equations and graphs.

Innovations are made in refining to gain various advantages. Degumming of soybean oil with 10% solutions of alkali phosphates before alkali refining considerably reduces losses occurring during the complete refining process (Lever Bros. & Unilever Ltd.—*Brit.* 661,703). Pretreatment of refuse palm oil with phosphoric acid and Glauber's salt permits attaining a light color in the final refined and bleached product (Babayan—*U. S.* 2,587,954). Use of alkali containing 0.005-0.01% potassium permanganate in the refining process also reduces the color of refined oil (Hirano & Kokura—*Japan* 518 [51]). In a process using sodium carbonate as the neutralizing agent, agitation due to evolved carbon dioxide during centrifuging is inhibited by running this step under pressure (Clayton—*U. S.* 2,607,788). A process for regeneration of frying oil is based on refining with a solution of mixed caustic and sodium carbonate (Kulikov—*Rybnoe Khoz.* 27, No. 5, 45). Used sunflower oil accumulated in fish canning is recovered for reuse by alternating washes with caustic and salt solutions. In the successive washes, the concentration of the caustic is decreased and that of the salt solution increased (Ivanov—*Ibid.* 25, No. 3, 16). Kroonen & Feuge (*J. Am. Oil Chemists' Soc.* 29, 65) find that "high shear," vigorous agitation, is most effective in removing acidic gossypol-like pigment from cottonseed oil in the "refining process." This process comprises mixing a small amount of caustic solution to once-refined oil and separating the soap stock. In this work, the effect of concentration of caustic, time, rate of agitation, and temperature are evaluated.

Lower alcohols are used in some alkali refining processes. For rice oil (Nojima—*Japan* 1819 [50]) and raw lanolin (A.-G. Vöslauer Kammgarn-Fabrik—*Austrian* 172,073), the fats are dissolved in benzene and petroleum ether, respectively, alkali solution and alcohol are added, and the soaps separate into the alcoholic-aqueous layer. In another process the alcohol is added to reduce the emulsion and aid in the centrifugal separation of the soap stock (Pueschal—*Ital.* 461,372).

Special technique and apparatus for refining are described. Automatic metering of oil and alkali, mixing, heating, and centrifuging for a continuous system are described by Kelly (*Paint, Oil & Color J.* 121, 1421). Special centrifuges for the process are patented (Aktiebolaget Separator—*Brit.* 673,632). For one continuous system the reference is available to the reviewer without details (Nakai—*Japan* 860 [50]). McClain (*U. S.* 2,579,946) makes use of water soluble inorganic salts as filter aid in refining so that oil can be recovered from the filter by dissolving the salt in hot water.

Distillation methods for removing free fatty acids are investigated. Obara & Oka (*J. Japan Soc. Food Nutrition* 3, 138) demonstrate that the molecular still can be used to separate various fractions of free fatty acids from highly acid rice oil and leave a residue of refined oil. Brooker & Hartman (*New Zealand J. Sci. Technol.* 33B, 488) report that, with coconut oil, the volatility of the free fatty acids and low molecular weight glycerides is not sufficiently different to permit separation by this technique. In a newly patented continuous system, distillation of free fatty acids is combined with adsorbent bleaching and deodorization stages (Mares—*U. S.* 2,594,953).

The Martinez-Moreno continuous system for removing free acids from olive oil with aqueous alcohol is described in detail by Rizzuti (*Olii minerali, grassi e saponi, colori e vernici* 24, 78). In other descriptions of like systems 70% methyl or ethyl alcohol is recommended for rice oil by Munakata *et al.* (*Japan* 2838 [50]) and 85% ethyl alcohol by Sagawa (*Japan* 179,842 [49]). Jaky (*Mezőgazdaság és Ipar* 3, No. 11/12, 8) demonstrates that for sunflower seed oil 90% alcohol is preferred for high acid oils and 96% for low acid oils. In this

work analyses of the extracts show differences in the amount of lecithin and sterols extracted with different concentrations of alcohol and from oils extracted by different processes. In one investigation on this process data on ternary systems of oleic acid, triolein, and 90 and 95% alcohols at 20° are recorded (Rigamonti *et al.*—*Chimica e industria* [Milan] 33, 619). Best results are associated with use of anhydrous or 95% methanol.

Other communications on deacidifying oils describe esterifying the free acids to form glycerides (Santelli—*Oleagineux* 6, 699); adsorption of the acids on resins (Venkatasubrahmanian & De—*Science & Culture* 17, 180); and emulsification followed by mechanical separation into purified oil and emulsion of fatty acids and impurities (Etablissements J. J. Carnaud & Forges de Basse-Indre—*Brit.* 585,566).

Various suggestions are made for bleaching oils. A gain in the economy of the process is obtained by first filtering the crude oil through partially spent adsorbent and completing bleaching with fresh adsorbent (Bailey—*U. S.* 2,618,644). A convenient method of bleaching solvent-extracted oil comprises contacting with adsorbent before evaporation of the solvent (Marmor & Moyer—*U. S.* 2,603,566). Several find it expedient to treat crude oils with acids before bleaching with adsorbents (Yamakita—*Bull. Inst. Chem. Research Kyoto Univ.* 24, 24; Tsuchiya—*Japan* 37 [50]; and Nakajima & Kosuge—*J. Nippon Oil Technol. Soc.* 4, 23). Others tell how to improve local clays for use in bleaching oils by treating the clay with inorganic acids (Alcala *et al.*—*Ion* 11, 135; Ramos & Vega—*Anales real soc. espan. fiz. y quim.* 48B, 247; and Takayasu—*J. Japan Soc. Food Nutrition* 3, 133). A comparison between some American and Japanese commercial clays indicates that the former are more efficient (Kimomura—*J. Oil Chemists' Soc. Japan* 1, 81). Bauxite treated with silica gel and calcined is suitable for decolorizing fatty oils (Heinemann—*U. S.* 2,563,650). Processes for bleaching oils and fats with oxidizing agents involve the use of persulfonic acid (Glorifet & Constolle—*Fr.* 965,495; Tsuchiya *et al.*—*Japan* 861 [50]); hydrogen peroxide (Kawai—*Japan* 2388 [50] and Nojima & Ishikawa—*Japan* 3633 [50]); chlorine dioxide (Woodward—*U. S.* 2,592,226, Woodward & Fenrich—*Chem. Eng.* 59, 174), and manganese trioxide and air (Uchida *et al.*—*Japan* 173,487 [46]).

In systems of decolorization of fats with propane, solvent and fat are counterflowed at a critical temperature to cause precipitation of color bodies and oxidized fats. Such a system for continuous decolorization of tallow is patented (Passino & Morfit—*U. S.* 2,621,198). This system is made applicable to decolorizing low grade fats and fatty acids by adding "ebony fat" to the charge (Brabets—*U. S.* 2,596,065). This ebony fat is described as a residue from a lower phase that is obtained in counter-current extraction with propane. A treatise on safety in propane fat decolorizing plants contains information on leakage detection, analysis of shop air, and explosion proof electrical fixtures (Anon.—*Soap, Sanit. Chemicals* 28, No. 4, 54).

In the literature on deodorization of fats and oils, the general papers that are merely being cited here are on the methods used in nine Indian factories (Ghose & Chakravarty—*Trans. Indian Inst. Chem. Engrs.* 3, 21), descriptions of two semi-continuous laboratory deodorizers (Allen *et al.*—*J. Am. Oil Chemists' Soc.* 29, 380), general information on deodorization (Bataille—*Bull. mens. IBERG* 6, 361), and description of a thin-film distillation apparatus for the purpose (Thompson—*U. S.* 2,611,741). Tests on deodorization of seal oil at 190-270° at 6 mm. pressure with steam indicate that optimum results with stability of the products are obtained at 210° for 30 minutes (Dugal & Cardin—*J. Fisheries Research Board Can.* 8, 189). Observations on fractions obtained by distillation of the volatile constituents removed from hardened whale oil during deodorization indicate that the most malodorous fraction contains lower aldehydes (C<sub>5</sub>-C<sub>6</sub>) and fatty acids (C<sub>7</sub>-C<sub>8</sub>) (Kuwada & Kaneyuki—*J. Oil Chemists' Soc. Japan* 1, 71). A new deodorization method comprises treatment with dilute sulfuric acid and steam, while electrolyzing (Yoshida—*Japan* 3632 [50]).

PRODUCTION OF ALCOHOLS, PHOSPHATIDES, VITAMINS, AND STEROLS. Physical characteristics and methods of preparation and utilization are discussed in two papers on fatty alcohols (Schon—*Soap, Perfumery & Cosmetics* 25, 65; Grillitsch—*Mitt. chem. Forsch. Inst. Ind. Österr.* 5, 91). One patent on equipment for production of alcohols from waxes is based on partial saponification under pressure, and in a second stage saponification is completed and alcohols are distilled off under vacuum (Paix & Cie—*Fr.* 959,651). Merley & Kofeet (*U. S.* 2,597,844) convert the acids of waxes to calcium soap, spread the mixture over granules of solid material and extract the

alcohols with acetone. Vaterrodt & Choyce (*U. S. 2,579,986*) spray the calcium soap-fatty alcohol mixture in filament form into a ketone solvent bath; the soap forms a light, flocculent precipitate which is easily removed from solvent-fatty alcohol solution. Another solvent method depends on dissolving the alcohols with propane at 100-150°F., removing the soap and stripping off the solvent (Black & Leaders—*U. S. 2,567,541*).

The communication on reduction of fatty acids to alcohols by hydrogenation deals principally with the catalyst for the purpose and gives conditions for operation with each catalyst. The catalysts are made from cadmium-nickel salts and copper chromite (Adams *et al.*—*J. Am. Chem. Soc.* 74, 2416), copper salts (Kunz & Fiore—*U. S. 2,590,105*), copper-zinc oxides, diatomaceous earth, and potassium dichromate or permanganate (Nobori *et al.*—*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 74, 363) and tin and zinc oxides (Yamafuji *et al.*—*Japan 2831* [50]). Hydrogenation of lead, tin, zinc, or cadmium soap also yields the corresponding fatty alcohol (Komori & Kotani—*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 223). Alcohols are also produced from fats or oils by reduction with lithium aluminum hydride (Micovic & Mihailovic—*Bull. soc. chim. Belgrade* 14, 256). Yields of 94-98% are claimed with this process.

The use of dialysis technique on fatty oils is patented (Lever Brothers & Unilever Ltd.—*Brit. 660,017*). Uses for the process are said to be extraction of phosphatides, vitamin A esters, polymers, partial glycerides, nickel catalyst, and other materials from the oils or fats. Heating palm oil to 200-500°F. for 10 minutes converts the carotene complexes therein to lower molecular weight forms that may be extracted with propane (Passino—*U. S. 2,615,927*). Vitamin A also is concentrated by chromatographic means. Processes using petroleum ether and sodium aluminum silicate (Baxter & Kascher—*U. S. 2,584,662*), and isobutanol and synthetic rubber (Lever Bros. & Unilever N. V.—*Dutch 68,577*) as solvents and adsorbents, respectively, are patented. Very favorable results are reported on production of vitamin A from whale-liver oil by molecular distillation followed by more intensive concentration by chromatographic technique (Agawa *et al.*—*J. Oil Chemists' Soc. Japan* 1, No. 1, 12). When halibut-liver oil is treated at 70° with six parts of methanol and one part of potassium hydroxide, the methanol layer is removed, and the residue is combined with light petroleum ether and is passed through an alumina column, the cholesterol and vitamin A are adsorbed (Kristjansson—*Fisheries Res. Board Can., Prog. Repts. Pacific Coast Sta. No. 88*, 51). After elution with ether, the cholesterol is isolated by crystallization. In a process for separating the components of lanolin, the unsaponifiable material is fractionated into cholesterol, isocholesterol, and alcohols (Bulbena-Sanz *et al.*—*Span. 194,365*). The sterols of wool fat and fish oils are also removed by formation of complexes with zinc chloride that are insoluble in organic solvents (Schuppen en Zoon—*Fr. 962,606*). In a crystallization method of production of cholesterol from lanolin, the sterols are precipitated from solution in 85:15 acetone:methanol solution by cooling; this precipitate dissolved in ethylene dichloride is reacted with oxalic acid at 180°F. and on cooling to 70-80°F., cholesterol crystallizes as an addition product (Vaterrodt & McNellis—*U. S. 2,598,469*). A similar method is used for recovering cholesterol from the ethyl acetate extract of still bottom residues of fatty acid distillations (Gebhart—*U. S. 2,610,195*). Another method of cholesterol production from still bottom residues is based on steam distillation (Kirschenbauer—*U. S. 2,598,269*). Various sterols can be extracted from crude vegetable phosphatides with methanol acidified with sulfuric acid (Mattikow & Perlman—*U. S. 2,585,954*).

Renner (*U. S. 2,599,016*) refines soybean phosphatides by extracting the crude preparations with 2-methoxy ethanol or 2-ethoxy ethanol. When commercial crude phosphatides are extracted with 6.5 ml. isopropanol per gram, the extract contains oil, lecithin, and cephalin whereas the inositol-containing material and about 77% of the sugar remains insoluble (Wik *et al.*—*J. Am. Oil Chemists' Soc.* 29, 345). Data on the composition of the fractions extracted with various volumes of solvents are tabulated. Lecithin is isolated from commercial soybean phosphatides or egg yolk oil by precipitation in alcohol solution with cadmium chloride, then removing cadmium by precipitation from methyl chloride solution with ammonia and extracting the residue with ether (Obata *et al.*—*J. Agr. Chem. Soc. Japan* 24, 29). Cephalin is isolated from the filtrate of the cadmium chloride-lecithin complex by precipitation with basic lead acetate and is freed from the lead salt complex with hydrochloric acid (*Ibid.* 33).

Separation of wax from fats and oils in the form of crystalline complexes with urea and thiourea is patented (Arnold *et*

*al.*—*U. S. 2,606,140*). The wax is recovered from the complex by decomposing with heat and dissolving the urea in solvents. Another method of obtaining wax from oils is to emulsify the oil in water with glycol and gelatin and separate the wax which floats. With this method Hitotsumatsu *et al.* (*Japan 180,820* [49]) separate about 25% wax from rice oil.

WINTERIZATION, SPLITTING, AND FATTY ACID FRACTIONATION. Boucher and Skau's (*J. Am. Oil Chemists' Soc.* 29, 455) study on the phase relations in solvent winterization of cottonseed oil in acetone-hexane mixture indicates the conditions required for reducing holding time during crystallizing of high melting point constituents. These conditions pertain to using higher oil concentration, lower chilling temperature, agitation, or combinations of these. In some cases vegetable oils may be winterized by addition of certain materials. Compounds recently patented for this purpose are aluminum stearate (Ninomiya *et al.*—*Japan 173,494* [46]), oil soluble polymers or derivatives of vinyl alcohol (Mattil—*U. S. 2,610,915*), and mixtures of coconut oil and lanolin (Ayers & Scott—*U. S. 2,607,695*).

In a study on production of lard oil by fractional crystallizing of the solid constituent from acetone, considerably higher stability is induced in the product by a preliminary slight hydrogenation of the raw animal fats used (Morris *et al.*—*J. Am. Oil Chemists' Soc.* 29, 441). The reduction in yield is slight but oil from unhydrogenated fat stabilizes with antioxidants to a few hours in accelerated test, whereas the products from slightly hydrogenated fat give stabilities of 63 to over 100 hours. A description of fractionation of menhaden oil from propane tells of recovering stearin, vitamins, and fractions useful for protective coatings (Dickinson—*Ibid.* 235). Among communications on fractionation of oils by molecular distillation there are two general reviews on the subject (Martens—*Seifen-Öle-Fette-Wachse* 77, 491, 517; Dini—*Olearia* 5, 285) and a patent on a still for the purpose (Hickman—*U. S. 2,578,999*).

The review on industrial splitting of fats, by Lascaray (*J. Am. Oil Chemists' Soc.* 29, 362) is a discussion of the mechanism of the process and contains applicable information such as effects of free fatty acids, stirring, temperature, catalyst, and water on the speed and completeness of the reaction. Cox's (*Trans. Inst. Chem. Engrs. London* 27, 123) experimental data of this type is prepared for application to operation of the Twitchell method continuously in a countercurrent column. In a stearic acid manufacturing plant, the induction period in Twitchell splitting is reduced by using an initial concentration of two normal sulfuric acids as catalyst and adding water as the reaction proceeds (Hartman—*New Zealand J. Sci. Technol.* 33B, No. 1, 5). Fukuzumi (*Japan 44* [51]) accelerates the Twitchell reaction by using normal sulfuric acid and one part of 1-chlorodibutyl-naphthalene sulfonic acid as splitting agents.

From a study of the autoclave fat splitting Yonese (*J. Chem. Soc. Japan, Ind. Chem. Sect.* 53, 313, 343) reports that the process is stepwise for mono- and diglycerides exist in the oil phase as intermediate products during the course of the process. New patents on autoclave splitting deal principally with method and equipment for continuous operation (Etablissements Fournier-Ferrier—*Brit. 666,785*; Barebey & Shields—*U. S. 2,522,899*). There are two new reviews on splitting of fats and preparation of fatty acids (Daodrio—*Ion* 12, 3; Wada—*J. Oil Chemists' Soc. Japan* 1, No. 1, 5).

A very common means of purifying or fractionating fatty acids produced by splitting is distillation. Existing continuous stills for the purpose are described by White (*Chem. Eng.* 59, No. 1, 163), Fichoux (*Oleagineux* 6, 483), and Berger (*J. Am. Oil Chemists' Soc.* 29, 81). In calculations of elements necessary in a fractionating column to segregate fatty acids of coconut oil into fractions of 90% minimum purity, Treub (*Rec. trav. chim.* 70, 1093) finds that 13 elements are required. LaCroix (*U. S. 2,576,946*) has designed a novel bubble cap suitable for a distillation column. A newly patented fatty acid still contains means for subjecting the vapors to centrifugal action under vacuum to cause separation of entrained material (Lawrence—*U. S. 2,610,142*). According to a new distillation system designed by Asch (*Brit. 667,388*) for very dark fatty acid mixtures, a primary distillation is followed by redistillation in the presence of fullers earth. Another means of obtaining light-colored acids from colored stock is to heat with a small quantity of boron trifluoride before the distillation (Terry & Warner—*U. S. 2,583,028*).

Other methods of fractionation of fatty acids depend on the difference in melting point or differences in solubility of the acids or complexes of the acids with urea. Ruef & Seidan (*Austrian* 170,289) use the fractional crystallization at low temperatures from petroleum ether in the production of con-

concentrates of the so-called essential fatty acids. Two methods for separating unsaturated and saturated acids depend on making flakes or a pasty crystalline mass of the mixed fatty acids and extracting with selective solvents at temperature and time compatible with the best separation (Jenness—*U. S. 2,593,458*; Schlenker—*U. S. 2,589,148*). For the same purpose, fatty acids and polar and nonpolar solvents are mixed and separated into two phases, the saturated acid concentrate in the nonpolar phase and unsaturated members in the polar phase (Pittsburgh Plate Glass Co.—*Brit. 658,967*). Dissolving the mixed acids in C<sub>6</sub>-C<sub>7</sub> hydrocarbons and raising the temperature to 400-500° F. at 250-600 lbs. pressure per sq. in. causes separation into two phases, one being rich in light-colored acid, the other containing dark acids and impurities (Lacey & Lead-ers—*U. S. 2,602,808*). Other methods of fractionation of fatty acids deal with the formation of insoluble complex compounds between urea and certain fatty acids. Details are recorded for the use of this process to separate linseed oil fatty acids in fractions of different degrees of unsaturation (Newey *et al.*—*U. S. 2,596,344*), for preparation of oleic acid from inedible animal fats and from olive oil fatty acids (Swern & Parker—*J. Am. Oil Chemists' Soc. 29*, 431, 614), for separation of free fatty acids from olive oil (Rigamonti & Riccio—*Fette u. Seifen 54*, 193), for removal of unpolymerized fatty acids from polymerized products, and for concentration of erucic acid from rape seed oil (Knafo—*Bull. mens. ITERG 6*, 323).

**HYDROGENATION OF OILS.** New fundamental information on hydrogenation of oils principally pertains to selectivity of the process. Janssen (*Chem. Weekblad 47*, 490) describes all oil hydrogenations by a mathematical equation containing constants representing diffusion of glycerides, activated adsorption, hydrogenation, and desorption. He explains selectivity of a hydrogenation process with regard to how these constants are affected by temperature, pressure, and poisoning of the catalyst. Lie & Spillum (*J. Am. Oil Chemists' Soc. 29*, 601) on experimentally finding more conjugation at high temperature hydrogenation than at low temperature, advance the theory that temperature influences selectivity through conjugation of the double bond. Sims (*Ibid.* 347) records that at high pressures selectivity of hydrogenation varies directly with the amount of agitation and inversely with the catalyst concentration. This is the reverse of that which is known for moderate pressures. Selective hydrogenation to convert polyunsaturated acids to monounsaturated acid is said to be accomplished with hydrogen at 100-230° and 1-20 atmospheres in the presence of copper catalyst (Miyake—*Brit. 670,906*). Analyses of products formed on partially hydrogenating methyl linolenate in acetone at room temperature indicate that double bonds at 15-16 carbons are easiest to hydrogenate, next come those at 9-10 position; and those at 12-13 position are most difficult to saturate (Ueno—*Fette u. Seifen 54*, 467). The analyses, giving content of the various fatty acids, including isoöleic acid, of various Indian fatty oils and their hydrogenated product are recorded by Belekar *et al.* (*J. Sci. Ind. Research India 11B*, 140). These data give an insight to the selectivity of the commercial hydrogenation in India.

Among innovations in the technique of hydrogenation the application of supersonic waves during the process seems most novel (Ohjyo—*Japan 862* ['50]). According to Möckel (*Chem. Ing. Tech. 24*, 153), the effect of these waves appears at the boundary between the gas and the liquid phases and makes possible in open equipment, hydrogenation that by ordinary methods requires pressure. Other general equipment innovations deal with development of a continuous system (Procter & Gamble Co.—*Brit. 654,692*, *658,188-9*), combining hydrogenation and deodorization stepwise in one set of apparatus (Armour & Co.—*Brit. 673,273*), and designing a hydrogenation plant to use the nitrogen and hydrogen mixture from cracked ammonia as a source of hydrogen (Jacob Jr. & Van de Erve—*U. S. 2,602,806*).

Olive oil extracted from press cake with carbon disulfide can be hydrogenated after the poisonous effect of sulfur on the hydrogenation catalyst is eliminated by heating the oil with iron and copper oxides, and hydrogen (Moreno *et al.*—*Anales real soc. espan. fis. y. quim. 47B*, 743). Overcoming the detrimental action of sulfur and nitrogen impurities in the hydrogenation process by use of alumina on which is adsorbed bivalent metals as catalyst is patented (von Fünér & Simon—*Ger. 807,419*). With trichloroethylene extracted oils, solvent residues in the oil of over 0.003% retard hydrogenation without affecting the selectivity of the process (Norris *et al.*—*J. Am. Oil Chemists' Soc. 29*, 28). The difficulty is ordinarily eliminated by common refining methods. With highly acid palm oils Holmboe (*Avhandl. Norske Videnskaps-Akad. Oslo I, Mat.*

*Naterv. Klasse 1951*, No. 5, 5) adds glycerol and with zinc-nickel catalyst is able to hydrogenate and regenerate the free acids into glycerides at the same time. Palm oil selectively hydrogenated to induce 12% isoöleic acid with a melting point at 37° is especially designed for use as a shortening (Loury & Jordan—*Oleagineux 7*, 139). A cacao fat substitute is prepared from the methyl esters of the head oil of the dolphin or pilot whale by hydrogenating and distilling off the portion boiling below 300° (Tomiyama & Takao—*Japan 180,897* ['49]). Tsuchiya *et al.* (*Repts. Gov. Chem. Ind. Res. Inst. 46*, 249; *Japan 1176* ['50]) hydrogenates sardine oil soaps and rice oil-alkali-refining-foots using Raney nickel by carrying out the process in the presence of considerable water. Sardine oil is converted to a petrolatum-like substance suitable for medicinal and cosmetic uses by polymerization followed by hydrogenation to the proper consistency (Tsuchiya & Kato—*Repts. Gov. Chem. Ind. Res. Inst. Tokyo 45*, 32). Methods of using hydrogenated cottonseed fatty acids in the cosmetic industry are discussed by Smith (*Am. Perfumer & Essential Oil Rev. 60*, 379).

Other communications related to hydrogenation of oils pertain to the catalyst. A review on hydrogenation catalyst by Bailey (*Ind. Eng. Chem. 44*, 990) contains the history and the technology of catalyst manufacture. Faulkner (*U. S. 2,609,346*) prepares nickel catalyst with solid high melting point fat in molded form. A new nickel-copper catalyst prepared in pellet form is claimed to be highly resistant to poisoning (Empresa Nac'l. "Calvo Sotelo" combustibles Liquidos y Lub.—*Span. 192,979*). Specially prepared mixed catalysts of nickel carbonate, cobalt carbonate, copper carbonate, and diatomaceous earth are used in hydrogenation of oils without a preliminary reduction of the catalyst (Ueno *et al.*—*J. Chem. Soc. Japan, Ind. Chem. Sect. 53*, 43, 140, 218, 252; *Japan 1118* ['51]). A catalyst comprising nickel dioxide on kieselguhr is said to be very stable and suitable for fatty oils (Endo & Kawakami—*Japan 181,347*). Introduction of acidified bleaching clay on completion of hydrogenation induces better removal of catalyst on filtration (Morris & Khym—*U. S. 2,602,807*). In a study on recovery of nickel from spent catalyst, best results are reported for digestion with a mixture of sulfuric and nitric acids (Belekar *et al.*—*J. Sci. Ind. Res. India 11B*, 28).

**ESTERIFICATION AND INTERESTERIFICATION.** All of the information recorded on alcoholysis of fatty material is useful for commercial application of the process. Pore (*Oleagineux 6*, 90) on finding that catalytic alcoholysis (methyl or ethyl) of palm oil is not complete even with five-fold excess alcohol and four days' heating, suggests that it is more convenient to use the calculated amount of alcohol, remove the ester layer, and repeat till esterification is complete. His (*Ibid.* 7, 21) measurements on rates of methanolysis show that simple triglycerides react slower than mixed triglycerides, saturated chains more easily methanolize than unsaturated, and the length of the chains is without effect. Paquet & Petit (*Ibid.* 2127) on observing that alcohol and fatty acids may esterify very easily if an inorganic acid or other catalyst is present, warn that in purification of fatty acids by crystallization from alcohol some esterification may take place. Rigid removal of material that may catalyze the reaction is recommended.

The new patents on alcoholysis are directed to obtain high yields. Iwasaki *et al.* (*Japan 173,087* ['46]) heat the reaction mixture to 300° at high pressure to accomplish 95-96% esterification. The use of absolute alcohol containing a small amount of sodium hydroxide is patented (van Loon & van Alkemade—*U. S. 2,588,435*). Aoki *et al.* (*Japan 173,473* ['46]) heat fatty acids containing a little sulfuric acid to 100° and introduce alcohol at the bottom. A catalyst for the process prepared by Sumiki (*Japan 2890* ['50]) by heating a mixture of sodium hydroxide, ethanol, and soybean oil, is said to induce 85% yield of fatty acid ethyl ester.

The literature on esterification of fatty acids with glycerol is reviewed by Stalman (*Seifen-Öle-Fette-Wachse 77*, 423). Savory (*Ann. faculte Sci. Marseille 20*, 39) records much useful and fundamental information pertinent to the manufacture of pentaerythritol esters of fatty acids. With p-toluene sulfonic acid as a catalyst no polymers develop during manufacture. Esterification starts as a two-phase system and rapidity is increased by improved contact caused by development of a mutual solvent, the monoester. Thus, yields and rapidity are greater with lauric than with stearic acid because of greater solubility of partial esters of the former. Phenol as a mutual solvent works well but is too difficult to remove; soap causes formation of emulsions, acrolein, and polymers. With mixed acids, random distribution is not attained because of lack of complete miscibility which is assumed in the postulation that polyesterification is at random. Manufacture of diesters by

blocking two hydroxyl groups with acetone or bromine is not successful. The monoesters of pentaerythritol are better emulsifiers than those of glycerol.

Naudet & Desnuelle (*Oleagineux* 6, 338; 7, 335) use the transesterification technique to improve coconut oil for deep fat frying and for soap making. The foaming tendency of the oil during frying is decreased by transesterification with peanut, soybean, or similar oils. Most marked decrease in foaming tendency, and removal of constituents that may cause irritation from its soap are obtained by transesterification with the methyl esters of peanut oil fat acids. During this process methyl esters of caproic, caprylic, and capric acids develop and distill off because of their low boiling point. A patent on this process is issued to Mueller (*U. S. 2,585,027*). Conversely, Jackson (*U. S. 2,615,159*) and Baur (*U. S. 2,615,160*) use the transesterification reaction to substitute one or two saturated lower molecular weight acids in a triglyceride of long chain acids. The products are useful in manufacture of waxes, suppositories, and other products. One patent on transesterification deals with accomplishing partial hydrogenation and transesterification at the same time (Martinez-Moreno—*Span. 193-123*). During the process the catalysts for both hydrogenation and transesterification are present. Alkali metal hydrides are patented as catalysts for transesterification (Eckey—*U. S. 2,558,547*). Catalytic transesterification is reviewed by van Loon (*Chem. Weekblad* 47, 494).

In a process of esterinterchange between fats and glycerol to make mono- and diglycerides, the purification and fractionation of the various esters is by stepwise phase separation from solution in polar solvents (Young & Black—*U. S. 2,608,564*).

### Fatty Products (Except Detergents)

**HOUSEHOLD FATS.** During the eleven years that the Federal Security Agency of our government was considering the bread standards, to be promulgated, the question of inclusion of certain commercial emulsifiers as standard ingredients has prolonged the discussion because the Federal Food and Drug Administration was not satisfied that their suitability for food purposes had been established. This has induced many studies. Some of the recent work appears during the year under review.

Some of the work is relevant to the suitability of partial fatty acid esters of sorbitan, and of polyoxyethylene glycols ("Spans," "Tweens," "Myrj"). According to Harris & Sherman (*Arch. Biochem. & Biophys.* 34, 249, 259), rats fed these at 25% levels in a synthetic diet are affected by severe diarrhea and increased mortality, except with polyoxyethylene monostearate. The authors state that sorbitan monolaurate is most harmful in this respect. At low levels in the diet the diarrhea does not develop. The toxic pathological observations with these compounds at over 5% levels in the diet are anemia, necrosis of the hind legs, irritation of the intestinal tract and of the tubular epithelium of the kidneys, and inhibition of gonadal maturation. Another investigation shows that polyethylene glycols are more toxic than glycerol as measured by LD50 on rats (Loesser & Sturmer—*Fette u. Seifen* 52, 87). In work seemingly to demonstrate innocuousness of polyoxyethylene compounds, Pratt (*Food Tech.* 6, 425) calculates that when used in all foods in which they are technically applicable the intake would not exceed 0.75 gram per person per day. This is considerably below the experimentally found toxic amounts. Culver *et al.* (*J. Pharmacol. Exptl. Therap.* 103, 377) fed the compounds to humans and found no evidence of storage in the body because practically all the polyoxyethylene moiety is excreted. The commercial products, Myrj and Tweens, did not interfere with oxygen uptake of kidney tissue as determined by the Warburg technique (Krantz, Jr., *et al.*—*Proc. Soc. Exptl. Biol. Med.* 81, 640).

Because, in past years, several investigators have claimed that the emulsifiers improve fat absorption, new workers have become interested in this property. However, it is not confirmed with either those having the polyoxyethylene moiety (Annegers—*Proc. Soc. Exptl. Biol. & Med.* 81, 277, Tidwell & Nagler—*Ibid.* 12), or those having the partial fatty esters of glycerol (Dasher—*Science* 116, 660). The compounds did not alter fecal fat, gastrointestinal motility, or fat splitting. In the tests with partial glycerides it is observed that the natural emulsifiers (bile salts, free fatty acids, etc.) create natural emulsifying conditions which are not augmented by the synthetic emulsifiers.

New evidence on the innocuousness of mono- and diglycerides as food ingredients is based on their natural occurrence in food and in the digestive system. Kuhrt *et al.* (*J. Am. Oil Chemists' Soc.* 29, 271; *Chem. Eng. News* 30, 2512) find

monoglycerides normally present in foods and the human intestinal tract. Their work on bread indicates that, due to development of monoglycerides during baking, breads from doughs containing lard have practically the same amount of monoglycerides as those to which the compound is added when mixing the dough. In a discussion on this subject, Coppock (*Brit. J. Nutr.* 5, 383) cites literature that also indicates presence in the bowels and that the absorption from ingestion is similar to that of natural fats. A committee of the National Research Council (published Dec. 1952) investigating safety of mono- and diglycerides also decided that they are normal, safe nutrients.

Opinions on emulsifiers in foods are also part of the text of editorials and general communications on chemicals in foods and adulteration. As an example of an opinion, Barnes (*Brit. J. Nutr.* 5, 377) suggests that the decision whether a substance should be permitted in food must rest also on considerations other than those of its toxicity. Such considerations may be within the field of nutrition rather than narrowed to limits of toxicity. The thought that when used as bread softeners the public would be deceived is another important consideration. On the basis of such consideration and the preceding reports, the bread standards, which are now in almost final form, permit use of partial glycerides, but polyoxyethylene derivatives are not approved as standard ingredients.

Some communication on partial esters of polyoxyethylene glycols for food purposes are not a part of the preceding controversy. A review on their functions in margarine, ice cream, soap, chocolate, and bakery products was prepared by Maes (*Mededel. Vlaam. Chem. Ver.* 13, 13). The possibilities of their economical manufacture in France is outlined by Aftalion (*Chimie & industrie* 67, 593). Preparation of the emulsifiers from palm and soybean oils and polyoxyethylene glycol is described by Senda & Oda (*Chem. High Polymers Japan* 7, 229). Their use to retard fat bloom in chocolate is reviewed (Easton *et al.*—*Food Technol.* 6, 21). The patents issued to Valko (*U. S. 2,606,838, 2,610,125*) indicate that complete esters of fatty acids and polyglycols are suitable for improving shortening, texture of ice cream, etc., just as has been recorded in the past for the partial esters of the glycols.

The improved dispersion of fat and air obtained when glycerol monostearate is added to a cake formula is described by Jooste & Mackey (*Food Research* 17, 185). In tests on the effect of various types of emulsifiers or detergents on flour proteins, both nonionic and cationic compounds show little effect; but anionics toughen the gluten and affect the consistency of the dough (Sullivan—*Cereal Chem.* 29, 282). The mechanism of this is not clearly understood. Other communications on bakery fats are on improving lard for cake baking by heat treating with alkali alcoholate to rearrange the triglycerides (Vander Wal & van Akkeren—*U. S. 2,571,315*); on the use of citraconic acid and other material in the shortening intended for puff pastry manufacture (Hennecke & Lamprecht—*Fette u. Seifen* 54, 147); on manufacture of dry shortening by spraying emulsified fats on sugar and other pulverized materials (Moriya & Kudo—*Japan 1274* [50]); on using solid monoglycerides for dry baking mixes (Jaeger—*U. S. 2,611,704*); on specifications for shortening used in the prepared cake mixes (Schroeder—*Trans. Am. Assoc. Cereal Chem.* 10, 141); and on a dry frosting mix which contains polyoxyethylene compounds and shortening (Melnick—*U. S. 2,598,282*).

The communications on frying fats pertain to the problems arising in their commercial utilization. Frying fats raised to a free fatty acid of 1.35% through open air heating drastically affect the shape, surface appearance, and fat absorption of cake doughnuts (Goodman & Block—*J. Am. Oil Chemists' Soc.* 29, 616). This effect is evident even after the free fatty acids are brought to a lower concentration by dilution with fresh fat. Also, in this work a seven-month commercial test in 10 large bakeries indicates that fat adsorption is eight percent greater with natural lard than with hydrogenated lard. In a discussion on preparation of high quality, deep fat-fried foods the text pertains to practical measures for inhibiting hydrolysis, polymerization, instability, discoloration, and off-flavor of the frying fat (Bates—*Food Eng.* 27, No. 12, 82). Data on the changes in physical and chemical characteristics of peanut oil, coconut oil, and hydrogenated fat when used for frying at 190-200° are recorded by Sen *et al.* (*Indian Soap J.* 17, 107).

The German food regulations regarding mayonnaise are published by Heesch (*Fette u. Seifen* 54, 509).

A newly patented method for continuously manufacturing margarine comprises chilling and emulsifying ingredients at the same time and homogenizing them by passing through



mesh screens before completely set (Rourke & Dow—*U. S. 2,611,707*). Setting to its final consistency is done with a minimum of interference by forces apt to cause shearing. A margarine that is said to be less heavy on the palate is made from fats from which high melting point glycerides are removed by crystallization (Wilson *et al.*—*U. S. 2,592,224*). Another innovation in margarine manufacture is emulsifying the fatty and aqueous portions in the liquid state but at such temperatures of the respective components that on mixing the temperature of the mixture is lower than the solidification point of the fat component (Zachariassen & Borek—*U. S. 2,605,185*). A margarine churn patented by Turgasen a few years ago is now described in a communication by Slater (*Food Eng. 24*, No. 2, 111). Use of a fatty acid-substituted protein as the emulsifier is said to produce a margarine resembling butter in spreading and other characteristics (Storrs & Froedge—*U. S. 2,609,300*). In tests on suitability of using synthetic vitamin A palmitate, 100 times the usual amount permitted normal growth, reproduction, and lactation without deleterious effects on test animals (Ames *et al.*—*J. Am. Oil Chemists' Soc. 29*, 151).

Other developments in the margarine industry relate to coloring materials and packages. Schuchardt (*Fette u. Seifen 53*, 689) recommends a 2:1 lactoflavin:carotene mixture to color it economically and to eliminate synthetic dyes from the product. A dye tablet for the same purpose contains yellow synthetic dyes compressed with starch (Adler & Ponath—*U. S. 2,600,381*). The newly patented margarine packages are designed to include a container for coloring matter which dyes the margarine on kneading the product while still packaged (Brown—*U. S. 2,607,697*; Hensgen—*U. S. 2,610,917*, *2,617,733*).

In an infant food composition the fat component is made by blending various food fats so that the blend contains 5% C<sub>12</sub>-C<sub>14</sub> saturated fatty acids, 50% unsaturated acids and the remainder saturated acids above C<sub>14</sub> but such that the saponification number of the total fatty acid mixture ranges between 190 and 200 (Bernhart & Hassinen—*U. S. 2,611,706*).

Esterification of monostearin with acetic acid anhydride yields acetostearins which are highly flexible, nongreasy solids at room temperature, and which are recommended for use as coatings for cheese, ice cream bars, meat, and poultry (Feuge *et al.*—*J. Am. Oil Chemists' Soc. 29*, 11; *Food Eng. 24*, No. 4, 191). Raw popcorn is preserved by mixing with hydrogenated coconut oil (Martin—*U. S. 2,604,407*). The difficulty in adhering sugar coatings to vitamin A and D pills of solid fat is overcome by coating the fatty pills with a layer of monostearin (Termansen—*Arch. Pharm. Chem. 53*, 727). Fat soluble vitamins are emulsified into milk with cholesterol esterified with radicals having free hydrophilic groups (Reerink & van der Vilet—*U. S. 2,583,290*).

Some communications are on fats in the pharmaceutical industry. Palm-kernel fat, freed of the soft portion by crystallization, is said to be superior to cacao butter as a suppository base because it is cheaper, odorless, and has a slightly higher congealing point (Münzel—*Schweiz. Apoth.-Ztg. 90*, 125). The ester formed by replacing one of the -OH groups of the propanediol side chain of chloromycetin with palmitic acid is less toxic than crystalline chloromycetin and still is therapeutically effective (Larkin—*Proc. Soc. Exptl. Biol. Med. 78*, 191). An equimolecular streptomycin-oleic acid mixture is 20% superior to dihydrostreptomycin as a bacteriostat against most bacterial species, and its effect lasts longer (Gros *et al.*—*Compt. rend. 232*, 764).

The effects of fats and oils on development of penicillin are recorded by Yasuda *et al.* (*J. Agr. Chem. Soc. Japan 25*, 310, 314, 361, 465, 469). The addition of soybean, rapeseed, sesame, cottonseed, peanut, lard, or other oils, or oleic acid to cultures after 24 hours' fermentation causes a marked increase in penicillin potency; whereas addition after 48 hours of fermentation results in an inhibition of mycelium growth and autolysis. In some cases bad effects from the oils are prevented by addition of three percent of lactose in the medium. Bad effects are slight with machine oil, rapeseed oil, or lard.

**GENERAL EMULSIFIERS AND DEMULSIFIERS.** Basic information on emulsifiers and emulsification is the text of a small number of communications. In a study on the effect of the amount of shear on particle size and interfacial phenomena it is observed that reduction of size of particle is dependent on speed of stirring, time, and composition, but for each system a limiting droplet radius is obtained after a definite time (Jürgen-Lohmann—*Kolloid-Z. 124*, 41, 77). Increasing amounts of emulsifiers decrease particle radius rapidly until a certain limiting value is reached. The minimum particle size is also

somewhat characteristic of the nonaqueous component. Francis (*J. Physical Chem. 56*; 510) on observing that emulsions of colorless liquid phases of equal refractive indices but different dispersions show brilliant colors by transmitted light, studies the usefulness of the phenomenon. These colors are a function of the temperature and composition. They are useful in approximating these factors as well as the refractive indexes of liquids above their normal boiling point, analysis of glycerol and other compounds, composition of binary or ternary systems, etc. Schönfeldts' (*Melliand Textilber 32*, 773) new method of estimating the stability of olein emulsions is based on rate of increase of oleic acid concentration in a series of samples taken periodically five millimeters below the emulsion surface. Physiological and pharmacological characteristics that may be involved are the texts of a discussion on emulsions used for air sterilization, insecticides, dust control, and smog control (Dautrebande—*Physiol. Revs. 32*, 214).

In the field of emulsion polymerization Jacobi (*Angew. Chem. 64*, 539) tells how particle size can be determined by titration. The knowledge obtained can be used for making emulsions of a certain medium particle size which is most compatible with the individual technical application. In one study on emulsion polymerization of styrene latexes, the kinetics of the reaction are studied with regard to fulfilling a certain equation (Wintgen & Jürgen-Lohmann—*Kolloid-Z. 122*, 144, 148). In this work the emulsion particle count is related to the absolute amount of emulsifier, and certain discrepancies are attributed to change in the structure of the emulsion at certain critical concentrations of emulsifier. Other studies on emulsion polymerization are not being cited here because the emulsifier, other fat derivative, or their contribution to the reaction is not the problem studied.

New emulsifiers or new methods of their manufacture appear mainly in patents. Partial esters of polyoxyethylene glycol and tall oil (Esposito—*U. S. 2,610,966*) and of pentaerythritol and fatty acid (Baker Castor Oil Co.—*Brit. 674,370*) are patented for use principally as hydraulic fluids, although structure and other uses mentioned indicate that they are also emulsifiers. Sorbitan and polyoxyethylene glycol derivatives of the fatty acids of lanolin are made for cosmetic uses (Griffin—*U. S. 2,608,563*). Special emulsifiers are formed on reacting ethylene oxide and di-alkylphenols (Cross & Enyeart—*U. S. 2,593,112*). An antifoam emulsion contains partial fatty esters of polyhydroxy compounds and benzene-soluble methylpolysiloxane (Currie & Hommel—*U. S. 2,595,928*). A coating composition suitable for application to wet insulating board contains partial polyethylene glycol-fatty acid esters (Wise—*U. S. 2,581,058*). A new emulsifier is made by condensing natural polyhydroxy fatty acids to estolides and partially esterifying polyhydric alcohols with these (Schoenfeld—*U. S. 2,590,046*). Glycerolysis of fat in tertiary aromatic nitrogenous bases increases the yield of monoglycerides up to 78% (Mattil & Sims—*J. Am. Oil Chemists' Soc. 29*, 59); mannitol and sorbitol can be reacted with fatty acids in pyridine to give mono-, di-, tri-, and tetraesters (Nicoud—*J. recherches centre natl. recherche sci. Lab. Bellevue 1950*, 227). In this work the mono- through hexalaurates of sorbitol and mannitol were prepared and their melting points and the surface tensions of their solutions are recorded. Other emulsifiers described are a mixture of rosin and fatty acids from lanolin (van der Waarden—*U. S. 2,577,218*), mixtures of certain partially hydrolyzed proteins and fatty acids (Gruenwald—*U. S. 2,584,123*), sodium caseinate having a pH of 6.8-7.2 (Peebles & Girvin—*U. S. 2,622,984*), and sulfited shellac (Saha—*J. Indian Chem. Soc. Ind. & News Ed. 13*, 262, 265).

The newly developed demulsifying agents are practically all derived from fat and for the most part are for use in production and processing of petroleum (Aquaness Corp.—*U. S. 2,597,204*; Petrolite Corp., Ltd.—*U. S. 2,589,061-2*, *2,589,196-201*, *2,594,541-2*, *2,599,538*, *2,602,051-69*, *2,602,077*, *2,602,087-8*, *2,605,230-33*, *2,606,882*; and Visco Products Co.—*U. S. 2,615,852-3*). The compounds are used to break emulsions in the recovery of petroleum from wells that are flooded, for breaking emulsions after the "Doctor treatment" of petroleum, for recovery of petroleum from emulsions, etc. Experiments with these indicate that petroleum in the flood water of a well can be reduced to values below 10% (Calhoun, Jr.—*Producers' Monthly 16*, No. 1, 15), and in certain fields additional production of petroleum from injected wells is valued at over twice the cost of compounds used (Breston & Johnson—*Ibid.* 24).

**CERTAIN FATTY ESTERS, ACIDS, KETONES, AND NITROGEN-CONTAINING AND HYDROCARBON DERIVATIVES OF FATS.** Some fatty acid esters were synthesized to obtain data on their prop-

erties that are useful in the analysis, in the determination of their structure, and for various investigations on natural fatty material. The new activities along this line are the synthesis of several symmetrical triglycerides (Craig *et al.*—*J. Am. Oil Chemists' Soc.* 29, 169), preparation of symmetrical diglycerides of single fatty acids (Baur—*J. Am. Chem. Soc.* 73, 3926), development of a procedure for making specific glycerides through esterifying dihydroxyacetone to a monomer, building and esterifying hydroxyl groups until the specific glyceride is obtained (Schlenk *et al.*—*Ibid.* 74, 2550), and synthesis of enantiomeric forms of A-cephalins and A-lecithins (Baer *et al.*—*Ibid.* 152, 158). Ester products made by substituting one or two lactate radicals in a glyceride and acylating the -OH groups of the lactate radicals are intended for use as plastic modifying agents (Filachione *et al.*—*U. S.* 2,584,998, Fein—*J. Am. Chem. Soc.* 73, 5870). Esters of tetrahydrofurfuryl and tall oil are manufactured for use as plasticizers (Weil & Tusa—*U. S.* 2,583,193).

Methods are being developed for preparing specific fatty acids, the compounds being intended for fundamental studies of their properties and reactions. New work of this type deals with isolation of several branched-chain acids (Cason *et al.*—*J. Org. Chem.* 16, 1170, 1177, 1181, 1187, 1193; *J. Biol. Chem.* 192, 405), synthesis of *cis*- and *trans*- forms of several fatty acids (Myers—*J. Am. Chem. Soc.* 73, 2100; Howton & Davis—*J. Org. Chem.* 16, 1405; Boughton *et al.*—*J. Chem. Soc.* 1952, 671; Ames & Bowman—*Ibid.* 677) oxidation of stearolic acid to 9,10-diketostearic acid (Khan & Newman—*J. Org. Chem.* 17, 1063), and isolation of methyl linoleate hydroperoxide (Zileh *et al.*—*J. Am. Oil Chemists' Soc.* 29, 244).

Fatty materials are modified for various commercial applications. Halogen-containing ether epoxides, made by the condensation of  $\alpha$ -epihalohydrins and monoglycerides, are useful as intermediates for manufacture of ingredients for varnishes, resins, lubricants, and detergents (Zech—*U. S.* 2,581,464). Saturated fatty acids are conveniently chlorinated by sulfuryl chloride in the presence of benzoyl peroxide (Savary & Desnuelle—*Bull. soc. chim. France* 1952, 213). Data on the kinetics and efficient means for hydrochlorination of lauryl alcohol are recorded by Kingsley Jr. and Bliss (*Ind. Eng. Chem.* 44, 2479). Products of the latter two citations are useful intermediates for numerous industrial preparations.

The oxidizing agents used in descriptions of the hydroxylation of fats, oils, and fatty acids are mixtures of ammonium persulfate and sulfuric acid (Ishii & Fujita—*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 207), combinations of hydrogen peroxide and various organic and inorganic acids (Ishii—*Japan* 2840 [1950], Ohno—*Japan* 3731 [1950]; Shinowara *et al.*—*Japan* 3732 [1950]); potassium permanganate (Maubec—*Fr.* 958,244); and electrolysis in the presence of sulfuric acid (Maruta—*J. Chem. Soc. Japan Pure Chem. Sect.* 72, 233, *Japan* 3133 [1950]). Conversion of the fatty acids of rice oil to methyl or ethyl esters followed by hydroxylating is said to yield a substitute for castor oil (Hitotsumatsu *et al.*—*Japan* 45 [1951]). As fundamental information Ishii (*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 240) has pyrolyzed hydroxylated oils and Chikamori (*J. Chem. Soc. Japan Pure Chem. Sect.* 72, 747) has diacylated dihydroxystearic acid with butyric, caproic, and lauric acids, respectively, and the characteristics of the products are recorded.

Fatty material is oxidized for other commercial purposes. Useful odd-numbered carbon chain fatty aldehydes and acids are formed on oxidizing normal fatty acids with peracetic acid in acetic acid at 85-90° (Gebhart & Ross—*U. S.* 2,585,129). Oil peroxides made by oxidizing fats and oils with air in the presence of enzymes derived from seeds are intended for bleaching flours or dough (Renner—*U. S.* 2,557,564, 2,573,358). A study of mild oxidation of various saturated fatty acids by Norbi (*J. Soc. Chem. Ind. Japan* 46, 146, 189, 220, 248) indicates that in mixtures the highest members are most labile, and lactones and hydroxy acids are the principal products. Catalytic oxidation of olefin provides dibasic acids such as azelaic and lower monobasic acids such as pelargonic and enanthic acids (Ölund—*Swed.* 131,987-8). A scheme for separation of such products comprises a vacuum distillation to separate the monobasic and lower dibasic acids, esterification of the still residue with propyl alcohol, and further fractionation of higher dibasic acid by distillation under reduced pressure (Cavanaugh & Weir—*U. S.* 2,560,156). Another means of obtaining dicarboxylic acid is by the alkaline pyrolysis of hydroxy fatty acids (Lane—*U. S.* 2,580,931, Mikeska—*U. S.* 2,614,122).

Pyrolysis is useful in preparation of some derivatives of fats. Heptanal and methyl undecylenate are made by the pyrolysis of methyl esters of ricinoleic acid (Soc. Organico—*Brit.* 668, 530). Fatty acids in the presence of certain catalysts are

decomposed by heat to ketones which may condense or break up to yield high boiling and gaseous materials (Demorest *et al.*—*Ind. Eng. Chem.* 43, 2569). Analysis of the pyrolytic products of olive oil indicates that the break in the oleic acid chain occurs near but not necessarily at the double bond (Petit and Bosshard—*Bull. soc. chim. France* 1952, 293). Electrolysis also causes decomposition of fatty material. This process is reviewed for fats and many other organic compounds by Weedon (*Quarterly Revs.* 6, 380). In applying this reaction to camellia oil in aqueous ethanol, 38% of the fatty acids turn into hydrocarbons, 2% into alcohols, and 12% into esters (Ono & Toyama—*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 359). In studying the reaction in the presence of compounds capable of polymerization, Goldschmidt & Stöckl (*Chem. Ber.* 85, 630) have confirmed the concept that acids decompose to carbon dioxide and alkyl radicals and the latter react with the polymerizable material such as styrene.

Nitrogen-containing derivatives of fatty material are sometimes made for a specific use and in the following, where no specific use is given, it is presumed that they are intended as intermediates for various preparations. Conditions are worked out for quantitative conversion of oleo, olive, castor, and tobacco seed oils to amides and glycerol by reaction with liquid ammonia under pressure (Roe *et al.*—*J. Am. Chemists' Soc.* 29, 18). Many *N*-alkenyl and *N,N*-dialkenyl derivatives of these are prepared and their properties are recorded (Roe *et al.*—*J. Am. Chem. Soc.* 73, 3642). Stearamidomethyl pyridinium chloride is prepared to study its possible esterification product with cotton (Weaver *et al.*—*J. Org. Chem.* 16, 1111). The freezing point of binary mixtures of acetamide with saturated fatty acids indicates that molecular compound formation takes place in the mixtures (Magne & Skau—*J. Am. Chem. Soc.* 74, 2628). Heating dihydroxystearic acid with alkylolamine yields compounds that serve as intermediates for many useful preparations (Swern *et al.*—*U. S.* 2,605,270). *N,N*-dipalmitoyl-benzene disulfonamide and like fatty acid derivatives are manufactured for use to coat enteric pills to prevent solution in the stomach but permitting solution in the intestines (Aelouy—*U. S.* 2,571,995). Amidoester waxes for polishing uses are condensation products of fatty acids and alkanolamines reacted with dibasic acids (Turinsky—*U. S.* 2,607,783). Imido esters from azolines and maleic adducts of fats can be used as rubber modifiers (Rowland—*U. S.* 2,580,047). Cyanostearic acid (N. V. de Bataafse Petroleum Maatschappij—*Dutch* 68,160), combinations of partial fatty acid esters of polyhydroxy alcohols with alkylene diamines (Matuszak & Hand, Jr.—*U. S.* 2,580,036), and mixtures of monoricinoleate and alkanol amines (Burgart—*U. S.* 2,566,925) are fat derived compounds which are used as ingredients for rust inhibitors. A corrosion-preventive mixture capable of being easily removed consists of a blend of soybean, sperm, and linseed oils (Costello—*U. S.* 2,611,711).

Stabilized fatty acid nitriles are prepared by reacting fatty acids or tall oil with gaseous ammonia in the presence of soaps of metals of group II of the periodic table (Drew & Funderburk—*U. S.* 2,589,232; Drew—*U. S.* 2,589,233). Apparatus for a similar process is patented (Armour & Co.—*Brit.* 654,462). The electrolytic reduction of fatty acid nitriles to the corresponding amines in a special apparatus is also patented (Janardhan—*Indian* 44,230). Numerous homologous fatty isothioureas are prepared and their germicidal activities are recorded (Bandelin & Tuschhoff—*J. Am. Chem. Soc.* 74, 4271). Marked germicidal activity is associated with derivatives of the C<sub>12</sub> and C<sub>14</sub> members.

FLotation, CORE BINDING, DRILLING FLUID, ETC., WITH FAT DERIVATIVES. References cited here are those that remained after classification of material under the specific divisions of this section. Optimum conditions, pH, concentration, etc., have been worked out for use of cetyl sulfate for the flotation of cassiterite ore (Edwards & Ewers—*Australian J. Sci. Research* 44, 627). A liquid core binder which is curable by heat and oxidation consists of partial polyalcohol esters of tall oil, drying oil, and asphalt (Simmers—*U. S.* 2,584,300). In laboratory investigations on use of linseed oil for core binding, it is found that baking at 230° for one hour produces desirable cores (Horspool *et al.*—*J. Applied Chem. London* 2, 283). Special fat derived surface active agents are added to petroleum well drilling muds to reduce their moisture loss (Doscher—*U. S.* 2,563,992). A polishing compound for printing rolls contains fatty oil, soap, vegetable gums, and powdered tale (Fumita—*Japan* 356 [1951]). A synthetic wax is made from tall oil, saturated fatty acids, and insoluble metal soaps (Cunder & Licata—*U. S.* 2,608,493). Textile material of animal fibers can be rendered water-repellent by *in situ* making of aluminum soap (Sookne & Brown—*U. S.* 2,599,590). The fabric is dipped in

dilute soluble soap solution, lightly rinsed, and then dipped in soluble aluminum salt solution.

**PROTECTIVE COATINGS, RESINS, AND PLASTICS.** Many general communications dealing with oils in protective coatings and plastic are informational on various phases of the industry, but, because they are in the nature of reviews or general discussions they are merely cited here with brief note on the text. Reviews on the mechanism of fat oxidation and polymerization were written by Kern (*Fette u. Seifen* 53, 746), Meier (*Chem. Ztg.* 76, 218), Wheeler (*Official Dig. Federation Paint & Varnish Production Clubs No. 322*, 661), and Carriere (*Ann. Faculté sci. Marseille* 19, 11). Powers (*J. Am. Oil Chemists' Soc.* 29, 420) discusses evidence for the formation of inter-polymers on heat-bodding of oils. Catalytic conjugation of oils to improve their drying properties is reviewed by Massoni (*Bull. mens. ITERG* 6, 147), von Mikusch (*Farbe u. Lack* 57, 341, 393), and Blokingh *et al.* (*Paint Oil Chem. Rev.* 115, No. 4, 18). Summaries on processing and utilizing castor oil in the coating industry were prepared by Griffiths (*Paint Manuf.* 22, 250), Wilson (*J. Oil & Colour Chemists' Assoc.* 33, 503), Cepeda (*Ion* 11, 523), Ijak (*Chim. peintures* 14, 188), and Sfiras (*Oleagineux* 7, 135, 221). The chemistry of sorbitol in regard to preparation of resins and varnishes is discussed by Colomb (*Ind. vernice Milan* 6, 55). The general and descriptive papers on alkyd resins treat: equipment for their manufacture (Yokell—*Paint Varnish Production* 42, No. 8, 23); modification of their properties through selection of oils (Stieger—*Fette u. Seifen* 54, 639); requirements for alkyds and polymerization (Jordan—*Chemistry & Industry* 50, 1208); pentaerythritol alkyds (North—*Paint Technol.* 16, 333); copolymers of oils, alkyds, and styrene (Hovey & Jerabek—*Official Dig. Federation Paint & Varnish Production Clubs No. 314*, 171); maleic oils (Kappelmeier *et al.*—*Peintures, pigments, vernis* 27, 481); and preparation and properties of varnishes containing maleinized oils (Gutkin—*Official Dig. Federation Paint & Varnish Production Clubs* 317, 371). Sethi & Aggarwal (*J. Sci. Ind. Res. India* 10B, No. 9, 205) describe varnish formulations containing aluminum, calcium, manganese, and zinc salts of polymerized acids of semidrying oils. Changes in composition of oil films during aging are reviewed by Drinberg & Rokhlin (*J. Applied Chem. USSR* 24, 239), infrared spectrophotometric observations of this process are recorded by Nicholls & Hoffman (*Official Dig. Federation Paint & Varnish Production Clubs No. 327*, 245).

A series of nine unpublished papers prepared at the Dept. of Paints and Lacquers of the Textilingenieurschule at Krefeld contain information on boleko oil, alkyd resins, enamels, copolymers of styrene and bodied oil, storage of drying oils, rosin esters, oxygen absorption, and commercial resins. They are briefly reviewed by Stock (*Deut. Farben-Z.* 6, 231). The information is intended for use by paint and varnish makers.

Factice, that is sulfur-vulcanized fatty oil, is discussed with regard to its function in rubber technology (Harrison—*Trans. Inst. Rubber Ind.* 28, 117).

Various techniques are used to gain fundamental knowledge regarding the mechanisms involved during thickening and drying of oils used in protective coatings. Various analytical techniques such as spectrophotometric analysis, molecular weight determination, etc., are applied for determining the successive changes that seem to take place during polymerization of sunflower seed oils (Barker *et al.*—*J. Oil & Colour Chemists' Assoc.* 34, 215). Migration of acids toward random distribution equilibrium, conjugation, dimer formation, disappearance of linoleic acid, etc., are demonstrated. Boelhouwer *et al.* (*Research London* 5, 336) confirm and demonstrate that cyclization occurs during polymerization of linseed oil. The bodied oil is fractionated, hydrogenated, the fatty acids converted to methyl esters, fractionated, converted to saturated hydrocarbons by dehydration, and cyclic components of these hydrocarbons are determined. By employing spectroscopic methods for estimating the conjugated and nonconjugated acids and by using new methods for determining mono-, di-, and trimeric methyl esters, a detailed study is made on the kinetics of polymerization of pure methyl linoleate (Pasehke *et al.*—*Ind. Eng. Chem.* 44, 1113). It is found that the various linoleates differ in speed of reaction and in ratio of dimer and trimer. These differences are attributed to the geometry of the various isomers.

The mechanism of oxidation of fats is studied with new methods for analysis of the products. Cannon *et al.* (*J. Am. Oil Chemists' Soc.* 29, 447) fractionates oxidized methyl linoleate by countercurrent distribution between 80% ethanol and a pentane-hexane mixture, and analyzes the fractions spectrophotometrically and by other means to determine type and amount of polymers, oxygen uptake, etc. Conjugated cis-trans

hyperperoxides are formed predominantly at 0° and conjugated trans-trans peroxides at room temperature. Unconjugated monohydroperoxide is formed to only a minor extent. In similar work Mukherjee (*Indian Soap J.* 16, 106) fractionates the products of oxidation by chromatography. His results confirm the theories that suggest oxygen attacks at a methylene group between double bonds to form hydroperoxide which rearranges with formation of conjugated double bonds. Treibs (*Fette u. Seifen* 54, 3) explains autooxidation of drying oils as follows: the primary product is peroxide; primary oxygen uptake occurs at 1,4 or 1,5 spacing; by hydrogenation the oxidates are reduced to oxy-cyclo-tautomeric moieties which become complete acetals; and migration of the double bond is also part of the mechanism with the polyunsaturated acids. Data obtained from spectral analysis of air dried dipentaerythritol fatty acid esters are interpreted as being in line with Farmers' theory of the mechanism of drying oil oxidation (Adams *et al.*—*Official Dig. Federation Paint and Varnish Production Clubs* 322, 669). In similar work on peanut oil, absorption bands indicating mechanisms such as development of hydroperoxides, their decomposition, diene conjugation, etc., are pointed out (Lemon *et al.*—*Can. J. Technol.* 29, 523). Kawahara *et al.*'s (*J. Am. Oil Chemists' Soc.* 29, 633) analyses of volatile cleavage products of oxidized methyl linoleate indicate much aldehydic material; acetaldehyde, propionaldehyde and  $\alpha$ -pentenal develop. This development of aldehydes in oxidized oil is suggested as a means of distinguishing oxidized from polymerized oils (Palumbo—*Ind. vernice Milan* 6, 113). In the tests used for aldehydes none are found in oils bodied in the absence of air.

Laboratory techniques to study some phases of the drying process are described. Privett's & Lundberg's (*Ann. Rept. Hormel Inst. Univ. Minn.* 1950-51, 7) studies on the kinetics of autooxidation are based on determination by liquid-liquid countercurrent extraction of the type of peroxide developed. The conjugated peroxides are concentrated in a nonpolar solvent phase, and nonconjugated peroxides in an alcohol phase. Catravas & Knafo (*Bull. mens. ITERG* 6, 43) precipitate the oxidized components with urea. They report that the more complex components contain both oxidized and unoxidized products. Chipault *et al.* (*Official Dig. Paint & Varnish Production Club No. 322*, 740; *Ann. Rept. Hormel Inst. Univ. Minn.* 1950-51, 18) record the rate of oxygen uptake, peroxide formation, and drying of glycerol, pentaerythritol and dipentaerythritol esters of oleic, linoleic, linolenic, and eleostearic acids during autooxidation. The rate is independent of the alcohol moiety. With conjugated systems setting is to a hard film at low peroxide value. Meier (*Farbe u. Lack* 58, 55) compared drying times of methyl esters of the same acids and licanic, ricinoleic, and ricinenic acids by determinations of the viscosity of their xylene solutions. Among the data the improved effect of conjugated systems is apparent.

Binde (*Farbe u. Lack* 58, 63) gives details on determination of viscosity of bodied oils by measuring rate of flow through a tube, by the speed of a rising air bubble through the oil, and by the falling speed of a steel ball. Equations and charts are included for converting data to absolute viscosity. Palumbos' (*Ind. vernice Milan* 6, 37) studies on viscosities of bodied oils show that they do not follow the law of Einstein which states that viscosity depends on the volume fraction of the more viscous ingredient. The discrepancy is explained as the result of solvation of the less viscous phase, and to the nonspherical nature of the macromolecules. Georgievskii & Shakhkel'dyan (*Zhur. Priklad. Khim.* 24, 772, 775) used viscosity measurements to demonstrate that linseed oil at 100° does not thicken in the absence of oxygen, that benzoyl peroxide destroys the induction periods, and that viscosity of linseed oil is related to the oxygen consumption, whereas, with tung oils more viscous products are obtained in the presence of benzoyl peroxide than without at the same oxygen consumption. Banks & Upton (*J. Oil & Colour Chemists' Assoc.* 33, 397) determine viscosity of bodied oil films during drying by a rolling-ball technique. They record data on linseed oil in which the induction period and the molecular weight changes are apparent.

Coating oils are also compared with regard to the characteristics of the films they produce. Elm (*Official Dig. Federation Paint & Varnish Production Clubs No. 322*, 701) measures the stress-strain properties of coating films by means of a special apparatus. The alkyd films give curves with consistent changes in the stress-strain characteristics during aging while pure oil film curves are inconsistent because of slow hardening. Pigments, when present, do not affect measurements. Oswald (*Ibid.* 308, 667) uses a special oven to study gas checking, frosting, and wrinkling of tung oil varnishes when dried in an atmosphere of nitrous oxide and in presence of other impuri-

ties. The faults are related to triene content, and are inhibited by heating the oil with pentaerythritol and by addition of phenolic resins. The latter is more suitable since the resulting films are more tolerant to mineral spirits and alkalies. A comparison of oxygen penetration during drying of oil films indicates more rapid oxygen penetration in greater amount per unit weight by thin films than by thick ones. (Carrick & Snoddon—*Ibid.* 322, 682). Tests on shrinkage of various films during drying indicate that it is greatest on the first day and is related to chemical reactions and progressive compaction of the film gel structure (Carrick & Permoda—*Ibid.* 692). The relative corrosion protection properties of various coatings are improved by the presence of pigments (Drimberg & Rokhlin—*Zhur. Priklad. Khim.* 24, 220, 233). Other data from these studies show that pentaerythritol ester films are superior to those of tung oil for coating metals susceptible to corrosion. Films of soybean oil, linseed oil, trilinolein, and trilinolenin are compared by Hess & O'Hare (*Ind. Eng. Chem.* 44, 2424) by determinations of weight gain, oxygen content, color, and alkali resistance. Yellowing is associated with the presence of linolenins; however, trilinolenin films are most alkali resistant.

Suggestions are made for improving the drying properties of certain oils. Special bodying procedures and removal of thinner fractions by distillation are used to obtain drying fractions from oils of rice (Shitamoto—*Japan 3730* [50]), pilchard (Joubert & Sutton—*J. Am. Oil Chemists' Soc.* 29, 287), and dolphin (Shmakova—*Rybnoe Khoz.* 27, No. 7, 58). For the same purpose crystallization procedures that remove nondrying constituents are used on oil of bonito (Doadrio & Lamo—*Anales real soc. espan. fis. y quim.* 48B, 169) and of cuttle fish (Tomiya—*Japan 520* [51]). Tobacco seed oil when used with alkyd, phenolic, and ester gums is said to yield better varnishes than comparable varnishes made with linseed oil (Rao et al.—*Paint Technol.* 16, 337). Heating olive oil in vacuum at 325° yields some polymerized resinous products (Petit & Bosshard—*Bull. soc. chim. France 1952*, 618). The mechanism in this process is believed to be a partial decomposition and polymerization of the decomposition products with undecomposed oil. Aenlle & Varela-Nunez (*Anales real soc. espan. fis. y quim.* 47B, 313) report that films made from sardine oil with cobalt or manganese driers are quite impervious to moisture.

The processes for converting castor oil or other oils containing hydroxy acids to drying products are based on dehydroxylation. Details of the methods involve use of definite temperatures, pressures, and catalysts. Processes are described using the following catalysts: phenol sulfonate (Dole & Keskar—*Proc. Oil Technol. Assoc. India* 6, 70), a combination of kaolin and sulfuric acid (Tsuchiya & Ohkubo—*Bull. Gov. Chem. Ind. Res. Inst. Tokyo Spec.*, No. 1-2; *Japan 181,411* [50]), phosphorous acid (Carter et al.—*Brit.* 671,368), and *p*-toluene sulfonic acid (Naudet & Desnuelle—*Bull. soc. chim. France 1951*, 655). Equipment is designed for continuous operation of the process (Colbeth—*U. S.* 2,567,925). Rubber-like gels useful as coating material are made from castor oil by heat treating followed by condensation with ethylene glycol (Council Sci. & Ind. Res.—*Indian* 43,149; Sen-Gupta & Aggarwal—*J. Sci. Ind. Res. India* 10B, 73). Fundamental studies of condensation of polyhydroxy acids to resinous substances as recorded by Basu (*J. Sci. Ind. Res. India* 10B, 79) contain information on activation energies, velocity constant, and structure of the products.

A method of improving drying qualities of oils is based on increasing the number of double bonds by chlorination and dechlorination. New details for such a process using *tert*-butyl-hypochlorite as the chlorinating agent and weakly alkaline salts for dechlorination are recorded by Teeter et al. (*J. Am. Oil Chemists' Soc.* 29, 367, 401; *U. S.* 2,557,159).

Tall oil and rosin acids are converted into drying oil products by esterification with pentaerythritol or other polyhydroxy alcohol (Ford, Jr. & Brewster—*Paint Oil Chem. Rev.* 115, No. 17, 14; Wittecoff & Roach—*U. S.* 2,572,086, 2,590,910; Bradley & Dannenberg—*Brit.* 674,841; Khudovkov—*Zhur. Priklad. Khim.* 24, 647). Esters of linseed oil fat acids and methyl-D-glycoside are said to be better for drying oil purposes than linseed oil (Gibbons & Janke—*J. Am. Oil Chemists' Soc.* 29, 467). Transesterification reactions from linseed oil to glycerol yields an oil compatible with turpentine and shellac for varnish making (Prakash et al.—*Proc. Oil Technol. Assoc. India* 6, 57).

The recently patented process for improving drying characteristics of oils by conjugating the double bonds makes use of quinoid compounds Aggarwal et al.—*Indian* 42,885, Radlove—*U. S.* 2,575,529), cobalt carbonyl (Blaser & Stein—*Brit.* 674,884), and alkalies (Grün—*Swiss* 270,751) to catalyze the

reaction. In producing this reaction in methyl linoleate by bromination followed by debromination the development of *cis,trans* systems from *cis,cis* is dominant; conversion of *trans,trans* to *cis,cis* is less apparent; whereas, there is practically no conversion to *trans,trans* (Jackson et al.—*J. Am. Oil Chemists' Soc.* 29, 229). An 8-*trans*, 10-*trans*-structure develops in ricinoleic acid dehydrated by distillation but not in processes using acid as the dehydrating agent (von Mikusch—*Ibid.* 114). This is also observed by Nichols, Jr. et al. (*Ibid.* 247) who report data on conjugation of linoleic acid. They observed that treatment with iodine causes *cis,trans*-conjugated isomers to change to *trans,trans*-products.

Some processes for improving drying of coating oils pertain to the catalyst used. Organic free radicals such as those containing three aromatic groups attached to oxygen or carbon, or two aromatic groups attached to nitrogen catalyze the process (Kaufmann & Strüber—*Fette u. Seifen* 54, 134). Aluminum alcoholates increase both the drying rate of the oil and the water resistance of the films produced (Schlenker—*Farbe u. Lack* 58, 351). Preparation procedures, optimum effective amounts for paint, and properties are recorded for several metallic soap drier solutions by Marwedel (*Ibid.* 395). A comparison of several metal soap driers for use with niger seed and safflower seed oils indicates that manganese and cobalt linoleates induce most rapid drying (Vidyarthi—*J. Sci. Ind. Res. India* 10B, No. 7, 170). Vogel (*U. S.* 2,569,206) aerates drying oils containing very small amounts of driers in order to inactivate natural oxidation inhibitors and destroy the induction period. Use of boron trifluoride as a polymerization catalyst results in bodied oils of light color and low acid number (Croston et al.—*J. Am. Oil Chemists' Soc.* 29, 331). Fast drying light colored films are produced from drying oils by heat treating with acetic anhydride (Vidyarthi—*J. Sci. Ind. Res., India* 10B, No. 9, 233). Bodying of oils is also improved by the presence of *cis*-1, 8-bis (*p*-hydroxyphenyl) methane (Geiger—*U. S.* 2,588,821) and sulfur (Boelhouwer et al.—*Chem. Eng. Sci.* 1, 117; *Dutch* 69,579; Slansky—*Paint Oil Chem. Rev.* 115, No. 19, 12). With the sulfur process, high alkali resistance in films is obtained.

Superbodied oils free from gel particles are prepared by Arvin (*U. S.* 2,607,784) by steaming just before the gelation point is attained. The process permits increase of viscosity without formation of gel. A bodying process designed by Hickman & Barnitz (*U. S.* 2,599,451) combines the process with recovery of vitamins and sterols by distillation. In the processes making use of peroxides to improve bodying, use is made of *tert*-alkyl peroxide (Wiebe—*U. S.* 2,588,902), *tert*-butyl-hydroperoxide (Opp & Werner—*U. S.* 2,574,753), and hydrogen peroxide, metal peroxide, or benzoyl peroxide (Kronstein—*U. S.* 2,599,397).

Descriptions on preparing modified drying oils, resinous products, and alkyds, suitable for protective coatings, linoleum, or other uses appear both in patents and literature communications (Carello—*Ital.* 461,821; Dazzi—*U. S.* 2,598,634; Jordan & Wittecoff—*U. S.* 2,579,499; Kass & Wicks—*U. S.* 2,577,770; Luce—*U. S.* 2,602,786; Oswald—*U. S.* 2,603,572; Rheineck—*U. S.* 2,569,495; Sarin et al.—*J. Sci. Ind. Res. India* 11B, 31; Schmutzler—*U. S.* 2,590,653-4; Sowa—*U. S.* 2,605,243; Stubblebine—*U. S.* 2,561,427; Toy & Brown—*U. S.* 2,586,885; Wittecoff & Roach—*U. S.* 2,572,085). Fundamental developments pertinent to their use pertain to correlation between properties of alkyds and composition of modifying fatty acids (Moore—*Ind. Eng. Chem.* 44, 2676), and data on effect of alkyds on the aggregation and dispersion of inorganic pigment suspensions (Gurevich—*Kolloid. Zhur.* 14, 93).

Procedures for improving drying oils by interpolymerization or reaction with styrene, butadiene, isoprene, vinyl compounds, and like material are very numerous (Armitage & Sleightholme—*U. S.* 2,586,593; Bednneau—*Rev. prod. chim.* 55, 1; Bezman & Browning—*Paint, Oil & Chem. Rev.* 114, No. 20, 10B; Bosch & Drubel—*Official Dig. Federation Paint & Varnish Production Clubs* No. 323, 894; Brit. Resin Products Ltd.—*Brit.* 674,155; Brunner & Tucker—*J. Applied Chem. London* 1, 563; Dow Chem. Co.—*Brit.* 656,994; Fisher et al.—*U. S.* 2,594,303; Gleason & Jaros—*U. S.* 2,581,094; Hammond—*U. S.* 2,563,784; Hillyer & Edmonds—*U. S.* 2,581,413; Kita & Wada—*Repts. Osaka Pref. Ind. Res. Inst.* 3, No. 3, 49; Marling—*U. S.* 2,587,497, 2,603,611; Meeske—*Verfkoniek* 23, 159; N. V. Bataafsche Petrol, Maatschappij—*Dutch* 68,954; Polly—*U. S.* 2,610,161; Port et al.—*U. S.* 2,586,860, *J. Polymer Sci.* 9, 493; Rust—*U. S.* 2,570,385; Schmutzler—*U. S.* 2,590,655; Sleightholme—*U. S.* 2,586,571-2; Tess et al.—*U. S.* 2,596,737; Wakely et al.—*Brit.* 672,224, Wynstra—*U. S.* 2,600,457). Petit & Fournier (*Bull. soc. chim. France* 1952, 287) and Falkenburg et al. (*J. Am. Oil Chemists' Soc.* 29, 7) demonstrate that no

true copolymerization between styrene and drying oils takes place during manufacture of styrenated oils. Homogeneity is attributed to mutual solubility. In one report advantage is taken of urea complex formation technique for separation of polymerized vinyl esters of fatty acids (Swern & Port—*J. Am. Chem. Soc.* 74, 1738). The saturated ester constituents are complexed with urea.

Other procedures for upgrading drying oils pertain to cooking with alkylphenolic resins (van Eijnsbergen & Pleysier—*Chim. peintures* 14, 255), treatment with alkylphenols and formaldehyde (DeGroot & Keiser—*U. S.* 2,568,118-19), use of polyamide resins (Speyer—*Paint Oil & Chem. Rev.* 115, No. 1, 7; Ralston *et al.*—*U. S.* 2,617,313), and reacting with polyisocyanates (Robinson & Waters—*J. Oil & Colour Chemists' Assn.* 34, 361) or with itaconic acid (Haines & Billelo—*Official Dig. Federation Paint & Varnish Clubs* No. 313, 125).

The varnishes prepared to dry to a wrinkle finish contain solvents, compounds, and oils generally used in normal varnishes but selection and treatment are in a manner to induce certain consistency, rate of evaporation of solvent, drying, etc., that will cause wrinkling (New Wrinkle, Inc.—*Fr.* 960,876; Waldie—*U. S.* 2,600,818; Moffett—*U. S.* 2,548,388; Kapur & Sarin—*J. Sci. Ind. Res. India* 10B, No. 7, 168). Insoluble metallic soaps are used to cause lacquer coatings to form transparent, dull, or matted film surfaces (Weidlich—*U. S.* 2,568,599). Water emulsion paints are made with normal coating oils, resins, and paint compounds, but selection is made so that the mixture will have emulsifying properties or an emulsifier is added (Heijmer—*U. S.* 2,567,433; Robinson—*U. S.* 2,586,092; Schulte & Herzog—*U. S.* 2,587,657; Henson & Edwards—*U. S.* 2,606,164).

**WATER INSOLUBLE METALLIC SOAPS, GREASES, AND OIL LUBRICANTS.** The literature on the physical properties of heavy metal soaps principally concerns those of interest for the manufacture of lubricating greases. Considerable data on the rheological properties of calcium soap are recorded graphically by Vinogradov & Klimov (*Zhur. Tekh. Fiz.* 18, 355; *Doklady Akad. Nauk S.S.S.R.* 71, 307). Strains under stresses, alternately, continually, and intermittently applied with a torsional elastometer are plotted to show changes caused by time under shearing stress, various periods of rest, temperature, etc. These data are discussed with regard to conformance with Hooke's law and influence of hysteresis, thixotropy, structure of the gels, and size of fiber micelles. Segalova *et al.*'s (*Kolloid Zhur.* 13, 461) data from work of similar utility comprise graphs of plastic strength, viscosity, and thixotropy of gels of calcium stearate and oleate with paraffin oil. The rheological properties of lithium soap grease are related also to fiber structure as determined by the electron microscope (Hotten & Birdsall—*J. Colloid Sci.* 7, 284). Lithium soaps of  $C_{14}$ - $C_{18}$  acids form rodlike micelles of 0.1 by 1  $\mu$  dimensions; the  $C_{12}$  are larger; those of unsaturated  $C_{18}$  acids are plump and of low gelling power; and lithium dihydroxystearate has high gelling power forming distinct intertwining fibrils. Moore & Cravath (*Ind. Eng. Chem.* 43, 2892) made use of electron microscopic micrograph technique to demonstrate that the softening of grease under stress of shearing results from breakdown of fibers into smaller particles. Lithium soap grease structure differences are also studied by a calorimetric technique (Evans *et al.*—*J. Applied Chem.* 2, 252). Solubilities and phase transformations are related to specific and latent heats. Similar technique is used on pure calcium, barium, and strontium stearates (Vinogradov—*Doklady Akad. Nauk S.S.S.R.* 58, 73). The soaps retain three percent moisture on air drying; exothermic effects of plastic modification appear at three different temperatures; and, on reheating, endothermic effects of structural changes in some cases are evident at four different temperatures.

Organic solutions of metallic soaps are studied also. Nelson and Pink (*J. Chem. Soc.* 1952, 1744) find that some of the soaps form unimolecular solutions in polar solvents. This work contains data on the micellar weights of soaps of various metals in toluene. Data on viscosity of benzene and toluene solution of aluminum mono- and distearate are graphically recorded by Inoue & Iida (*J. Chem. Soc. Japan Pure Chem. Sect.* 73, 71, 73). The influence of thixotropy, form of micelles, and temperature on the course of the curve are discussed. The dipole moments of several trivalent metallic soaps in benzene and in solutions containing alcohol have been determined (Banerjee & Palit—*J. Indian Chem. Soc.* 29, 175).

New infrared spectrum studies of the structure of aluminum soaps have confirmed that the mono- and di-soaps are discrete chemical compounds; whereas, tri-soaps do not exist (Harple *et al.*—*Anal. Chem.* 24, 635). According to Nelson and Pink (*Nature* 169, 620) tri-soaps of iron actually exist.

General communications on metallic soaps which tell of preparation, properties, and application are written by Wolff (*Bull. mens. I.T.E.R.G.* 5, 302; *Peintures, pigments, vernis* 27, 611), and Smith (*Am. Perfumer Essential Oil Rev.* 59, 123). Another paper is on lithium soaps particularly with regard to making greases for special purposes (Vamos & Hadfy-Kovacs—*Magyar Kem. Lapja* 5, 269).

An organized series of mixers and centrifuges is patented for manufacturing metallic soap and converting it continuously into lubricating grease (Cornell—*U. S.* 2,584,424). For making anhydrous aluminum and magnesium soaps Hunn (*U. S.* 2,582,833) reacts the powdered metals and fatty acids in alcohol solution in the presence of mercury compounds as catalyst. Aluminum soaps of aromatic and aliphatic anions such as aluminum benzoate stearate are made for use in grease, as a coating-flattening agent, or as a water proofing agent (Hotten—*U. S.* 2,599,553). Aluminum soaps of naphthenic and dimerized linoleic acids are used as gelling agents for diesel fuel (Dean—*U. S.* 2,620,345). A tall oil calcium soap, made with 50-100% more lime than is required to produce a neutral soap, is intended for use in film-forming compositions (Mahler—*U. S.* 2,616,814). A combination of metallic soaps with lubricating oil to form gels of desirable texture by special heat treatment and homogenization is patented by Moore & Saarni (*U. S.* 2,588,556). A lithium soap grease for packaging in an aerosol dispenser is made to a desirable physical structure of the soap fiber in excess oil and then some of the oil is leached from the grease with a solvent (Browning—*U. S.* 2,580,654). Bailey & Whitney (*U. S.* 2,598,154) manufacture grease by dispersing the soap in oil under pressure in the presence of a volatile diluent which is afterwards flash evaporated in a manner to provide cooling.

The innovation in some greases pertains to the choice of the cation of the soap. Special combinations of soaps of lithium and potassium are used to induce good initial penetration qualities (Whitney—*U. S.* 2,623,017). Special blends of sodium-barium greases give good structural stabilities (O'Halloran—*U. S.* 2,588,279; O'Halloran & Kolfenback—*U. S.* 2,588,280). Greases of superior high temperature properties are derived from calcium soaps in combination with soaps of metals of lower molecular weight (Sproule *et al.*—*U. S.* 2,607,735). A grease made in brick form contains sodium soap and heavy mineral oil and is intended for lubrication of heavy machinery (Sproule & King—*U. S.* 2,591,630). A hard brick grease contains sodium and calcium soaps and a small amount of ester of fatty alcohol and adipic acid to inhibit cracking (Ogden *et al.*—*U. S.* 2,588,326).

Special greases particularly for use at high temperatures contain metallic soaps of acid mixtures containing some very high melting members (Morway *et al.*—*U. S.* 2,581,127, 2,583,435-6, 2,586,693, 2,589,973, 2,591,586, 2,599,343, 2,599,383, 2,610,947, 2,618,598; Teeter & Nelson—*U. S.* 2,590,801; Nelson—*U. S.* 2,590,786). Hydrogenated fish oils, rapeseed oil, and certain waxes are sources for these fatty acids. Branched chain high molecular weight acids and aromatic compounds with fatty side chains are also mentioned. Calcium soaps of hydroxy fatty acids are used in greases having high dropping point (Sproule *et al.*—*U. S.* 2,607,734). The metal soaps used by Worth *et al.* (*U. S.* 2,595,566-7) for grease-making are complexed with urea or are oxidized. Patents were issued also for using tall oil or rosin as the acid component of the metallic soaps intended for grease manufacture (Sato—*Japan* 172,077 [46]; McCarthy—*U. S.* 2,580,570).

Various substances are added to lubricants to improve certain properties. The new additives for improving and stabilizing the gel structure are esters of polyalkylene glycols (N. V. de Bataafsche Pétrol, Maatschappij—*Dutch* 67,825; Sterman—*U. S.* 2,585,182), oxy acids of phosphorus (Butcock—*U. S.* 2,585,321), a mixture of partial fatty acid esters of sorbitan and a substituted glyoxalidine (Nelson *et al.*—*U. S.* 2,581,132), amines prepared from fatty acids (Bryant & Frost, Jr.—*U. S.* 2,594,286), alkali metal salts of fatty amates (Bryant & Giordano—*U. S.* 2,604,449) and a choice of amino fatty acids, fatty acid sulfonates, and others (Abrams & Stross—*U. S.* 2,599,683). Sirianni & Puddington (*U. S.* 2,583,607) improve the structure of soap greases by addition of dibasic carboxylic acids of two- to six-carbon atoms. Styrene polymers and organosilicon compounds are used to thicken and waterproof grease (Sirianni *et al.*—*U. S.* 2,583,603-6). The newly patented pour point depressants are alcohol esters of liquid fatty acids (Morita—*Japan* 172,148), certain aluminum soaps (Wakama & Hara—*Japan* 181,436 [50]), esters of acetic acid and fatty alcohols (Bartlett—*U. S.* 2,575,992). Dropping point, consistency, and surface activity of soap greases are improved by addition of colloidal titanium dioxide (Maltz—*Ger.* 803,781

*Cl 23c*). The communications on lubricant viscosity modifiers describe the use of a combination of phosphorus pentasulfide-treated sperm oil and styrene-isobutylene copolymers (Smyers & Young—*U. S. 2,595,819*), alcohol esters of acids derived from carbonization of coal (Montgomery *et al.*—*U. S. 2,568,965*), liquid dialkyl esters of bis (hydroxylalkyl) sulfides (Ballard *et al.*—*U. S. 2,603,604*), and dicarboxylic acid ester of nonadecyl alcohol (McKeever—*U. S. 2,599,468*). The grease additives for extreme pressure lubrication are sulfurized sperm oil (Cyphers & McNulty—*U. S. 2,580,005*), heterocyclic acids (Morway & Kolfenbach—*U. S. 2,581,126*), and fatty alcohol esters of dibasic acids (Morway and Smith, Jr.—*U. S. 2,588,273*), soap of phosphated hydrogenated castor oil (Knowles & Eckert—*U. S. 2,600,058*), metal soaps of acids with less than seven carbon atoms (Schott & Armstrong—*U. S. 2,583,394*), and boron trifluoride treated fatty material (Kipp—*U. S. 2,611,742-6*). The materials added to lubricants to inhibit corrosion are alkaline earth sulfonates (Eckert—*U. S. 2,610,946*), addition products of amino bicyclohexyl and fatty acid phosphate (Vaughn—*U. S. 2,605,226*), fatty, unsaturated hydrocarbon and phosphorus sulfide reacted together (Musselman—*U. S. 2,606,182*), combination of propylene glycol esters of coconut oil fatty acids and bis (methyl cyclohexyl) dithiophosphate (Sproule & King—*U. S. 2,587,545*) and oleic acid salts of amino alcohols (Matuszak—*U. S. 2,587,546*). The new detergent additives for removing deposits from piston rings are sulfonated detergents (Martes—*U. S. 2,623,016*), wool grease treated with phosphorus sulfide (Brennan & Williams—*U. S. 2,582,958*), and thiuronium salts of phosphonic acids of fatty or aromatic organic compounds (Mikeska—*U. S. 2,605,278*). The new antioxidants suitable for lubricants are fatty nitriles which have been treated with phosphorus sulfide (Bartleson—*U. S. 2,584,977*, Musselman & Lankelma—*U. S. 2,587,642*), thienylthio carboxylic acids (Brooks—*U. S. 2,581,626*), bis (5-methyl-2-hydroxyphenyl) sulfide (Morway and Young—*U. S. 2,595,161*), an ion exchange resin (Armstrong & Butcosk—*U. S. 2,605,225*), trioleyl phosphate (Oberright—*U. S. 2,589,326*), and compounds prepared by treating halogenated fatty acids with sodium selenide (California Research Corp.—*Brit. 655,608*).

In regions without petroleum resources, efforts are made to convert fatty oils to petroleum lubricant oil uses. Data on the efficiencies of domba, hongay, and mohua oils and their oxidized and polymerized products as motor lubricants are recorded by Thiagarajan & Srikantan (*J. Indian Chem. Soc. Ind. & News Ed. 13*, 201, 210, 219, 227). Lamel & Wist (*Austrian 172,065*) mixed the fatty oils with petroleum oils under influence of ultrasonic waves. Another means of blending fatty with mineral oils for lubricating uses is to arylate the fats according to the Friedel-Crafts reaction (Compagnie française raffinage—*Fr. 973,170*). Refluxing vegetable oils with 10% sulfuric acid is said to yield good lubricant oil (Ueno—*Japan 173,337* [46]). Hydrogenation of castor oil followed by partial decarboxylation by heating with aluminum chloride or boron trifluoride produces a light lubricant (Maruta *et al.*—*Japan 172,139* [46]). Yields of lubricating oils by pyrolysis of various fatty oils with several catalysts are recorded by Tokunaga (*J. Fuel Soc. Japan 29*, 243, 289). Squalene, a by-product of fish liver oil fractionation, is recommended as a lubricant either unprocessed or processed by hydrogenation or by polymerization (Fukushima *et al.*—*Japan 180,491* [49]; Aoyama—*Japan 38* [50], Akiyama & Tsuchiya—*Bull. Govt. Chem. Ind. Res. Inst. Tokyo Spec. No. 8 and 9*; Yamasaki—*Japan 2115* [50]).

A comprehensive treatise on the oils used in the woolen textile industries contains information on oil shrinkage, carding, static control, oil removal, and effect of oil on dyestuff and on spinning (Ryberg—*Am. Dyestuff Reporter 41*, 189). Fundamental data on preparation of bone oil useful for textile and metal cutting lubrication by removing "stearin" through crystallization from acetone is recorded by Petrovskii & Komarova (*Myasnaya Ind. S.S.S.R. 23*, No. 5, 76). In this work solutions of from 5 to 90% bone oil in acetone are crystallized at temperatures from 10 to  $-19^{\circ}$  and composition and characteristics of the fatty components in the solid, oil in acetone, and acetone in oil phases are determined. The newly patented cutting oils are pine, hinoki or cryptomeria oils emulsified in aqueous soap or sulfonated oil solutions (Morimoto—*Japan 3726-7* [50]), sea eel oil saponified with lye, polymerized at  $250-80^{\circ}$ , and mixed with aqueous ammonium hydroxide solution (Yamagishi *et al.*—*Japan 172,605* [45]), a mixture of hydrocarbon polymers, soft wax, and halogenated fatty acids (Perry & Talley—*U. S. 2,621,159*), and a blend of light petroleum oil with fatty material such as lanolin, oleyl alcohol, and olein (Jahn—*U. S. 2,605,224*). Lubrication of metal stock for wire drawing is

achieved with a mixture of borax and partial fatty acid esters of polyhydroxy alcohols (Orozco & Roy—*U. S. 2,573,585-6*). In a comprehensive treatise on steel wire drawing, lubrication with lime, soap, phosphate coating, soap powder, graphite, and powdered copper are discussed (Boshin—*Kinzoku 21*, 342). Cottonseed, palm, and coconut oils, and alkyl esters of dibasic acids used as surface lubricants for tin plate are made to adhere to the metal by use of emulsifying agents (Allen—*U. S. 2,579,777*). A hard and tenacious lubricant for coating electrical conduits contains higher saturated fatty acids (Couchman—*U. S. 2,597,706*). A twister-ring lubricant comprises petroleum oil and a minor proportion of normal fatty amino-phenol (Morway & Young—*U. S. 2,604,452*).

## Deterioration

REVIEWS ON THE SUBJECT. The new general discussion and review papers on fat spoilage are written on rancidification of fatty oils (Carola—*Olii minerali grassi e saponi colori vernici 29*, 3), mechanisms of oxidation of fats (Ishii—*J. Oil Chemists' Soc. Japan 1*, 85), chemical and physical agents causing alterations in fats (Valverde & Guillema—*Actas y trabajos Congr. peruano quim. 2*, 603), fat studies and antioxidants in the U.S.A. (Marcuse—*Fette u. Seifen 54*, 530), flavor deterioration of fats (Lips—*Food in Canada 12*, No. 6, 9) application of antioxidants (Raeithel—*Z. Lebensm.-Untersuch. u. Forsch. 95*, 246), selection and application of antioxidants to a variety of foods (Bentz *et al.*—*Food Technol. 6*, 302), use of propyl gallate as an antioxidant (Molinari—*Olii minerali grassi e saponi colori vernici 25*, 70), and pharmacological evaluation of antioxidants (Lehman *et al.*—*Advances in Food Res. 3*, 197). A paper on "chemicals in food" deals principally on use of antioxidants to stabilize fats and vitamin A against oxidative deterioration (Lea—*Chemistry & Industry 1952*, 178).

TESTS FOR DETERIORATION AND ANTIOXIDANTS. Several investigations concern improvement of existing methods for measuring deterioration. In the iodometric estimation of peroxides in fat Hartman & White (*Anal. Chem. 24*, 527) recommend a 10% solution of citric acid in a mixture of tert-butyl alcohol and carbon tetrachloride in place of the acetic acid-carbon tetrachloride mixture which is usually used. This alteration with exclusion of air eliminates high blank titration and may eliminate the need of running a blank. The photometric ferric thiocyanate method of Hills and Thiel is modified by extracting the fat with benzene, making the extract miscible with aqueous reagents by addition of methanol and mixing ferric chloride with ammonium thiocyanate before adding it to test solutions (Smith—*J. Sci. Food Agr. 3*, 26). This permits better reproducibility in the fat peroxide estimations. Alcala & Quijano (*Anales real soc. espan. fis. y quim. 48B*, 255) recommend addition of sodium bicarbonate to the reaction mixture of the Wheeler peroxide method so that the adverse effect of air is inhibited by the carbon dioxide evolved. The dichlorophenol-indophenol method also gives high peroxide values owing to interference by atmospheric oxygen (Hartman & White—*J. Sci. Food & Agr. 3*, 112).

The color developed on fats and pure compounds in the thio-barbituric test, the Kreiss test, and the Hartmann-Glavind test for fat spoilage was measured spectrophotometrically (Glavind & Hartmann—*Acta Chem. Scand. 5*, 975). The color in the first two develops from various complex compounds, whereas that of the latter is a specific reaction for peroxides. Lea's (*J. Sci. Food & Agr. 3*, 586) comparisons of peroxide estimations show that the iodometric, the 2,6-dichlorophenolindophenol, and the ferric thiocyanate methods are all affected by atmospheric oxygen, but the latter gives the best reproducibility. In comparison of rancidity in pork by peroxide value and organoleptic characteristics the flavor is more closely associated with peroxide value than is the odor (Naumann *et al.*—*Food Technol. 5*, 496). Schmalzfuss (*Fette u. Seifen 53*, 689) recommends that reports on spoilage characteristics of fats be standardized. He proposes peroxides be recorded in Lea value, acidity in milligrams potassium hydroxide required for neutralization, ketones in micrograms of methyl nonylketone, aldehyde in micrograms of heptaldehyde, and epihydrinaldehyde also in micrograms; all being based on one gram of fat.

A new method for estimating spoilage of fats is based on determination of carbonyl groups by means of reaction with hydroxyl amine (Drozdov & Materanskaya—*Myasnaya Ind. S.S.S.R. 23*, No. 3, 73). The result is corrected for the amount of acidity in the original sample.

The rapid  $\alpha$ -naphtholphthalein colorimetric test for water-insoluble acids, previously used for butter, is modified for

application to cream by using a mixture of ethanol and petroleum ether for extracting the fat for analysis (Harper & Armstrong—*J. Dairy Sci.* 35, 342).

A report on collaborative work on the determination of the antioxidant propyl gallate in fats by the ferrous reagent method indicates that average recovery is 90% and nordihydroguaiaretic acid and tocopherols do not interfere but gallic and tannic acids do (Kahan—*J. Assoc. Off. Agr. Chemists'* 35, 186).

**MECHANISM OF DETERIORATION.** According to Treibs & Rothe (*Chem. Ber.* 84, 370) autoxidation of 1,3- and 1,4-spaced unsaturation of fatty acids results in formation of peroxides, not hydroperoxides, as primary products; whereas with oleic acid hydroperoxides are formed and there is some migration of the double bond in the molecule. A comparison of the oxidation of ethyl, propyl, and butyl oleates indicates that maximum peroxide formation decreases from ethyl to butyl oleate (Feuell & Skellon—*J. Chem. Soc.* 1952, 59). Also, in this work, it is shown that oleic (cis-) esters react more rapidly than elaidic (trans-) esters. In the fat autoxidation work of Glimm *et al.* (*Fette u. Seifen* 54, 462) the changes in characteristics and the development of hydrogen peroxide are studied. At maximum peroxide value, the acid and saponification values have risen, and the iodine value has dropped to a value equivalent to that of the thiocyanogen value. Under anhydrous conditions, water is split off and this moisture is necessary for the progress of the reaction. On standing five to six weeks, hydrogen peroxide develops but never exceeds one percent. On development of hydrogen peroxide the saponification value decreases and the acid value increases. In following the autoxidation of various fats by polarography Nagami *et al.* (*J. Pharm. Soc. Japan* 71, 813, 818) observe a reduction wave due to the double bond of oleic acid, besides two distinct waves and a maximum wave due to unstable peroxides that form in the initial stage of autoxidation. These unstable peroxides turn to stable peroxides which can be determined by chemical methods but not by polarography.

An entirely different hypothesis on the rancidification reaction is proposed by Saletore (*Rept. Proc. Symposia on Fuels, Fats & Oils and Res. Ind. India* 1950, 141). He has observed that some samples of sesame oil develop rancid odor at peroxide value of about 60 whereas others at 175 did not have a disagreeable odor. Since the degree of oxidation and rancidity do not seem related, he presumes that nitrogen of the air is involved. His analyses show 21-129 milligrams per 100 grams of fixed nitrogen in various oils which is not due to protein, extraneous matter, bacteria, or enzymes; he also demonstrates that the fixed nitrogen is increased in samples by aeration.

In analyses on volatile cleavage products of autoxidized soybean oil, acetaldehyde, propionaldehyde, 2-pentenal, and hexanal are identified and strong evidence for presence of crotonaldehyde is presented (Kawahara & Dutton—*J. Am. Oil Chemists' Soc.* 29, 372).

**FACTORS THAT AFFECT STABILITY OF FATS.** A comparison of peroxide value and stability of olive oils shows that they develop considerable amounts of peroxides (Hadorn & Jungkuntz—*Mitt Gebiete Lebensm. Hyg.* 42, 281). It is presumed that the high peroxide development and the high squalene content in olive oils are related. Differences in the stabilities of individual animal fats are assumed to be related to the natural antioxidants present (Petrovskii—*Myasnaya Ind. S.S.S.R.* 23, No. 3, 30).

Various processing operations are investigated for their effect on the stability of fatty products. The changes in fatty acid composition and natural tocopherol content in cottonseed oil fractions obtained in winterizing are such that they counterbalance one another and lead to the same final stability in each product (Mack *et al.*—*J. Am. Oil Chemists' Soc.* 29, 14). That is, the winterized fraction contains sufficiently more tocopherol to give it a stability equal to that of the more saturated stearin fraction. In fish oil recovery by boiling, pressing, drying, and extraction, major spoilage occurs in the drying operation (Perepletshik—*Rybnoe Khozyaistvo* 24, No. 5, 38). In this work methods for shortening or elimination of drying are suggested. A difference in susceptibility to oxidation of hydrogenated oils is attributed to different quantities of highly unsaturated fatty acids remaining in the products (Ueno & Shigeno—*J. Chem. Soc. Japan Ind. Chem. Sect.* 53, 228).

The changes in characteristics and compositions of fats in meats during home storage and cooking are tabulated by Chang *et al.* (*J. Am. Oil Chemists' Soc.* 29, 334, 378). Peroxidation occurs in freezer storage. Roasting causes development of peroxides, the drippings being highest. Very high peroxide

values developed during storage decrease during cooking; but drippings, especially from pork, have a rancid odor. The loss of linolenic acid during roasting or frying is not significant.

Privett (*Ann. Rept. Hormel Inst. Minn. 1950-51*, 11) demonstrates that considerable oxidative changes may occur in meats before the meat becomes unpalatable through proteolytic deterioration. This work is intended to show that errors in fatty acid analyses of natural meat fats may be caused by presence of oxidized fatty acids. He (*Ibid.* 6) also demonstrates that a catalyst for oxidation of fat is present in pork tissue. It can be extracted with 50% ethanol salt solution. Another study of the oxidation catalyst in pork tissue indicates that significant quantities of lipoxidase cannot be demonstrated, and that myoglobin and hemoglobin may be the predominant prooxidants involved (Tappel—*Food Research* 17, 550). In a study of lipovitellin of egg yolk, uncatalyzed oxidation of the lipid part did not seem inhibited by the protein moiety, but the protein gave considerable protection against the catalytic action of copper and of hemin, but not against the weaker catalytic action of hemoglobin (Lea & Hawke—*Biochem. J.* 50, 67). The oxidation in these tests is accelerated as acidity is increased, and further acceleration is caused by the presence of salt.

The rate of oxidation of bacon in freezer storage is directly related to the concentration of the salt in the bacon (Gaddis—*Food Technol.* 6, 294). Thome (*Svenska Mejeritidningen* 42, 195, 207) in recommendations for preserving butter quality suggests that for direct consumption the product should not be salted, whereas, for storage salting should be with salt containing some sodium carbonate and sodium acid phosphate and the pH should be at least six but no greater than seven.

Autoxidation of linoleic acid during x-ray irradiation is reduced under anaerobic conditions or in the presence of cysteine (Mead—*Science* 115, 470). Peroxidation of fats induced by high velocity electrons is greater at higher temperatures, but the after effect, i.e., accelerated oxidation after treatment, is maximum in fats treated with the high-velocity electrons at  $-20^{\circ}$  (Hannan—*Nature* 169, 152; Hannan & Shephard—*Nature* 170, 1021).

Moisture, ammonium chloride, and excess (0.3%) vitamin E increase rate of peroxidation of chicken fat; whereas, certain low concentrations (optimum at 0.03%) of vitamin E and absence of moisture render the fat most stable (Phillips & Williams—*Food Technol.* 6, 74). Addition of vitamin E to the diet of cockerels increases the stability of the fat deposited in the skin; but feeding choline or betaine has no effect. Feeding tocopherol to dairy cattle at the beginning of the winter feeding improves the ability of the milk and butterfat to resist development of oxidized flavor, but is ineffective when the cows are shifted to tocopherol feeding towards the end of the winter season (Krukovsky & Loosli—*J. Dairy Sci.* 35, 834).

Of two papers on general fat preservation information, one tells how the stability of 12 fatty food items is increased 43-4300% with the use of antioxidants (Bentz *et al.*—*Food Technol.* 6, 302), and the other assesses commonly approved antioxidants for stabilizing steam-rendered lard (Gemmill—*Food Eng.* 24, No. 5, 102).

The antioxidant properties of a series of aromatic hydroxy, amino, and quinoid compounds were investigated in two laboratories. Täufel's & Rothes' (*Fette u. Seifen* 53, 381) investigations are on olive oil as the substrate. In general the aromatic hydroxy compounds are more effective than the aromatic amino or quinoid compounds. The antioxidant effect of a hydroxy compound is further enhanced by addition of one more OH or NH<sub>2</sub> group, by quinone formation, and by distribution of OH or NH<sub>2</sub> groups among the rings of polynuclear groups. Meiers' & Mebes' (*Farbe u. Lacke* 53, 215) tests of these compounds are made on linseed oil and the criteria are weight gain and drying time. The efficiency of the antioxidants parallels their reducing power, as measured by their normal oxidation-reduction potential. With the nitrogen compounds, nitrogen is lost during the oxidation. With the amino compounds drying rate does not parallel increase in weight; the former is much slower. Tests on antioxidants for stabilizing lard and cottonseed oil are recorded by Moore & Bickford (*J. Am. Oil Chemists' Soc.* 29, 1). At 0.10% content the order of increasing effectiveness in cottonseed oil is: control, di-tert-butyl-*p*-cresol, sesamol, nordihydroguaiaretic acid, norcinnendrin, hydroquinone, and propyl gallate; and for lard: control, lecithin, gum guaiac,  $\alpha$ -tocopherol,  $\gamma$ -tocopherol, butylated hydroxyanisole, di-tert-butyl-*p*-cresol, sesamol, norcinnendrin, hydroquinone, nordihydroguaiaretic acid, and propyl gallate. In tests on comparative evaluation of 89 antioxidants for inhibiting oxidation of carotene, the most effective

are hydroxy- and amino-substituted diphenylamines, *p*-substituted phenylenediamines, and derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline (Bickoff *et al.*—*Ibid.* 29, 445). Kartha (*J. Sci. & Ind. Res. India 11B*, No. 6, 263) suggests that antioxidants be tested for resistance to destruction and for efficiency in dilute solution of substrate oil. A non-volatile and stable solvent for the purpose is coconut oil that has been oxidized with potassium permanganate and washed to zero iodine and acid values.

Mack & Bickford (*J. Am. Oil Chemists' Soc.* 29, 428) report that  $\alpha$ - and  $\beta$ -conidendrols are equally efficient antioxidants and are superior to butylated hydroxyanisole, di-*tert*-butyl-cresol, hydroquinone, and others for vegetable oils, lard, GR-S type polymers, and vinyl type monomers. Because the 3-*tert*-butyl-4-hydroxyanisole has been reported more effective than the 2-isomer, Mahon and Chapman (*Anal. Chem.* 24, 534) have devised a procedure for estimating the 3-isomer in commercial preparations. For frozen stored cream containing copper, Gelpi, Jr. *et al.* (*J. Dairy Sci.* 35, 93) find that ethyl caffeate is more efficient than butylated hydroxyanisole alone or with synergists. The anti-rancidity properties of nordihydroguaiaretic acid in various lards and the baked products containing the protected lards are recorded by Dalmau (*Afinidad* 28, 205). Improvement is obtained with citric acid as a synergist. The antioxidant affords greater protection in cake than in crackers because of the latter's alkalinity. In a specific test on the influence of pH on antioxidant properties of nordihydroguaiaretic acid and hydroquinone, the efficiency is found to diminish gradually at pHs from 5 to 9.2 and is practically nil at 9.2 (Spetsig—*Svensk Kem. Tid.* 64, 191). In a test on whole milk powder, the effect of using synergists (ascorbic or citric acid) with nordihydroguaiaretic acid is not noticeable until after nine months' storage (Busch *et al.*—*J. Dairy Sci.* 35, 524).

Various alkyl esters of gallic acid are demonstrated to be good antioxidants for lard; whereas, the acid itself is found to be unstable at baking temperatures (Rutkowski—*Koeczniki Państwowego Zakładu Hig.* 3, 71). In tests by Bickoff *et al.* (*J. Am. Oil Chemists' Soc.* 29, 51) with pyrogallol derivatives all those that are more effective than pyrogallol in protecting carotene in mineral oil are much less effective than pyrogallol in lard and, with two exceptions, are also less effective in coconut oil. A kinetic study of the antioxidant reaction of tocopherol indicates that it reacts with the initially unstable form of peroxides rather than the final more stable form (Dubouloz *et al.*—*Oleagineux* 7, 265). An antioxidant for butter is extracted from whey (Thomé *et al.*—*Meddelande No. 32*).

The effectiveness of sulfur compounds for improving the keeping quality of fats and oils has been recorded. Heating lard with 0.05% sulfur for four hours at 180° combined with a subsequent addition of 0.02% gallate antioxidant considerably improves the keeping quality (Bertram & Wynia—*J. Am. Oil Chemists' Soc.* 29, 629). Alkylmercapto ketones are also shown to be effective antioxidants for lard (Thompson *et al.*—*Ind. Eng. Chem.* 44, 1659). In an investigation of many sulfur compounds, sym-diphenyl-thiourea, sodium sulfite, sodium thiosulfate, benzenthionol, cysteine-HCl, cystine, and *S*-methylisothiourea sulfate are found effective (in decreasing order); thionalide, thiourea, and 1-phenyl-2-thiourea accelerate autoxidation, and many other sulfur compounds tested have only slight or no effect (Sumiki *et al.*—*J. Agr. Chem. Soc. Japan* 25, 237).

Successful use of an antioxidant is reported for the protection against rancidification of the skin fat of frozen stored turkeys (Klose *et al.*—*Food Technol.* 6, 308), and for the fat of frozen creamed turkey (Lineweaver—*Ibid.* 1). Similar tests on cold-stored herring indicate that antioxidants are ineffective (Banks—*J. Sci. Food Agr.* 3, 250).

Tests on 78 samples of spices show that all, except one sample of ginger, are effective antioxidants for lard (Chipault *et al.*—*Food Res.* 17, 46). Rosemary and sage exhibit pronounced antioxidant effects. The petroleum ether extracts of the spices, with few exceptions, are ineffective.

A new antioxidant, 3,4-bis(*m,p*,dihydroxyphenyl)-*n*-hexane is more toxic than nordihydroguaiaretic acid when measured by the decrease in body weight produced in rats (Takata *et al.*—*Vitamins* 5, 126, 203, 206). In this work another antioxidant, 2,6-bis(4-hydroxy-2-methyl-5-isopropylbenzoyl)-*p*-cresol is found to be less toxic than antioxidants now in use in margarines. Itaconic acid, another oxidation inhibitor, at two percent levels in the diet is not toxic to rats (Booth *et al.*—*J. Biol. Chem.* 195, 697). High doses of tocopherol acetates diminish the storage of vitamin A in the livers and kidneys of rats fed moderate amounts of  $\beta$ -carotene (Swick & Baumann—*Arch. Biochem.*

*Biophysics* 36, 120). Vitamin E (tocopherols) is said to play a significant role as an antioxidant *in vivo* (Dam.—*Fette u. Seifen* 54, 633).

The newly patented methods for stabilizing fats, oils, or vitamin A pertain to the use of various aromatic substituted ethanolanilines (Hill & Baldwin—*U. S.* 2,576,458), a mixture of tocopherol and palmitoyl ascorbate (Rigby—*U. S.* 2,582,395), *p*-toluene sulfonic acid (Schwab *et al.*—*U. S.* 2,583,602), gallic acid esters of C<sub>8</sub>-C<sub>12</sub> aliphatic alcohols (Tollenaar—*U. S.* 2,586,274), iminodisuccinic acid (Cowan & Evans—*U. S.* 2,594,294), substituted coumarins (Chenicek & Gleim—*U. S.* 2,599,810), acetondicarboxylic acid (Schwab *et al.*—*U. S.* 2,605,186), a mixture of propylene glycol with an alkylated hydroxyphenyl ether with or without alkyl gallic acid ester (Magoffin—*U. S.* 2,607,745-6), phytic acid (Evans *et al.*—*U. S.* 2,610,973), and azo dye yellow OB or yellow AB (Ohoka—*Japan* 686 [51]). Patents on inhibiting rancidity in soap pertain to use of a mixture of isosafroegenal and sodium silicate (Tomiya *et al.*—*J. Oil Chemists' Soc. Japan* 1, No. 1, 17), and freshly precipitated aluminum hydroxide (E. A. Kollontay Chem. Fabrik—*Austrian* 165,888).

**FLAVOR REVERSION.** Processing operations have been investigated for their influences on the flavor reversion of oils. The work of Evans *et al.* (*J. Am. Oil Chemists' Soc.* 29, 61) is principally on the effect of the processing stages as related to the content of copper and iron in the oil. These metals are capable of promoting the flavor reversion. In general, refining removes 95-98% of the metals from the oil, but deodorization sometimes increases the iron content 40 fold. The deodorization process is the most critical and sometimes a very damaging process to the stability and quality of soybean oils. Lips *et al.*'s (*Can. J. Technol.* 30, 1) work of the same type pertains to the effect of different refining procedures. Refining of solvent-extracted oil while still in the solvent yields oil no different in stability than standard refining. Treatment of soybean oil with activated magnesia or with hydrochloric acid after alkali refining is detrimental to flavor stability. The adverse influence of deodorization on flavor stability is demonstrated also with rapeseed oil (Delobez & Mestreit—*Bull. mens. ITERG* 5, 468). A means for retardation of reversion flavor in hydrogenated fats is based on treatment with or passage of the oil through activated alumina, activated bauxite, or activated aluminum silicate previous to the hydrogenation (Lange & Folzenlogen—*U. S.* 2,589,097). A process for protecting fatty and phosphatide-containing products from getting an unpleasant taste and odor comprises heating them to 80° with reducing sugars and adding alkali to raise the pH to about nine (Sjorstrom & Larsson—*U. S.* 2,609,297). This process is intended for margarine and dairy products.

In a study of flavor of canned Florida Valencia orange juice, several polyunsaturated fatty acids have been identified which might be involved in off-flavor development of the product (Swift—*Food Res.* 17, 8).

**MICROBIOLOGY AND FATS.** In a study of fishy flavor due to trimethylamine oxide development in fats no mechanism has been visualized for development of the compound other than reduction by micro-organisms associated with bacterial spoilage (Lea & Rhodes—*J. Sci. Food & Agr.* 2, 556). This compound is rapidly reduced by autoxidizing unsaturated fats at 100°.

Ketone rancidity of fats is of microbiological origin; *Penicillium glaucum* being quite active for producing ketones from C<sub>4</sub> to C<sub>14</sub> fatty acids (Thaler—*Angew. Chem.* 62, 40). For this type of rancidity Mukherjee (*Arch. Biochem. Biophys.* 33, 364) claims that oxygen is necessary and suggests that the mechanism includes hydrolyses, oxidation of the acid, desaturation of saturated acids by dehydrogenase, and decomposition. Oily-flavor development in butter, however, is attributed to formation of  $\alpha,\beta$ -unsaturated carbonyl compounds (Holm *et al.*—*Medd. Statens Mejerforsok No. 37*, 14). Oily-flavored butter from ripened cream contains the  $\alpha,\beta$ -unsaturated carbonyl compounds in quantities related to the intensity of the off-flavor. Putrefactive and cheesy types of off-flavor in butter are attributed to microbial decomposition in the serum rather than the fat (Diatchenko—*Lait* 31, 308, 505).

Methods for studying the bacterial hydrolysis of fats have been developed by Goldman & Rayman (*Food Res.* 17, 326). Fats in emulsions containing less than 10 grams of fat per 100 ml. of solution are completely hydrolyzed by *Pseudomonas fluorescens*; at 20 grams of fat per 100 ml. of emulsion 90-95% of the fat is hydrolyzed. The lipolytic power of different strains of *Pseudomonas* vary widely in both rate and extent of hydrolysis.