72% transmittancy of the feed to 99% T. of the final effluent.

Table I summarizes the entire process. The analyses are a fair average over many runs and do not indicate finished stocks from the particular sweetwater shown. It should be noted however that with very highly colored sweetwaters from the splitting of poor crude oils or foots somewhat less spectacular results would be obtained. Dilution of such sweetwaters with better grade stock minimizes a low throughput and a dark finished glycerol. Addition of another cation-anion exchanger and/or a decolorizing resin bed would be recommended to process such materials for the production of C.P. glycerol.

TABLE I

Note: Analyses shown are averages.

| | Sweetwater | Crude Glycerol | Deionized Glycerol |
|---|---|---|---|
| % Glycerol | 9.1 | 94.5 | 95.02 |
| R. I. at 25°C | 1.3435 | ........ | 1.4662 |
| % Ash | 0.2 | 1.4 | 0.006 |
| Color | ........ | Dark Brown | 2.5Y-0.2R |

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

## Report of the Literature Review Committee *

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### Introduction

STATISTICS AND OUTLOOK. The immediately following economic information on fats and oils was compiled from late 1951 issues of the publication "Fats and Oils Situation" which was issued by the Bureau of Agricultural Economics of the United States Department of Agriculture.

Production of fats and oils in the year which began October 1, 1951, probably will total over 12.5 billion pounds, 0.2 billion above the record of a year earlier, which in 1950-51 was 3% more than the year before and 42% above the 1937-41 average.

During the 1950-51 year imports of fats and oils and production from imported materials was slightly larger than that of the year before; exports were 19% more than in the previous year.

Domestic disappearance of fats and oils in 1950-51 was 125 million pounds greater than the year before and almost 700 million more than two years ago. Owing to population increase, however, at a per capita basis of 68.6 pounds it was slightly less than the year before but still more than two pounds greater than in 1948-49. Food uses at 43.3 pounds were down 1.3 pounds, while non-food uses at 25.3 pounds increased 0.9 pound per person.

Prices of the major edible vegetable oils have declined in recent months as supplies have been large in relation to demand. The index number of wholesale prices of 26 major fats and oils, excluding butter, in the first half of January, 1952, was 170% of the 1935-39 average compared to 176 in December and 241 in January, 1951.

The economic treatises on fats and oils that appeared during the year were on current domestic and world economic situations as related to fats and oils (Prichard—*J. Am. Oil Chemists' Soc. 28,* 453-5); possibilities for improving the economic status of animal fats through research (Lundberg—*Proc. 2nd Conference on Research Am. Meat Inst. Mar. 23-4,* 112); trade, production and source information on 30 vegetable oils (Shearon—*Chem. Eng. News 29,* 4065); world fats and oils supplies and American soybeans (Quintus—*Oil Mill Gaz. 56,* No. 3, 13); drying oils trade (Andrews—*Oil & Chem. Rev. 114,* No. 8, 10); the fat supply of France (Ferrara—*Olearia 4,* 407); and import and production in Japan (Toyama—*Fette u. Seifen 53,* 65). Because of increasing production of synthetic detergents (syndets) there appeared several treatises on the economics of soaps versus the syndets (Snell—*Chem. & Eng. News 29,* 36; *30,* 30; *Brit. Silk Rayon J. 27,* No. 315, 45; Snell & Kimball—*Soap Sanit. Chemicals 27,* No. 6, 27; Killeffer—*Chemistry & Industry 1951,* 350; Flett—*Soap Sanit. Chemicals 27,* No. 3, 35). Solid soap and syndet productions, respectively for 1951, were 2,780 and 1,500 million pounds as compared to 2,955 and 1,250 million pounds during 1950. The great bulk of syndet production was from petroleum-base alkyl aryl sulfonates. The production was hampered by shortages of the supply of sulfur and benzene for manufacture, and of tripolyphosphate and tetra sodium pyrophosphate for building. These situations should be considerably eased by 1953. The economics and future of the German soap and syndet industry were also reviewed (Harz—*Seifen-Öle-Fette-Wachse 76,* 572).

General papers of economic interest were written on the cultivation of oleagenous plants in Italy (Baldacci & Fischetti—*Olearia 4,* 371); the vegetable oils of Java (Meijer—*Oliën, Vetten en Oliezaden 30,* 187, 198, 210); and inedible oils for technical uses of India (Dutt *et al.*—*Indian Soap J. 16,* 71).

### TABLE OF CONTENTS

A. INTRODUCTION.

Statistics, outlook, fat from waste, synthetic fat, microbiological fat, and comprehensive literature.

B. PRODUCTION.

Animal fats, fish fats, vegetable fats, tall oil, refining, bleaching, deodorization, winterization, fractionation, splitting, hardening, and transesterification.

C. PRODUCTS (except detergents).

Household fats, emulsifiers, demulsifiers, protective coatings, resins, lubricants, and preparation of fatty acid, ester, fatty ketones, nitrogen containing, and hydrocarbon derivatives of fats.

D. DETERIORATION.

Reviews, testing, mechanism, factors affecting stability, flavor reversion, microbiological decomposition of fats.

E. PHYSIOLOGY AND BIOCHEMISTRY.

Reviews, fat nutrition, fat absorption, intermediate metabolism, lipids in disease, and lipids in relation to microbiology and enzymes.

F. CHARACTERISTICS AND COMPOSITION.

Analyses of source, chemical characteristics, physical tests, composition, and detection of adulteration.

G. DETERGENTS.

Manufacture, constituent analysis, physical properties, performance tests.

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Treatises on culture and properties of specific oils were written on sunflower seed oil (Clagett *et al.—No. Dakota Agr. Expt. Sta. Bimonthly Bull. 13*, 173); growing soybeans in North Dakota (Stoa—*Ibid. 12*, 131); chemical and physiological properties of sesame oil (Budowski & Markley—*Chem. Revs. 48*, 125); cultivation of safflower and garden pepper cress for oil production (Favilli—*Olearia 5*, 83), cultivation of safflower in French Morocco (Miege — *Olearia 3*, 91); a study of three African oil-palm trees (Poerck—*Oleagineux 5*, 689); and oil production from African palms in Honduras (Reif—*J. Am. Oil Chemists' Soc. 28*, 152). The communications on utilization of various oils were on cacao butter (Jekel—*Österr. Apoth.-Ztg. 4*, 661); elder tree seed oils (Heller—*Seifen-Öle-Fette Wachse 77*, 161); Canadian erucic acid oils (Grace *et al.—Can. J. Tech. 29*, 71, 276, *J. Am. Oil Chemists' Soc. 28*, 522); train oil for lacquers (Scheifele—*Fette u. Seifen 53*, 201); menhaden oil (McLeod—*Fish Meal and Oil Ind. 3*, No. 6, 10); oiticica oil (Hrabe—*Chem. Obzor 25*, 181); olive oil foots (Moreno—*Ion 10*, 579); pumpkin oil (Sappok—*Fette u. Seifen 53*, 344); *Sardinia pilchardus* oil in varnish (Montequi & Montequi—*Anales real soc. espan. fis. y quim. 47B*, 33); safflower seed oil in edible fat products (Saltolft & Dollear—*J. Am. Oil Chemists' Soc. 28*, 335); shark liver oil (Vita—*Semana med. 1951*, 421); a symposium on soybeans (Various authors—*Nogaku 3*, 240, 245, 250, 254, 258); tobacco seed oil in relation to coatings (Greaves—*Paint Oil Colour J. 120*, 320; Rao *et al.—Paint Tech. 16*, 241); tomato seed oil (Pareja—*Farm. Chilena 24*, 397); uses for wool fat (Hadert—*Fette u. Seifen 53*, 289); and use of vegetable oils in tanning (Das—*Indian Soap J. 16*, 131).

Some general papers were on processes and research in fats and oils. These concerned chemical engineering in the edible oil industry (Goss—*Chem. Eng. Progress 47*, 489); extraction, refining, hydrogenation, fat splitting and soap making (Schwitzer—*Internat'l Chem. Eng. & Process Inds. 32*, 227); apparatus and processing (Niewiadomski—*Przemysl Chem. 6*, (29), 223; Namyslowski—*Ibid.* 236); recent advances in processing (Rigamonti—*Chimica e ind. 32*, 53); fat research in Spain (Moreno—*Fette u. Seifen 53*, 125); new developments in fats and oils in U.S.A. (Baldwin—*Ibid.* 509); fat research in Australia (Winter—*Ibid.* 516); methods of producing vitamin A containing oils in Norway (Domart—*Bull. mens. ITERG 5*, 199); whale oil production at Cape Lopez, Gabon, Africa (Budker—*Bull. Museum natl. hist. nat., Paris, 22*, 549); and description of a British Columbia plant for processing whale (Granberg—*Fish Meal and Oil Ind. 1*, No. 9, 8).

Recovery of Fat from Waste. A method of recovering fatty acids from soap-manufacturing waste water depended on pH control of the waste in a large chamber where suspended solids settle and the fatty acids that float are collected (Gibbs—*Proc. 5th Ind. Waste Conf. Purdue Univ. Eng. Bull. Extension Service No. 72*, 400; *Waste Eng. 22*, 72). The recovery of lanolin from wool scouring waste was reviewed (Gernert—*Seifen-Öle-Fette-Wachse 77*, 388). Fatty acids were extracted from a pasty residue remaining after recovery by distillation of the hydrocarbon-fatty acid solution used in ball mill processing of metallic powders (Akers & Hamlin—*U. S. 2,501,806*).

Poor grade fats were extracted from the waste buckwheat leaf meal residue of rutin manufacture (Krewson & Couch—*J. Am. Oil Chemists' Soc. 28*, 382) and from the waste of soy sauce manufacture (Nakatani & Nishiyasu—*J. Agr. Chem. Soc. Japan 19*, 663).

Synthetic and Microbiological Fats. Fundamental information on how production of protein, fat and carbohydrate by *Chlorella pyrenoidosa* through photosynthesis could be controlled was reviewed (Milner—*J. Am. Oil Chemists' Soc. 28*, 363). Engineering problems concerned with large scale culture of *chlorella*, plant design, cost estimates, etc, were discussed. A newly isolated mold of the *Fusarium* group isolated from birch sap produced surface culture with 52% fat on the dry basis (Aristowskaja *et al.—Przemysl Chem. 5*, 552). It was shown that *Saccharomyces cerevisiae* yeast could be commercially extracted; but, the fat could not be conveniently refined to an edible product (Brasch—*J. Am. Oil Chemists' Soc. 28*, 396).

Two communications contained general information on the chemistry and physiology of fats obtained by paraffin oxidation (Schulte & Weisskopf—*Chim., Switz., 5*, 1; Horski—*Przemysl Rolny i Spozywczy 4*, 95). The German synthetic fats for replacement of fats used in leather were listed and described (Brown *et al.—J. Am. Leather Chem. Assoc. 46*, 483, 505).

New Comprehensive Literature. During the period under review the following new books have come to the writer's attention:

Industrial Oil and Fat Products, 2nd. Ed., by A. E. Bailey. Interscience Pubs., New York, 992 pp.

The Lipids, Vol. I. Chemistry and Biochemistry, by H. J. Deuel, Jr. Interscience Pubs., New York, 982 pp.

Continuous Processing of Fats, by M. K. Schwitzer, Lenard Hill, London, 354 pp.

The Modern Soap and Detergent Industry. Vol. I. Theory and Practice of Soap Making. Vol. II. Manufacture of Special Soaps and Detergent Compositions. Edited by E. I. Cooke. Tech. Press, London.

Synthetic Detergents, by J. W. McCutcheon. MacNair-Dorland Co., New York, 435 pp.

Soap Making, by R. L. Dutt. General Printers & Publs., Calcutta, 143 pp.

Oil, Fat and Soap, by B. Levitt. Chem. Pub.. Co., New York, 238 pp.

Seifen-Industrie-Kalender. Edited by H. Heller. Delius Klasing & Co., Berlin, 268 pp.

Also as literature of general nature there appeared an annual review on the chemistry of lipids (Mattil—*Ann. Rev. Biochem. 20*, 87), a lecture on history of chemistry of fats during 1900-1950 (Hilditch—*Chemistry & Industry 9*, 154), a technical symposium on fatty acids (Peck *et al.—Proc. chem. Specialties Mfrs. Assoc. June, 1950*, 151), and a description of the French ITERG organization (Desnuelle—*Fette u. Seifen 53*, 1).

## Production

Animal and Fish Fats. Fundamental information applicable to simple rendering operation was developed by Mirkin & Manerberger (*Myasnaya Ind. S.S.S.R. 22*, No. 2, 9). Their best yields and lowest free fatty acid content of product were obtained when the fatty tissue was soaked six hours in ice water before rendering; shorter soaking time or higher temperatures reduced quality and yield. Their data on rendering bones showed the relationship between the yield and free fatty acid development depended upon rendering temperatures. A method for producing oil from eggs comprised hard boiling, removing the yolks, and rendering the yolks in liquid material (Cooper—*U. S. 2,555,731*).

Other animal fat preparation processes involved extraction with water-immiscible solvents. Animal material was alternately treated with organic solvents and water for the extraction of fat, and glue or gelatin (Tour—*U. S. 2,562,221*). A similar process was also described by Gernert (*Seifen-Öle-Fette-Wachse 76*, 509, 531). A continuous process employed hexane as the solvent (Langhurst—*U. S. 2,554,109*). In two other processes for solvent extraction of rendering residues, liquefied normally gaseous hydrocarbons were preferred in one to produce relatively low colored products (Leaders—*U. S. 2,548,434*), and in the other process, the inventor particularly emphasized continuous operation, economy in reuse of vapors for heating, and means for reducing stickiness (Leslie—*U. S. 2,571,143*). Brain, spinal marrow, and pancreas which contain sphingomyelins and cerebrosides were extracted with vegetable oils to produce emulsifiable fatty products suitable for ointments (Organon—*Dutch 67,255*). Animal raw material for production of vitamins, enzymes, or hormones was dehydrated and defatted by azeotropic extraction with dichloroethylene (Levin & Lerman—*J. Am. Oil Chemists' Soc. 28*, 441).

New techniques for extraction of fats from fish were designed according to the raw materials and products desired. Valen (*U. S. 2,534,640*) steam cooked fish and pressed the cooked material to produce oil, glue water, and feed cake. In a continuous fish and fish offal plant the raw material was cooked to 40-50% moisture, and the oil was extracted by a spray of heavy chlorinated hydrocarbon solvent (Bradford—*U. S. 2,536,345*). The critical range of 40-50% moisture permitted the solvent to coagulate the protein, which then floated on the solvent. Yamada & Ishida [*Science (Japan) 21*, 467] described a method using ultrashort waves for rendering fish muscles. In this process the protein selectively absorbed energy so as to become 10°C. warmer than the oil, and as heat coagulation of protein took place, the moisture and oil separated as an emulsion. An enzyme method of releasing oil from fish livers at pH of 1.9-2.5 made use of the other parts of the fish viscera as the enzyme source (Lane—*U. S. 2,550,570*). A plant with a capacity to process 50,000 lbs. of fish livers per day by the alkaline digestion process was described by Granberg (*Fish Meal and Oil Ind. 2*, No. 1, 14).

Butter production was the subject in several literature items. In a new continuous process, high concentration creams were cooled to 14°C. to obtain a complete phase inversion of the fat emulsion, it was then heated to about 30°C., and then the butter was re-cooled to the storing temperature (Stigen—*U. S. 2,569,203*). In another continuous process the butter was mixed with a 0.5% acid solution before final separation in order to obtain a clearer product (North—*U. S. 2,550,288*). The effect of each step of the continuous process on water-insoluble fatty acids and butyric acid was determined by Hillig *et al.* (*J. Assoc. Off. Agr. Chem. 34*, 720, 777). There was very little difference in the final product as compared to that of barrel-type churn in this respect. Neutralization of cream did not increase water-insoluble or butyric acids in butter churned therefrom. Hiscox's and House's (*J. Dairy Res. 18*, 291) investigations on reworking and blending of stored butter principally indicated that the practice would stimulate dormant bacteria and hasten the deterioration of the final butters.

A new metal butter churn had etched or scored inner surfaces to hold moisture and thus inhibit the butter from sticking (Henrard—*U. S. 2,571,573*).

The reports on wool fat processing contained information on scouring wool, recovery of the fat, and separating the constituents. Fong *et al.* (*Textile Research J. 21*, 540) scoured wool under neutral conditions with 3% *n*-butyl alcohol solution, increased the concentration to 7% in the washings, and the grease and dirt separated. After readjusting the *n*-butyl alcohol content of the separated solution by distillation, it was reused for scouring. Haidee (*Mon. farm. y. terap., Madrid, 57*, 177) recovered lanolin from soapy scouring solutions by decomposition with acid and air blowing to float the fatty material. The fatty material was dissolved in benzene, washed with alkali-alcohol solution, and the benzene was distilled off. For the same purpose, Shawcross (*U. S. 2,522,140*) passed the soapy emulsion through granular hydrogen-ion-exchange material on which wool fat was precipitated and from which it could be extracted with organic solvents. A review of wool fat recovery patents was compiled by Gernert (*Textile-Praxis 6*, 434).

Other wool fat processes dealt with separation of the constituents. Vaterrodt & Choyce (*U. S. 2,579,986*) saponified with 75-85% lye in the presence of lower alcohol, converted the acids to the calcium salts and recovered fatty alcohols by solvent extraction. Nozoe's (*Japan 178,375*) process was similar and it also included segregation of hydroxy acids from the acid fraction by adsorption on acid clay. Black *et al.* (*U. S. 2,567,541*) designed apparatus for saponification of such fat and waxes and extraction of the alcohols with liquefied gaseous hydrocarbons. In a similar process, Porter (*U. S. 2,499,877*) neutralized the saponified wool fat to pH 8.5-11.0 and extracted alcohols with a chlorinated hydrocarbon solvent. There were two methods of isolating cholesterol from wool fat alcohols, one depended on selective crystallization from methanol solution (Hewett—*Brit. 646,227*) and the other on precipitation from the same type solution with metal chlorides (Hackmann—*Rec. trav. chim. 69*, 433).

VEGETABLE FATS. Past research work on storage of seeds was reviewed by Jensen *et al.* (*Oil Mill. Gaz. 55*, No. 8, 55) and Milner (*Food Tech. 5*, 25). These recognized the role of fungi in the deterioration of damp seeds and discussed chemical preservatives for control of spoilage. In large scale storage tests losses of oil and development of free fatty acids in stored cottonseeds were correlated with initial moisture (Jensen *et al.*—*J. Am. Oil Chemists' Soc. 28*, 241). In spite of aeration to control temperatures the rate of formation of free fatty acids was rapid except in those cases involving seeds of initially low or medium moisture and low free fatty acid content. In one series of papers spontaneous heating and ignition of stored bagged palm kernels were studied. Bowes & Thomas (*J. Sci. Food & Agr. 2*, 65) and Bowes (*Ibid.* 79) record temperature and humidity changes during one year of commercial storage and suggest that the heating was mainly due to respiration of microflora developing on the material. In other papers of this series the autoxidation of the fat adsorbed on the bags was observed and the oxygen consumption, product formation, heat evolved, etc., determined to serve in designing precautions to avoid ignition of palm kernel stacks (Burgoyne & Thomas—*Ibid*, 8, 20; Burgoyne—*Ibid.* 157). Grapeseeds were stabilized for storage by drying to 5-10% moisture content, washing with brine and redrying (Badische Anilin- & Soda Fabrik—*Ger. 801,645*). The treatment inhibited deterioration of the oil.

Some studies on cottonseed processing concerned production of high quality by-product feed unrestricted feeding to nonruminants requiring reduction of free gossypol. Batson's *et al.* (*J. Am. Oil Chemists' Soc. 28*, 468) work showed that free gossypol was removed in the common cooking procedures used in hydraulic mills, and, in screw press processing removal principally occurred during passage through the screw-press. Gribbins (*Ibid.* 41) recorded the effect of time, temperature and moisture on free gossypol reduction and correlated these into equations useful for processing raw seeds, whole meats, and solvent extracted flakes. Milligan & Bird (*Poultry Sci. 30*, 651) also studied such processing variants on cottonseed and showed their relationship to nutritive value by chick feeding tests. For chick feed, a 160°F. cooking temperature was optimum and exceeding 200°F. was deleterious to the nutritive value.

Several other seed treatments were made to gain special advantages. Peanuts could be dipped in cold lye solution to remove skin color before processing so as to produce a light colored protein by-product, but small losses in oil and kernel weight were caused by the treatment (Pominski *et al.*—*J. Am. Oil Chemists' Soc. 28*, 513). Vacuum treatment to rupture oil-bearing cells, or preliminary extraction of proteins and solubilization of cellulose were recommended in oil seed processing to induce optimum extraction of oil, vitamins, sterols, and phosphatides (Loew—*Olearia 4*, 294). Reuther *et al.* (*J. Am. Oil Chemists' Soc. 28*, 146) in studies on effect of moisture in solvent extraction showed that low moisture flakes developed more fines and reduced percolation rate of solvent because of particle size; excess moisture inhibited oil extraction from the cottonseed hulls and slowed the percolation rate because of softness and pliability of the flakes. Optimum moisture content of flakes was 9-10%. A combination pressing and solvent extraction system for seed oils comprised a heat treatment, moisture conditioning, and flaking step between the extraction stages to produce soft, porous, and flexible flakes which resist development of fines during the solvent extraction step (Dunning—*U. S. 2,551,254*). A pre-extraction treatment, comprising heating seeds in vacuum below protein denaturing temperatures with electric short waves, was patented (Neiss—*Ger. 803,609*). A newly patented oil seed pressing assembly had means for cooking, drying, and then conveying seed to the press without heat loss (Weigel—*U. S. 2,533,858*).

Filhes (*Oleagineux 6*, 151) studied physiochemical factors involved in the common palm oil extraction method used in Africa. The fruit was boiled one-half hour, pitted, pulped and mixed in warm water, and the oil decanted. Yields were 78-80% of the total oil.

Fundamental data useful for designing equipment and processing methods for solvent extraction were recorded. Reiners *et al.* (*J. Am. Oil Chemists' Soc. 28*, 518) designed laboratory apparatus to correlate operation of basket-type extraction systems with laboratory tests. It was used to determine the effects of solvent flow rate on oil extracted and production of fines on application to corn germ. Wingard & Phillips (*Ibid.* 149) recorded quantitative data relating extraction rate and temperature for soybeans, cottonseed, and flaxseed extracted with several solvents. In general the time required for extraction to a 1.0% residual oil varied inversely with the square of the extraction temperature in degrees Fahrenheit. Similarly, but less extensively, Antonioli & Turriziani (*Ann. Chim. Rome, 41*, 255) determined the extraction of oils from seeds by two petroleum naphthas (boiling at 80-120° and 120-150°C.) at temperatures of 25, 50, and 75°C. Similar data by Martinenghi (*Olearia 5*, 5) on castor seeds and solubility of castor oils of various acidities were basic to design of rational extraction cycles in which oil was recovered from miscella by the phase separation produced by cooling.

Flow rates of hexane miscella were correlated with viscosity and density of the miscella, bulk density of soybean flake bed, and average diameter of the flakes (Cornell & Katz—*Ind. & Eng. Chem. 43*, 992). The data were relevant to operation of extraction systems in which the solvents were gravity flowed through beds of seed material. Data on vapor pressures of soybean oil-hexane solution by Smith (*J. Am. Oil Chemists' Soc. 28*, 356, 360) were useful for miscella distillation operations. Ayers & Scott (*Ibid.* 348) reported that methylpentanes were superior to hexane for extraction of seed oils because they were more efficient solvents and produced a better quality oil.

Russell (*Iowa State Coll. J. Sci. 25*, 348) who earlier recorded fundamental information on extraction of soybean flakes with trichloroethylene in a Redler conveyor supplemented this line of work with data on milkweed seed, sorghum germ, safflower seed, and cottonseed flakes extraction. Thickness of flakes, reduction of oil content, and optimum moisture for extraction were recorded. Arnold & Breuklander (*Proc. Iowa Acad. Sci. 57*, 157) preferred dichloromethane over trichloroethylene among the chlorinated extractants, because it was more easily and economically distilled from the miscella. They developed graphs showing the relation between boiling point and specific gravities of dichloromethane-soybean oil mixtures to serve for distillation operations. Vapor toxicity observations of trichloroethylene were reported by Forssman (*Arkiv Hig. Rada 1*, 257) and Adams *et al.* (*Arch. Ind. Hyg. & Occupational Med. 4*, 469). Although these data were not functional to the operations they are pertinent to the commercial use of the solvent.

A comprehensive report on the fundamental information for extraction of cottonseed with isopropanol was reported as the experimental data through which a plant was developed (Harris & Hayward—*Bull. Agr. Mech. Coll. Texas 6*, No. 9, 67 pp.). This contained optimum conditions of primary extraction and liquid-liquid purification, heat and material balances, and general properties, solubilities, and equilibrium data of the solvent systems involved. The fundamental information for extraction of peanuts with ethanol by Mayolle (*Bull. mens. ITERG 4*, 453) comprised critical temperatures of two-phase separation for peanut oil-alcohol miscella of oils of various acidities and the efficiencies of centrifuge separations at 21°C.

General descriptive papers on extraction equipment were a review of processes (Depmer—*Fette u. Seifen 53*, 699; Christiansen—*Ibid* 99), a review of principles, operations, methods, etc., of 14 commercial systems (Cofield—*Chem. Eng. 58*, 127), description of the Kennedy and Botarro systems (Paleni—*Fette u. Seifen 53*, 385), review of methods with regard to physiochemical factors involved (Filhes—*Oleagineux 5*, 705), the Wurster & Sanger, Inc., equipment (Smith—*J. Am. Oil Chemists' Soc. 28*, 274), a combination prepressing and solvent extraction plant (Brady—*Oil Mill Gaz. 56*, No. 1, 73), the Blaw-Knox Construction Co. equipment (McCubbin—*J. Am. Oil Chemists' Soc. 28*, 310, *Can. Chem. Processing 35*, 468), a small rotary extractor (Martinenghi—*Olearia 4*, 285), and the Exsolex process (Dunning—*Oil Mill Gaz. 56*, No. 1, 64). Distiller's dried grains were successfully extracted in a basket-type soybean solvent extraction plant to yield an oil similar to corn oil except for higher color and refining loss (Walker—*J. Am. Oil Chemists' Soc. 28*, 195).

Several solvent processing innovations were described. A process for fractionating cottonseed by Vix *et al.* (U. S. *2,579,526*) comprised disintegrating in organic solvent without rupturing the pigment glands, mixing with more hydrocarbon solvent of such specific gravity that glands and hulls settled and the fine meal tissue, free of glands, remained suspended in the liquid. The oil and suspended meal that were isolated from the liquid were of good quality. A process designed for small cottonseed plants comprised mixing a slurry of rerolled, cooked flakes and hexane followed by filtering and countercurrent washing (Spadaro *et al.*—*Oil Mill Gaz. 56*, No. 1, 77). Operational data were recorded. Such data were also determined for extraction of the flakes with hexane-water mixtures (Bendler & McNeil—*J. Am. Oil Chemists' Soc. 28*, 164). Extraction at 6 : 1 and 1 : 5 hexane : meal and water : meal ratios, respectively, reduced oil in meal to about 1%, and meal was easily filtered from miscella and air-dried to an easily handled non-sticky cake. New equipment was designed to extract oilseeds with liquefied normally gaseous hydrocarbons (Leaders—*U. S. 2,548,434*; Dickinson—*U. S. 2,560,935*; Rubin—*U. S. 2,564,409*). A new process for castor oil extraction comprised leaching with heptane above miscibility temperature and cooling to layer in oil-rich and oil-poor phase (Sly—*Australian 137,130*). The principle of azeotropic distillation of a mixture of solvent and suspended seed material was patented for simultaneous defatting and dehydration (Levin & Worsham—*U. S. 2,539,544*).

Other processing innovations dealt with design of equipment. In equipment designed by Straight (*U. S. 2,550,947*) seed material was swept progressively down spaced superposed baffles and then lifted in horizontal columns through which solvent was passed countercurrently to the seed. Smets (*U. S. 2,569,199*) made use of passing different charges of solvent successively through a traveling bed of solids. Bilbe (*U. S. 2,545,938*) made use of the countercurrent extraction principle in a U-shaped apparatus, while Hamacher & Barns (*U. S. 2,547,577*) used screws to pass the solids horizontally and then vertically. Other new systems were a rotary type (Raffineries Nord-Ocean—*Fr. 943,064*), one in which the solids charge was passed over stages by means of paddled wheels (Fitts *et al.*—*U. S. 2,567,474*) and another in which two extractions were made and between the extractions the solids were dried and reground (Arnaud—*Ital. 454,621*). On some new solvent plants the writer found references but did not have descriptive information. Two of these were systems for seed materials in general (Andrews—*Brit. 654,036*; Gallais—*Fr. 951,140*); and two were designed especially for olive pomace (Salino & Monti—*Ital. 444,223*; P. H. Barriere Fils—*Fr. 943,552*).

Some innovations were small improvements in commercial equipments. Crockin (*Chem. Eng. 57*, No. 11, 160) sprayed water containing a surface-active agent into the miscellas in order to cause fines to swell and become slimy, thus facilitating their removal by continuous centrifuges. New valve mechanisms were designed for withdrawing solids from extraction towers (Anderson — *U. S. 2,548,333*; Zies & Weigel — *U. S. 2,549,997*). Details of equipment, method, and costs for applying the spray-drying principles to desolventization of soybean oil-trichloroethylene miscella were described by Barr (*Iowa State Coll. J. Sci. 25*, 153).

TALL OIL. Tall oil production methods include extraction from waste sulfite lye skimmings, purification, and separation of constituents. A review of patents on these covering the time interval from 1936 to 1946 was published by Jakobson (*Svensk Papperstidn. 53*, 369).

All other literature coming to the writer's attention during the year was in processing patents. Stephenson (*U. S. 2,561,150*) and Hasselstrom & Stoll (*U. S. 2,575,013*) refined crude tall oil skimmings by washing with solutions of sodium sulfate and sulfuric acid; and similarly Gates & Radeker (*U. S. 2,525,892*) used phosphate salts and acid. On separating fatty acids from tall oil, Davis & Spurlin (*U. S. 2,558,543*) mixed with an aqueous alkali an organic solvent mixture in a manner to preferentially saponify the fatty acids and separate the rosin acids; Dunlap & Sievert (*U. S. 2,565,484*) oxidized the crude tall oil to increase the viscosity and segregated the constituents by liquid-liquid extraction with use of furfural and petroleum naphtha as solvents: Christenson & Harpt (*U. S. 2,573,890*) used liquid phase extraction after conversion of the fatty acids to methyl esters and the rosin acid to soaps as a means of segregation; Koonce & Perry's (*U. S. 2,538,103*) system depended on selectively reacting rosin acids with diene compounds to increase the boiling point of the resin compounds so the fatty acids could be separated by distillation; and Kalman (*U. S. 2,532,101*) precipitated rosin acids from tall oil by reaction with cyclohexylamine; subsequently the soluble fatty acid salts of the reagent were recovered by hydrolysis with acid. The unsaponifiable matter of tall oil, suitable for preparation of sex hormones, was isolated by saponification of the tall oil and extracting sterol from the soaps with isopropanol-water-naphtha mixtures (Christenson & Gloyer — *U. S. 2,530,809-10*).

REFINING, BLEACHING, AND DEODORIZATION. Several inventors degummed oils with aqueous solutions of surface active agents as a preliminary to alkali refining (Mattikow—*U. S. 2,576,957-8, 2,525,702*; Folzenlogen—*U. S. 2,563,327-8*; Rider & Gershon — *U. S. 2,544,725*). These processes pertained to separation of crude phosphatides, operation on solvent extracted oils while still in the miscella stage, and reducing losses in the subsequent alkali refining step. Partially esterified polyhydroxy fatty acid esters were used as the surface active agents. For the same purpose Ayers (*U. S. 2,561,330*) used methanol-water solution and the treatment was performed on the oil miscella. Another process for the same purpose comprised treating with aqueous sodium hydroxide or calcium chloride solution and passing through a Votator machine (Parkin & Walker—*U. S. 2,564,407*). A rice bran refining process contained a step in which the oil was aerated in the presence of sulfuric acid before alkali refining in order that the final product would be clear and light colored (Sakurai—*J. Chem. Soc. Japan 52*, 193).

Some experimenters determined optimum conditions for alkali refining of certain oils. With cottonseed oil the darker oils required more vigorous agitation; 20° Bé caustic could be used below 85° F. without large refining losses; and with higher concentrations of caustic use of minimum amounts and low temperatures were necessary to avoid high refining losses (Cavanagh—*J. Am. Oil Chemists' Soc. 28*, 377). In cottonseed oil refining tests by Sharma & Lal (*Proc. Ann. Convention Oil Technol. Assoc. India 2*, 30), 9.3% caustic effected the greatest removal of color at 30-40°C.; at 50°C. 30% caustic was best but the former gave better decolorization. In similar investigations on peanut and sesame oils the optimum refining temperature for the former was 60°C. and alkali solutions recommended were of strengths increasing as the acid number of the oil increased; and with the latter oil 25% alkali and 50°C. temperature were optimum (Ram *et al. Ibid. 3*, 25). Reduction of oil losses was claimed in patents on refining oils with alkali-methanol solutions (Ofner—*Hung. 135,577*), and with alkali refining in the presence of salicylic acid (Lange—*U. S. 2,551,496*). Solubility and phase equilibrium data were developed as basic information for extracting the free fatty acids from grapeseed, walnut, and linseed oils with methanol (Rius & Crespi—*Anales real soc. espan, fis. y quim. 47B,* 243). Stills were also designed for removal of free fatty acids from oils (Egger & Webster—*U. S. 2,575,051;* Dini —*Ital. 455,242*).

Free fatty acid acidity of oils was also eliminated by re-esterification. Naudet (*Bull. mens. ITERG 5,* 51) discussed such a process with regard to the effect on melting point, plasticity, and for eliminating frothing. Paleni (*Olearia 5,* 149) reviewed his 20 years of experience with the use of the process. Goday & Catalá (*Ion 11,* 17) demonstrated that the process could be used with oils with acid numbers as high as 65. A patented process of this type comprised adding mono- and diglycerides and heating to above 200°C. (Hazama—*Japan 179,338*).

Some oil refining descriptions pertained to improving edibility. Mustard oils contaminated with toxic argemone oil were rendered edible by emulsifying with ferric chloride solution, allowing to settle, and filtering the decanted oil through fuller's earth (Prakash *et al.*—*Current Sci., India, 20,* 16). Edibility of marine animal and fish oils was improved by a polymerization treatment (Werner—*Fette u. Seifen 53,* 133; Hugel—*Ibid.* 264). It was pointed out that there was insufficient pharmacological data on the polymerized compounds. Undesirable flavor-imparting materials were removed from medicinal vitamin A oils by dissolving in a non-polar saturated hydrocarbon solvent and passing the solution through anhydrous gamma alumina (Taylor—*U. S. 2,573,509*). Commercial treatments for improving residual olive pulp oils were reviewed by Paleni (*Olearia 5,* 75) and Santelli (*Ibid.* 165).

Malodorous *Mesua ferrea* seed oil was made suitable for soap stock and technical uses by treatment with hydrochloric acid and potassium chlorate (Gupta—*J. Sci. Ind. Research, India, 10B,* 24). Alkali coconut oil-foots was heated with alum powder and settled to yield a layer of useful technical oil (Morita —*Japan 179,240*). A useful oily product was prepared from lecithin by treatment at 239° in vacuum with alkali alcoholate solutions (Pollak—*U. S. 2,554,955*).

Many deodorization methods were described. Bleaching of cottonseed oil in hexane with activated clay and carbon were recommended because of efficiency and low oil losses (*Feuge* & Janssen—*J. Am. Oil Chemists' Soc. 28,* 429). Sanders (*U. S. 2,555,098*) claimed that bleaching of oil before rather than after drying, more effectively removed color. Yamakita & Fujii (*Bull. Inst. Chem. Research Kyoto Univ. 20,* 64) pretreated the oil with dilute acid for the same purpose. Christenson & Harpt (*U. S. 2,569,124*) steamed the oil during the bleaching with absorbent earth. Samuel (*Fr. 948,401*) used earths and carbon with ultrasonic agitation for bleaching oils. The new chemical bleaching processes made use of, respectively, hydrogen peroxide (Ohya—*Japan 179,245*), and electrolytic release of hydrogen from chemicals added to the oil (Nomata —*Japan 177,360*) as the bleaching agents.

Some oil bleaching information dealt with bleaching clays. Four native clays of India and their sulfuric acid-activated products were evaluated for bleaching vegetable oils (Mukherjee & Roy—*Indian Soap J. 16,* 281). A patented activating process for oil bleaching clay made use of treatment with sulfuric acid (Christiansen—*U. S. 2,553,239*). Fatty oils were recovered from spent clays by making a slurry with naphtha, water, and emulsifier, steaming and separating into layers (Gee —*U. S. 2,577,079*). The upper solvent layer contained the recovered fatty material. McClain (*U. S. 2,579,946*) used water soluble, oil insoluble filter aids for filtering oils so that adsorbed oil in waste filter aid could be released by addition of water and recovered.

Various means were used to deodorize fats and oils. Oils were treated with the aqueous portion of a distillate of pine roots and washed with water (Koyanagi—*Japan 177,505*). The odor of shark-liver oil was removed by heating with alcohol or propylene glycol and skim-milk powder (Patel & Sreenivasan —*J. Sci. Ind. Research, India 9B,* No. 5, 130). Odorous nitrogen compounds in chrysalis oil were removed as the acid amides by the reaction with ketene gas produced from acetaldehyde (Takama—*Japan 178,834*), by mixing with the milky fluid obtained from green figs (Uchida *et al.*—*Japan 177,092*), by heating with silver powder (Hamajima—*Japan 179,027*), and by heating with alkali fluorides (Hamajima—*Japan 179,028*). Soybean oil was deodorized and stabilized by blowing with a mixture of air and steam (Carleton—*U. S. 2,578,670*)

The innovations in the common steam deodorization were a new apparatus for the process (Miller—*U. S. 2,559,129*), use of a deairing step for the steam water used in such equipment (Tsuchikawa—*Japan 178,220*), and a removable sleeve was put in the distillation column of an oil deodorizer in order to facilitate removal of fouling matter (Castle & Beal — *U. S. 2,530,376*).

In an investigation on 13 commercial metals and alloys in regard to their suitability for construction of oil deodorizing equipment, aluminum and nickel alloys had the least effect on the stability of the oils, iron had some effect, copper was extremely bad, and molybdenum decreased the proöxidant effect of stainless steels (Beal & Lancaster—*J. Am. Oil Chemists' Soc. 28,* 12). However, the metals, when coated with an oxidized film of oil, were nearly equivalent to a glass surface in effect on stability. Another publication on deodorizers had general information on materials of construction, methods, and means of detecting leaks (White—*Ibid.* 438).

An analysis of the distillate obtained from the deodorization of palm kernel oil indicated the presence of fat, methyl nonyl ketone, methyl hendecyl ketone, and methyl nonyl carbonyl (Calas & Duffault—*Bull. mens. ITERG 5,* 147).

WINTERIZATION, FRACTIONATION, AND SPLITTING. Systematic phase relation data have been recorded for cottonseed oil using a hexane and an 85:15% acetone:hexane mixture and for peanut oil only with the mixed solvent (Boucher & Skau—*J. Am. Oil Chem. Soc. 28,* 483, 501). The data afforded preliminary basis for plant design, selection of optimum conditions, and recognition of limitations for pilot plant research on solvent winterization of the oils.

In vegetable oil fractionation work with selective solvents most interest was on the use of furfural as the solvent. Farr (*Oil Colour Trade J. 114,* 729) recorded data correlating the iodine number (unsaturation) of the fractions with ratios of the solvent to oil used in the process on soybean, linseed, and fish oils. Such data were guides for regulating practices to obtain fractions of specific characteristics from semidrying oils for replacement of linseed oil in the paint industry. In similar work on fish oils de Lamo *et al.* (*Pubs. inst. quim. "Alonso Barba" 4,* 295) used furfural:oil ratio of 4:1 and recorded the characteristic of fractions obtained at different segregating temperatures. The data on critical solution temperatures of oil-furfuryl alcohol systems by Angelescu & Esanu (*Acad. Rep. Populare Romane Bull. Stiint. Ser. Mat. Fiz. Chim. 2,* 387) also pertained to solvent fractionation. The data was on rape, cucurbit, sunflower, tobacco, soybean, poppy, walnut, hempseed, linseed, and olive oils. Many patents on oil fractionation with furfural and other polar solvents were assigned to the Pittsburgh Plate Glass Co. (*U. S. 2,539,661, 2,546,132, 2,573,-891, 2,573,896-900*). In these, equipment was described, fundamental data on oil miscibility in many polar solvents was recorded and methods of operation to remove "break" constituents — sterol, vitamin, and phosphatide concentrates — and to fractionate several oils were presented. Another patent issued to this concern (*Brit. 644,917*) described means of protecting the oils in this type equipment by a blanket of inert gas.

Segregation of oil constituents by crystallization from solutions was done with several solvents. Bloomer (*U. S. 2,571,663*) described the fractionation of soybean oil into fractions of iodine number greater and less than the original oil by fractional crystallization from ethanol. Cording & Shaines (*J. Am. Oil Chemists' Soc. 28,* 344) used isopropanol solvent similarly to prepare wool greases of prescribed viscosities. Flow sheet, fundamental data, and method for separation of stearin from olein and unsaponifiable by crystallization from petroleum solvent were in a patent issued to Neudert & Lange (*Brit. 650,720*). Patents issued to Swift & Co. (*U. S. 2,552,797, 2,553,288, 2,576,841*) contained apparatus designs and processing methods for removing color material, and crystallizing oils from liquefied normally gaseous hydrocarbons into fractions of different melting points. The solubility relationships of methane-propane-glyceride systems as recorded by Bogash and Hixson (*Chem. Eng. Progress 47,* 347) were pertinent to solvent crystallization of fats. These showed that phase separation of trisaturated glycerides or acids from propane solutions could be induced by the addition of methane. Two methods of fractionating fatty acids comprised converting these into ethyl esters (Pool & Sedgwick—*U. S. 2,543,055*) and amides (Myers —*U. S. 2,575,526*), respectively, and crystallization from organic solvents. Other newly reported methods on fractionating fatty acids were on distillation procedures (White & Strawn—*U. S. 2,521,766;* Potts & Olson—*U. S. 2,573,727;* Acker—*Can. Chem. Processing 35,* 716).

The nonglyceride and nonfatty acid constituents of oils were recovered by various procedures. Vogel (*U. S. 2,523,794*) concentrated sterols by saponifying fats with ammonia and extracting the sterols from the ammonium soaps with organic solvents. Myers (*U. S. 2,520,470*) selectively extracted unsaponifiable from fatty acid stock with alcohols, ketones, and organic acids of not over three carbon atoms. Feinstein & Ringel (*U. S. 2,557,956*) separated sesamin from sesame oil by chilling a petroleum ether solution of the oil to 0°C. The sesamin was intended for admixing with pyrethrum extracts to combat insect pests. Carotenoid pigments were recovered from palm oil acids or other esters by dissolving in alcohol, cooling the solution to precipitate the fatty material and recovering the carotenoid concentrate from the solvent (Gebhart—*U. S. 2,572,467*). Linseed phosphatides were segregated into choline-rich and inositol-rich fractions, respectively, by liquid-liquid extraction using alcohol and hexane as solvents (McGuire & Earle—*J. Am. Oil Chemists' Soc. 28,* 328).

The mechanism of autoclave fat splitting was investigated on beef tallow, coconut oil, and peanut oil (Sturzenegger & Sturm—*Ind. Eng. Chem. 43,* 510). All three fats hydrolyzed at 280° in about 0.5 hours, and reaction velocities were nearly independent of the oil-water ratio used. A new system of fat splitting comprised saponification with ammonia to produce ammonia soaps and glycerol, and, after separation, the fatty acids were recovered by treatment with carbon dioxide (Frankel—*U. S. 2,558,515*). Trutter (*J. Applied Chem. 1,* 452, 454) studied the mechanism of splitting wool fat with alkali solutions and graphically represented the characteristics of the reaction. When about one-third of the fat was saponified the rate of reaction was diminished because the alcohols liberated compete with the esters for places in the interfaces of saponification agent and fat.

Other splitting information dealt with catalytic reagents for the common process. The use of reagents containing substantial amounts of sulfonic acids of polyisopropyl benzene (Griesinger—*U. S. 2,575,807*) and sulfonic acids of monoalkylnaphthalene (Tomiyama *et al.—Japan 178,506*) were patented for the process. Halogenated derivatives of alkylphenol sulfonic acids were found to be superior splitting agents than the unhalogenated compounds (Fukuzumi & Ozaki—*J. Chem. Soc. Japan, Ind. Sect. 52,* 154). The splitting agents used in the Spanish industry were reviewed by Doadrio & Montequi (*Anales real soc. espan. fis. y quim. 46B,* 233).

Hardening of Oils. The theoretical aspects of hydrogenation were comprehensively reviewed by Kaufmann & Baltes (*Fette u. Seifen 53,* 525). Blekkingh (*Faraday Soc. Discussion 1950,* No. 8) in discussing the catalyst mechanism of the process indicated that adsorbed hydrogen may be split to atomic hydrogen, this causing isomerization in oils while molecular hydrogenation takes place at the same time. Selectivity of hydrogenation and isomerization during the process were discussed in connection with the above ideas.

Data on formation of isomers and their reduction during hydrogenation were recorded for several fatty acid esters. In the hydrogenation of oleates as much as 38% *trans* isomers developed while the first 10% stearate was formed (Feuge *et al.—J. Am. Oil Chemists' Soc. 28,* 420). In general the *trans* isomer formation was accelerated by increasing temperature, increasing catalyst concentration, and decreasing dispersion of hydrogen; and hydrogenation always resulted in equilibrium of *cis* and *trans* isomers at 67% concentration of the latter. Daubert *et al.* (*J. Am. Chem. Soc. 72,* 1233, 4356; *J. Am. Oil Chemists' Soc. 28,* 177, 183) observed isomer formation in methyl esters of oleic, linolenic, and β-eleostearic acids. They found that the relative reactivities of various unsaturated acids towards hydrogenation may be represented by the following whole numbers: oleic and isoöleic 1, isolinoleic 5, linoleic 27, and linolenic 27. Several isomers of each of the acids were isolated from the partially hydrogenated oils. Thompson's (*J. Am. Oil Chemists' Soc. 28,* 339) similar work on mixtures of tung and linseed oils showed that eleostearin was many times more reactive than normal linolenin but as eleostearin decreased its reactivity also decreased until at the 1-2% level it was only slightly more reactive than normal linolenic for equivalent concentrations. He found that the conjugated linolein formed during the hydrogenation was many times as reactive as normal linolein. These data were discussed with relation to hydrogen selectivity. Comparable work was also done on a fatty acid with four conjugated double bonds, parinaric acid (Riley—*J. Chem. Soc. 1951,* 2579). The hydrogenation removed conjugated tetraenes with insignificant production of conjugated triene or conjugated diene.

The literature on hydrogenation equipment comprised a newly invented hydrogenation plant (Holmboe—*U. S. 2,536,603*), accessory equipment to blend fat still hot from hydrogenation with oil under hydrogen atmosphere (Harrington—*U. S. 2,546,502*). and a description of a pilot plant apparatus for hydrogenating fatty acids (Hempel & Kozerski—*Przemysl Chem. 6,* 299).

New hydrogenation techniques dealing with hardening of fatty acids were described. All of these involved esterifying the acids with a lower alcohol or glycerol before the hydrogenation (Kirby — *U. S. 2,547,014;* Schicht — *Brit. 642,715; Brit. 642,718;* Tsutsumi—*Japan 176,379*).

Some hydrogenation literature pertained to the catalyst used. Special catalysts containing nickel, alumina, silica, and diatomaceous earth were said to induce bleaching as well as hardening (assigned to Lever Bros. Co.—*U. S. 2,566,362; Brit. 645,551*). The presence of moisture in nickel-clay catalyst improved the hardening reaction for highly acid oils (Tsutsumi —*J. Chem. Soc. Japan Ind. Sect. 52,* 191). Funaki & Funaki (*Japan 179,931*) patented alkalization of acid clays intended for making nickel-clay hardening catalyst.

A recently described process for hardening of oils by elaidinization made use of fuming sulfuric acid as the catalyst (Dahmen *et al.—Chimie & industrie 64,* 557).

Transesterification. β-Oleodistearin when heated in inert atmosphere at 300° was converted to a mixture of glycerides of such proportion of each as to indicate that random distribution of the fatty acids was approximately attained (Crawford & Hilditch—*J. Chem. Soc. 1951,* 1194). One patent on a commercial transesterification process pertained to recovery of glycerol in the presence of sodium methylate (Price & Sprules—*U. S. 2,543,421*).

## (Products (except detergents)

Household Fats. A new shortening product comprised a mixture of edible beef tallow and lard which was deacidified and deodorized by steaming at 425°F. (Anderson—*U. S. 2,536,865*). A shortening homogenizer designed especially for blending solid fats was patented (Harrington—*U. S. 2,546,502*). In a description of a modern animal shortening plant, particular emphasis was placed on new efficient materials-handling techniques and instrument control of time and temperature for refining, deodorization, and blending the fats (Miller—*Food Eng. 23,* No. 8, 88).

Various materials were suggested as additives to improve mixing qualities of shortening with other ingredients or improve the quality of the finished baked product. An additive for cake shortening comprised a mixture of sorbitan monostearate and partial esters of condensed ethylene oxides and fatty acids (Johnston—*U. S. 2,569,527*). Lecithin and cephalin were converted to suitable shortening modifiers by hydrolysis with inorganic acid to remove choline and colamine and convert them to phosphates (Hansen—*U. S. 2,550,558*). Another method of improving shortening comprised treating it with air in the presence of enzymes which catalyze oxidation without generating undesirable catalytic by-products (Renner—*U. S. 2,573,358*). Monoglyceride, a common shortening improver, was studied with regard to its effect on starch, flour, and bread (Strandine *et al.—Cereal Chem. 28,* 449). Small quantities decreased swelling or hydration of starch granules and inhibited the release of water-soluble starch, increased the softness of bread, and decreased the rate of crumb firming during storage. The mechanism in part was due to the capacity of monoglyceride to inhibit release of the water-soluble fraction from starch granules, thus keeping this cementing substance in discontinuous aggregates and preventing its release on the gluten strands around the starch granules.

The aim in some shortening patents was to provide dry powdered products for ready-mixed baking mixes. Salo & Huber (*U. S. 2,555,902*) divided solid shortening into $\frac{1}{8}$ to $\frac{1}{2}$ inch particles, mixed these with flour and submitted this to a special mixing process to further reduce the particle size and mix the ingredients. Hansen (*U. S. 2,557,283*) used hard fat of melting point 130-160°F., finely comminuted, and coated with a mixture of calcium lactate, calcium sulfate, and corn starch. A dry shortening for pastry mixes contained water, corn starch, corn oil, propylene glycol, and calcium acid phosphate (Wade —*U. S. 2,557,524*). Bogin & Feick's (*U. S. 2,555,467*) shortening powder made use of methyl cellulose and sodium carboxy methylcellulose as the carrier for the fat. Another method of handling the problem of mixes was to grind hard shortening directly into the mixing apparatus containing the flour, sugar, salt, leavening agent, and other ingredients whereby it became quickly and uniformly distributed (Lang — *U. S. 2,579,326*). Also in this connection there was invented a packaging machine in which the ingredients were continually mixed so that the shortening was uniformly delivered with the other ingredients into the packages (Reed—*U. S. 2,573,872*).

Three articles on salad oils treated different aspects of the product. Francois & Sergent (*Bull. mens. ITERG 5,* 39) prepared various mixtures of peanut, rape, mustard, and soybean oils and recorded the tendencies to solid glyceride appearance in the oils. Peanut oil and mixtures containing it had the greatest tendencies to clouding when stored at cold temperatures. Zuccaro *et al.* (*Food Research 16,* 30) cautioned that resistant bacteria or yeast when coated with salad oil as in French dressing might survive the normal pasteurization process for the product and could produce spoilage of food. Musher (*U. S. 2,554,870-2*) induced intense olive flavor in various salad oils by treating them with brine in which ripe olives had been cured.

New methods of making margarine emulsions were described. A continuous plant contained drum coolers, multiplex rolling machines, machines which press the mass through perforated plates, and a final kneading and mixing machine (Van den Bergh's en Jurgen's Fabrieken. N. V.—*Dutch 67,620*). Nelson & Kuhles (*U. S. 2,557,135*) prepared an 80% edible fat emulsion in a melted state, mixed with an innocuous liquid, submitted this to a spray drying operation to evaporate the innocuous liquid and to reduce the temperature, and mechanically worked the solidified particles to a plastic margarine mass. Herlow (*U. S. 2,585,874*) first emulsified the aqueous ingredient phase of margarine with some oil to form an oil-in-water emulsion and then worked this into the main body of fat in such manner that fat became the continuous phase. Wilson & Oakley (*U. S. 2,558,204*) improved the plasticity of margarine by melting the emulsion, cooling, and finally kneading. Another patent of Wilson *et al.* (*Brit. 650,481*) dealt with emulsification under conditions in which the higher melting components of the fat were in a crystalline state. A subsequent treatment for the above process comprised mechanical shearing treatment and forcing through screens to impart uniform consistency to the final product (Rourke & Dow—*Brit. 650,482*). Other improvements in margarine manufacture dealt with addition of ethyl esters of fatty acids of less than 18 carbon atoms to increase similarity to the composition of butter (Pardun—*Seifen-Öle-Fette-Wachse 76,* 377, 397, 417, 440) and several patents on coloring the products (Metheny *et al.*—*U. S. 2,539,457;* Herlow—*U. S. 2,546,748;* Drew *et al.*—*U. S. 2,559,411*).

Some investigators displayed interest in the quality of margarines. Good German products decreased 15% in vitamin A potency during the 12-14 weeks of storage, and thereafter the decrease in vitamin A was very rapid (Wodsak—*Fette u. Seifen 53,* 533). Tests on Canadian margarines indicated a very consistent vitamin A content averaging 4,062 international units per 100 grams (Murray *et al.*—*Can. J. Tech. 29,* 147). Another report on vitamin A in margarine showed that the vitamin and carotene were very stable in antioxidant-supplemented products and that the emulsifying agents increased their dispersibility in the product (Deuel *et al.*—*J. Nutr. 43,* 371). In this work the environmental factors were more capable of augmenting physiological response in feeding tests to carotene than to the preformed vitamin A. A bacteriological study of margarines indicated that the bacterial population was similar in magnitude and variety to that of many other processed foods (Foltz & Lord—*Food Res. 16,* 216).

The consistency of the product was the principal interest in peanut butter manufacture, and this consistency depended on the character of the fat constituent. Mitchell (*U. S. 2,562,630*) stabilized the consistency by addition of 2-5% hydrogenated fat, and cooled and stored it in a manner to induce beta crystallization of the fat. Avera's (*U. S. 2,552,925*) stabilized peanut butter fat in such semicrystalline condition as to induce softness and spreadability to the product.

EMULSIFIERS AND DEMULSIFIERS. The reviews on emulsions were on preparation of emulsions (Brown & Myers—*Soap Sanit. Chemicals 27,* No. 7, 43), theory of emulsions (Schmalfuss—*Fette u. Seifen 53,* 134), hydrocarbon emulsions (Russ—*Seifen-Öle-Fette-Wachse 77,* 173), viscosity of emulsions (*Ibid. 271*), Brownian movement in emulsions (*Ibid.* 317), and creaming of emulsions (*Ibid.* 342).

Some communications contained new fundamental information on the properties of emulsions. The work of Gros & Feuge (*J. Am. Oil Chemists' Soc. 28,* 1) was an evaluation of the ability of monoglycerides to reduce interfacial tensions with various nonaqueous phases. These reductions, by 0.5% monostearin, between water and mineral oil, cottonseed oil, and amyl acetate were, respectively, 96, 24, and 1%. In general various glycerides were equally effective with cottonseed oil, whereas with mineral oil the monostearin was more effective than comparable lower fatty acid derivatives and less than that of monolinolein. The effects of temperature were related to the concentration of the emulsifier in the nonaqueous phase; the largest temperature effect being with the lower fatty acid monoglyceride. The fundamental work by Sherman (*J. Soc. Chem. Ind. 69,* S70, S74) was on the influence of the dispersed phase concentration and pH on the viscosity of water-in-oil emulsions. Up to water content of about 50% with 2-5% emulsifier there was no marked rise in viscosity; with increases beyond this critical limit the changes were pronounced, the emulsions exhibited plasticity, and mobility rose rapidly to a maximum. With nonionic emulsifying agents the mobility and stability of the emulsions were unaffected by pH until the pH rose above 7.0 at which inversion and complete loss of viscosity occurred. Similar work by Saha (*J. Indian Chem. Soc. 28,* 23) contained a record of interfacial tension, size frequency of droplets, and jelling characteristics which characterized the dispersing ability and emulsifying capacity of oleate soap for water and oil systems.

Most of the new patents on emulsifiers pertained to partial esters of fatty acids with polyhydroxy alcohols. Fatty monoglycerides were prepared by reacting fat with excess glycerol and were purified by crystallization from a mixture of ethanol and chloroform (Young & Black—*U. S. 2,553,288*). A procedure for fatty diglycerides comprised reacting a glycidyl ester of a fatty acid with fatty acids in organic solvent solution (Kester—*U. S. 2,523,309*). Improvement in partial ester emulsifiers was obtained by reacting them with polybasic acids such as maleic, malic, fumaric, or sebacic (Bertram—*U. S. 2,552,706*), or by etherifying them with alcohol amines (Katzman & Epstein—*U. S. 2,496,875;* Ackelsberg—*U. S. 2,531,190*). A new generally usable defoamer was a partial ester of polyglycol and ricinoleic acid (Parry—*Brit. 640,464*), and one for defoaming antibiotic culture fermentations was a mixture of a partial glyceride of animal oil with or without mineral oil (Brown & Farbak—*U. S. 2,550,450*). A liquid buffing or polishing composition for metal contained diglycol stearate as the emulsifier and disperser for water and abrasive powder (Onkey—*U. S. 2,540,376*).

Simultaneously submitting certain fatty oils to polymerization and deodorization treatments yielded products suitable as emulsifiers (Tsuchikawa & Nishimura—*Japan 179,024*). In a review on preparing oil-emulsion drilling fluids, soaps, lignosulfonates, starch, and carboxymethylcellulose were the emulsifiers mentioned (Perkins—*Petroleum Engr. 23B,* No. 4, 60). An emulsifier for technical uses was prepared by sulfonating a mixture of cetyl alcohol and fine mineral oil (Nishio—*Japan 176,325.*) The emulsifiers in two aqueous wax emulsions were, respectively, stearic acid and a volatile emulsifier (Buckman & Rendall—*U. S. 2,504,920*), and N,N-dihydroxyethyl aryl sulfonamide diester of a fatty acid (Aelony—*U. S. 2,505,931*).

Desnuelle *et al.* (*Bull. soc. chim. France 1951,* 197) recorded the interfacial tensions of monoglycerides of peanut oil, lecithin, and mixtures of these with water and also the properties of their unimolecular films. Water precipitated hydrates of lecithin from mixtures of the emulsifiers. Methods of using the commercial partial esters of sorbitans ("Spans" and "Tweens") to solve prescription incompatibilities were worked out for some mentholated lotions, resinous tinctures, and other medicinal emulsions (Stoklosa & Ohmart—*J. Am. Pharm. Assoc. Pract. Pharm. Ed. 12,* 23). A qualitative test for "Tweens" in cosmetics depending on reaction with silicotungstic or phosphomolybdic acids was described giving limitations and listing cosmetic ingredients which might interfere or yield false positive tests (Newburger—*J. Assoc. Off. Agr. Chem. 34,* 109). A quantitative method for determination of polyoxyethylene stearate depended on formation of a complex with the amylose fraction of potato starch, and the amylose not involved was converted to iodine-amylose complex which was determined colorimetrically (MacAllister & Lisk—*Anal. Chem. 23,* 609).

Some of the communications and patents on rubber, synthetic rubber, and polymerization dealt principally with the soap emulsifiers used in the industry. McKeand (*Ind. Eng. Chem. 43,* 415) recorded considerable data on the influence of soaps on the gelling characteristics of Hevea latexes. Soaps improved gelling and gel strength, but decreased mechanical strength of those poor gelling and high strength latexes which had been preserved with sodium pentachlorophenate and ammonia. Nonionic emulsifiers caused a similar decrease in mechanical stability but not a corresponding improvement in gel properties. Data by Kolthoff *et al.* (*J. Polymer Sci. 6,* 73) on the effect of soap on the rate of polymerization of 75:25 butadiene:styrene mixtures showed that the polymerization was constant to about 60% conversion and proportional to the square root of the amount of soap used. A method for the determination of the moment of disappearance of soap micelles in emulsion polymerization depended on measuring the changes in electrolytic conductivity (Klaassens *et al.*—*J. Polymer Sci. 7,* 457). Tests on using soaps from hydrogenated fat stocks as emulsifiers in the manufacture of synthetic rubber indicated that poor results were caused by high heavy metal contamination of soaps. Similarly, Sear & Palit (*Nature 166,* 603) found that polymerization of styrene in presence of ferric soaps was inversely proportional to the square root of the ferric soap present. In a newly patented emulsion polymerization process, 0.5-1.5 parts of soap were first used to obtain 25-30% conversion, and then the soap content was increased to 3-6 parts for obtaining 100% conversion to polymers (Davison & Dunn—*U. S. 2,579,908*). Soaps of rosin derivatives were said to be particularly applicable for emulsion polymerization because they were efficient for the process, they were readily washed from the polymers, and the rubber products were transparent, of high tensile strength and suitable tackiness (Borglin & Ray—*U. S. 2,569,447-9;* Drake—*U. S. 2,569,884*).

The new demulsifiers for separation of petroleum oils from water emulsions that were prepared from fats and other organic compounds used in making surface active agents, consisted of partial esters, sulfonated compounds, alkyd-like derivatives, pyridinium derivatives, and other derivatives with surface active properties (Aquanox Corp.—*U. S. 2,540,437-9;* Petrolite Corp. Ltd.—*U. S. 2,505,948; 2,517,092-3; 2,518,668; 2,524,889-92; 2,541,990-2,542,013; 2,543,223; 2,543,489; 2,549,434-9; 2,552,528-34; 2,554,667; 2,557,081; 2,558,510-13; 2,560,333; 2,562,878; 2,564,191-2; 2,565,549-50; 2,568,115-19; 2,571,116-19; 2,572,885-6; 2,574,538; 2,574,543-5;* Standard Oil Development Co.—*U. S. 2,543,871;* Visco Products Co.—*U. S. 2,568,736-48; 2,572,868;* Wayne—*U. S. 2,547,188*). Pincus *et al.* (*Ind. Eng. Chem. 43,* 521) evaluated the capacity of many surface active agents for breaking tar-water emulsions.

PROTECTIVE COATINGS, RESINS, AND PLASTICS. The historical review and general information papers on these subjects were written on recent advances in protective coating chemistry (Wittcoff—*J. Am. Oil Chemists' Soc. 28,* 399), recent methods of drying oil improvement (Scheifele—*Deut. Farben-Z. 5,* 37), isomerization of oils (Baltes—*Fette u. Seifen 52,* 462), theories on drying of linseed oil (Scheiber—*Ibid. 53,* 16), chemistry of oil bodying (Petit—*Schweiz. Ver. Lack- u. Farben-Chem. u. -Tech. Bull. No. 12,* 5), the importance of the proportions of linoleic, linolenic, and/or eleostearic acids in drying oils (Hilditch—*Paint Ind. Mag. 66,* No. 4, 13), dehydration of castor oil (Scheifele—*Farbe u. Lack 57,* 149; Plisov & Thomson—*J. Applied Chem. 23,* 205), pentaerythritol-tall oil esters for the paint industry (Gourley—*J. Oil & Colour Chemists' Soc. 33,* 175), esterification in the drying oil industry (Reid—*Ind. Eng. Chem. 43,* 1942), polyurethanes and styrene copolymers (Armitage & Hammond—*Chem. & Ind. 1951,* 1082), styrenated oils (Baltes—*Fette u. Seifen 53,* 160; Rinse & Korf—*J. Oil & Colour Chemists' Soc. 32,* 593; Petit & Fournier—*Peintures, pigments, vernis 26,* 357), and water-in-oil emulsion varnish and paint (Bosch *et al.*—*Am. Paint J. 35,* No. 17A, 25).

Among studies on the mechanism of autoxidation of oils several investigations were on monounsaturated acids. Hilditch (*Nature 166,* 558) believed that oleates alone did not undergo autoxidation below 50°C., but in the presence of linoleate, autoxidation occurred on this compound to form peroxide radicals which propagated the oxidation of the oleates. Analysis of products of air-oxidation at 80°C. of a monounsaturated acid by Dal Nogare & Bricker (*J. Org. Chem. 15,* 1299) indicated that carbon dioxide, dihydroxy acid, lower acids, esters resulting from epoxide groups and the carboxyl group of dihydroxy acid, and other unidentified materials were formed. In similar work Knight *et al.* (*J. Am. Oil Chemists' Soc. 28,* 188, 498) autoxidized methyl oleate under ultraviolet irradiation at 35, 70, and 100°C. At 35°C. oxygen added to one of the carbons of the double bond to form a *trans* hydroperoxide; no normal methyl oleate peroxides were evident. In this work, the oxygen introduced was determined by analyses for carbonyl, hydroxyl, oxirane, ester, and carboxyl oxygens on samples withdrawn at intervals and also by difference from carbon and hydrogen analyses. In the late stages of autoxidation the two methods did not check, probably because of formation of ethers which could not be determined. Zilch *et al.* (*Anal. Chem. 23,* 775; *J. Am. Chem. Soc. 73,* 2861) attacked the same problem using analyses by countercurrent distribution techniques to determine the products formed. They isolated unoxidized methyl oleate, a component consisting primarily of methyl oleate hydroperoxide, and a component consisting of peroxides, acid scission products, and other oxidized substances. The data supported the view that monohydroperoxides were the first stable products formed and that the carbon to carbon bond was not attacked until subsequent oxidation.

The above workers (*J. Am. Oil Chemists' Soc. 28,* 285) used the same technique for studying autoxidation of methyl linoleate. The four major fractions segregated were an alcohol-soluble component of about 40% conjugated components with diene and triene conjugation in about equal proportions, an alcohol-soluble component with 60% diene conjugation, a hexane-soluble fraction almost exclusively diene conjugation, and an unoxidized linoleate. There was no evidence of monohydroperoxide, but dimers formed very early in the process. Oxidation and separation of primary products were also performed on methyl eleostearate (Allen & Kummerow—*J. Am. Oil Chemists' Soc. 28,* 101). The results obtained were interpreted to confirm the view that double bonds gave different initial products during oxidation, for the unsaturated system of the radical added oxygen at either of the three double bonds to produce polymers through peroxide bridges. In tests of the relative stability of α- and β-eleostearic acids, the former required storage at 4° and the latter at −40° to inhibit conversion to viscous liquids (Planck *et al.*—*Proc. Am. Tung Oil Assoc. 1950,* 37).

The investigations of Kaufmann *et al.* (*Fette u. Seifen 52,* 276; *53,* 142) on the mechanism of autoxidation of oils were done on various drying oils; and the effects of air, light, temperature, and driers were recorded in relation to the characteristics of the films, oxygen absorption, and carbon dioxide and moisture evolved. The films did not dry in vacuum or under carbon dioxide, although tung oil acids were isomerized to the β-form. Carbon dioxide and moisture evolved after a certain critical amount of oxygen was absorbed, siccative driers accelerated the process and increased oxygen absorption. The results were interpreted to fit the mechanism which involves peroxide formation, and then formation of dioxane systems. These papers also contained general information on effect of processing, natural inhibitors, and catalysts for autoxidation.

Krasnovskii & Gurevich (*Doklady Akad. Nauk S.S.S.R. 75,* 715) related speed of autoxidation of oils in light on metal oxides to the photoactivity of ultraviolet light and the formation of lattices on adsorption of films on the oxides, and they expressed these promoting effects by equations. Honn *et al.* (*J. Am. Oil Chemists' Soc. 28,* 129) also observed that autoxidation was rapid in closely packed monomolecular layers absorbed on porous surfaces.

Other studies on drying oil films were on the character of the film produced. Meier (*Farbe u. Lack 57,* 186) recorded that linseed films increased 62% in weight in 18 days. In this work, water and dilute salt, sugar, and hydrochloric acid solutions dissolved some water-soluble components from films and also inhibited the weight-increase of the films. A method of measuring the thickness of experimental coatings, developed by Kaufmann & Herminghaus (*Fette u. Seifen 53,* 672), was based on including a radio-active isotope in the film material and measuring the radio-activity of the final film. Moore (*Ind. & Eng. Chem. 43,* 2348) correlated properties of various drying oil compositions in alkyd coating material with respect to drying time, hardness, and yellowing of films. The hardness was directly related to the polyenoic acid content without regard to linoleic-linolenic ratio; and yellowing was quantitatively related to the amount of linoleic acid plus five times the linolenic acid present. Changes in the ratio between dienoic and trienoic acids, or between conjugated and nonconjugated unsaturation, did not affect hardness, although conjugation hastened the drying. Salomone's (*Ind. vernice, Milan 4,* 142) observations on yellowing of three fractions of linseed oil obtained by solvent segregation were interpreted to indicate that yellowing was related to mucilage or other impurities present.

Some investigators developed information on improvement of the drying characteristics of oils by isomerization to conjugated double bonds. Desnuelle & Massoni (*Compt. rend. 230,* 965) attributed the smaller tendency to diene conjugation of linoleic acid in certain oils to the presence of isolenoleic acids of configuration forms resistant to the process. They also indicated that the spectroabsorption criterion in such work should not be taken as positive. This latter statement was confirmed by Nichols *et al.* (*J. Am. Chem. Soc. 73,* 247) when they found that some conjugated linoleic acids have lower specific extinction coefficients than products prepared by certain common procedures. The recently described methods of conjugating double bonds of fats were by heating 30 minutes at 320° (Ueno & Sakurai—*J. Chem. Soc. Japan, Ind. Sect. 52,* 256), and heating at 170-200° in the presence of nickel or cobalt catalyst containing a small amount of sulfur (Stejskal —*U. S. 2,553,429*). Blekkingh (*Chem. Weekblad 46,* 362) cautioned that linseed oil should be isomerized under conditions which inhibit formation of monomeric ring compounds so that after-tack does not occur in the final film products.

The methods of converting castor oil to drying oil products dealt with dehydroxylation of the hydroxy acids in a manner to develop conjugated unsaturation. Desnuelle *et al.* (*Bull. soc. chim. France 1950,* 1180; *Compt rend. 231,* 776) recorded analyses during the course of the processes with various catalysts. These data were plotted to serve as applicable fundamental information for the process. The predominant products were conjugated diene and oxy compounds. Similar work by Pillai & Janardhanan (*Indian Soap J. 16,* 51) and by Kochar & Dutt (*Ibid.* 97) indicated that highly acid isomerization catalyst caused excessive condensation and thermal decomposition. Two patents on improved dehydroxylation of castor oils dealt with carrying out the process in the presence of antioxidants (Coffey & Walton—*U. S. 2,517,765,* Schecter—*U. S. 2,552,872*). Pulverized 2-naphtholsulfonic acids were patented as catalyst for the process (Lewis Berger & Sons, Ltd. —*Brit. 644,406*). Dole & Keskar (*Current Sci., India, 19,* 242) report that aromatic sulfonic acids of a single ring structure were superior as catalysts to polyring aromatic sulfonic sulfuric acids. Zeolite matter was also patented for the process (Matsubayashi & Shiozawa—*Japan 179,397*). The drying properties of grape seed oil were improved by hydroxylation with enzymes or by chemical means (Salomone—*Olearia 4,* 367).

Several other methods were used to improve the drying properties of oils. The literature reviewed in the preceding section of this paper under fractionation of oils and the patent by Vogel (*U. S. 2,569,136*) told how drying fractions could be segregated from semidrying oils by preferential solubility in polar solvents. Adams *et al.* (*U. S. 2,569,595*) patented use of special adsorbants to extract color from polymerized oils. The unsaturation of oils was increased by bromination with N-bromosuccinimide followed by debromination (Bergström & Hansson—*Acta Chem. Scand. 4,* 435; Hsing & Chen—*J. Chinese Chem. Soc. 18,* 79). In work on improving the drying qualities of tobacco seed and safflower seed oils, the extent of improvement obtained by heating with resorcinol and sodium bisulfite, hydroxylation with selenium oxide, and isomerization with various catalysts, respectively, were evaluated with regard to the varnishes made from them (Sharma *et al.*—*J. Sci. Ind. Research, India 10B,* 33). Soybean oil paint vehicle was improved in drying characteristic by the presence of lime (Lewis *et al.*—*U. S. 2,550,703*). New patents were also issued on improvement by esterifying the fatty acids of oils with polyhydroxy alcohols or their etherified products (N. V. de Bataafsche Petrol. Maatschappij—*Dutch 67,571;* Wicks—*U. S. 2,558,025;* Wayne—*U. S. 2,566,268;* Jordan & Herban—*U. S. 2,572,035*). Investigational reports on these showed that products of xylitol with fatty acids of soybeans average 4-5 esterified hydroxy groups, and they were superior to the original oil (Teeter *et al.*—*J. Am. Oil Chemists' Soc. 28,* 299); diglycerol esters were superior to the triglycerides as drying oils (Northwestern Paint & Varnish Production Club—*Official Digest Fed. Paint & Varnish Prod. Clubs No. 310,* 827); and suitable paint oil was made from tall oil by esterification with pentaerythrite, treatment with maleic acid, and copolymerization with styrene (von Nikusch—*Farbe u. Lack 56,* 91).

Wrinkling in film-forming drying oils was treated in the literature both as a desirable and as an undesirable property. Drying oils were modified to give desirable ornate wrinkle finishes by partial chlorination and treatment with unsaturated lower organic-inorganic compounds (Williams—*U. S. 2,529,528*) and by the presence of finely divided copper (Williams—*U. S. 2,528,936*). The tendency of oils to cause undesirable wrinkling in protective coatings was inhibited with small amounts of dialkyl or dibenzyl disulfide (Coffey & Lukas—*U. S. 2,566,169*), with small amounts of antioxidants (Colomb —*Ind. Vernice, Milan 5,* 34), by adding reaction products of dibasic acids and linoleic acid dimer (Goebel & Moore—*Paint Varnish Production 41,* No. 8, 20), and upon reducing mineral oil thinner in the paint products made from the wrinkling drying oil (Boller & Lichthardt—*Farbe u. Lack 56,* 528). Kaufmann & Strüber (*Fette u. Seifen 53,* 543) suggested that wrinkling of drying oils was caused by a greater uptake of oxygen on the surface than in the lower parts of the film, thus expanding the upper film to a greater degree. They found that proöxidants, partial prepolymerization, and presence of aerosols inhibit the phenomena; whereas antioxidants and dust particles cause the faster surface drying. Frosting and gas checking of films of drying oil-alkyd resin products was inhibited by additions of small amounts of alkylated phenol-aldehyde resins (Dannenberg—*U. S. 2,559,347*).

New oil bodying information was published. Hess & O'Hare (*Paint & Varnish Prod. 31,* No. 4, 19) recorded the effects of air flow, agitation, and temperature on oxidation polymerization of drying and nondrying oils. Linolenic and linoleic groups acted similarly in this work whereas the oleic, eleostearic, and 9,11-linoleic constituents gave different results. Rhodes' & Davalle's (*J. Am. Oil Chemists' Soc. 28,* 466) evaluation of polymerized safflower oil placed it intermediate between comparable products of linseed and soybean oils. Oils for painting colors were only partially bodied in open tanks to allow absorption of oxygen from the air in a manner to induce emulsifying properties in the product (Schlick—*Ger. 801,643-4*). According to Fisher (*U. S. 2,567,106*) oils were bodied by exposure to a high-frequency electrical field in place of the conventional heating. Two patented procedures for bodying made use of boron trifluoride as a catalyst for the process (Konen & Clocker—*U. S. 2,547,760*); Bradley —*U. S. 2,550,961*). An investigation with this catalyst in the polymerization of ethyl oleate indicated that combinations of boron trifluoride and phosphoric acid were very active catalysts and dimers were the only polymers formed from oleates (Topchiev & Vishnyakova—*Doklady Akad. Nauk S.S.S.R. 71,* 493). Other patented catalysts for the bodying process were metallic selenites and tellurites (Turk & Boone—*U. S. 2,530,923*).

Improved bodied products were prepared by cobodying oils with other polymerizable unsaturated radicals or compounds. The allyl compound polymer patents were on allyl esters of fatty acids (Pollack—*U. S. 2,536,568*), fatty acid esters of polyallyl alcohol (Adelson & Gray—*U. S. 2,555,775;* Bent—*U. S. 2,541,148*), and copolymers of fatty oils and polyallyl ethers (Roach—*U. S. 2,555,834*). Those on copolymerization of styrene or styrene derivatives with fatty oil products dealt with polymerization in a solvent (Nye—*U. S. 2,556,336*), inclusion of polyallyl ether as a third component (Roach—*U. S. 2,562,537*), the presence of a monocyclic-α terpene to prevent gelation (Wakeford & Hewitt—*U. S. 2,567,137*), use of the fatty component in the form of a partial ester of a polyhydric alcohol (Wakeford *et al.*—*Brit. 640,836*), as the ester of pentaerythritol (Robinson—*Brit. 651,560*), or as a maleic acid modified oil or using maleic acid as an additional component (Rust & Canfield—*U. S. 2,524,022;* Root—*U. S. 2,559,465-6;* Malinowski—*U. S. 2,561,313;* Wakeford—*Brit. 640,832*), and use of isopropenyl compounds as an additional component (Marling—*U. S. 2,577,709*). In other patents the fatty material was copolymerized with conjugated olefin material in general (Marhofer—*U. S. 2,552,684;* Bloch & Hoffman—*U. S. 2,523,609;* Tracy—*U. S. 2,554,280*), cyclic diene hydrocarbons (Bobalek—*U. S. 2,549,767;* Moffett & Hoya—*U. S. 2,551,387*), and unsaturated amines containing at least one alkenyl radical (Danforth—*U. S. 2,566,515*). Communications containing reports of practical experience and theoretical discussions of making the above polymers with description of the products were on products from vinyl esters of fatty acids (Port *et al.*—*J. Polymer Sci. 7,* 207; Rheinieck—*J. Am. Oil Chemists' Soc. 28,* 456), vinyl and allyl esters of fatty acid products (Harrison & Wheeler—*J. Am. Chem. Soc. 73,* 839), styrene-oil products (Falkenberg—*J. Am. Oil Chemists' Soc. 28,* 496), and 2-chloroallyl linoleate-styrene copolymerization (Dyer & Meisenhelder—*J. Am. Chem. Soc. 73,* 1434). Kappelmeier *et al.* (*Verfkroniek 23,* 263; *Deut, Farben-Z. 5,* 233; *Paint Technol. 15,* 477; *Paint, Oil & Chem. Rev. 114,* No. 3, 16) analyzed styrenated drying oils by solvent segregation and determining the saponification value and other characteristics of the fractions. These results were discussed in relation to theoretical and technical considerations.

The alkyd product inventions were a reaction product of drying oil, polyalcohol ester with monoalkenyl, and polycarboxylic acid (Rust—*U. S. 2,570,385*), a product of maleic anhydride, fatty acid ester of unsubstituted alcohol, and boric acid (Kosmin—*U. S. 2,569,420*), polymers of maleic-fatty acid adducts and bisazolines (Rowland—*U. S. 2,547,497-8*), method of reacting nondehydrated castor oil with maleic anhydride (Ullmann—*U. S. 2,502,606*), condensation products of rosin, maleic anhydride, linseed oil, diethylene glycol, and glycerol (Adams—*U. S. 2,537,949*), resinous product of pentaerythritol, rosin acids, and α,β-unsaturated polycarboxylic acid or anhydride (Rheinieck—*U. S. 2,569,495*), alkyd resins modified with unsaturated fatty acids (Wittcoff & Roach—*U. S. 2,572,085-6*), synthetic fatty acid-polyhydric alcohol esters modified with phthalic anhydride and lead (Jordon & Wittcoff—*U. S. 2,579,499*), a rosin, maleic acid, and glycerol product (Kobbe—*Ger. 801,737*); alkyd resin modified with (hydroxymethyl)melamine and 4,4′-biphenyldi-sulfonylazide to yield a foam resin (Ott—*U. S. 2,532,240*), oil-modified and cellulose-derivative-modified alkyd resin (Scholz & Taylor—*U. S. 2,553,682*), and means of improvement of maleic adducts by solvent segregation (Heiberger—*U. S. 2,537,134*). The communications giving practical information on alkyds were on making varnish with the products from grape seed oil (Zaccarini—*Ind. vernice, Milan, 5,* 51) and with oiticica oil (Letts—*Ibid. 2,* 295); making the resins with safflower oil (Thurmond *et al.*—*J. Am. Oil Chemists' Soc. 28,* 354) and with linseed, tobacco seed, safflower and coconut oils (Kapur & Sarin—*J. Sci. Ind. Research, India, 10B,* 94).

Other resins-drying oil compositions were made by reacting oils with diallyl isopropylidenebis-(phenoxyacetate) (Rust & Canfield—*U. S. 2,563,873*), with 2-furaldehyde and mesityl oxide (Harvey—*U. S. 2,565,685*), with acrolein (Whetstone—*U. S. 2,568,426*), with oxygen gas previously passed through ketene or diketene (Keenan—*U. S. 2,555,976*), with crotonaldehyde (Fitzpatrick—*U. S. 2,554,528*), with phenols (Greenlee—*U. S. 2,542,664*), with drying hydrocarbon oils, and aldehydes, or ketones (Geiser—*U. S. 2,565,654*), with phenol-formaldehyde resins (Müller—*Deut. Chem. Ztg. 2,* 207), with diamines (Bradley—*U. S. 2,555,111*), and with urea (Eckey & Abbott—*U. S. 2,574,864*). The last produced a resin intermediate.

Technical information on drying oils, their derivatives, and adducts made from them was recorded with respect to the making of caulking compounds (Figliolino—*Paint Varnish Prod. 41,* No. 6, 17) and linoleum (Schmidt—*Farben, Lacke, Anstrichstoffe 4,* 373), and for use as core-bonding agents (White—*Oil Colour Trades J. 114,* 1342). A patented core-binding agent contained drying oil and small amounts of metal drier and peroxide compound (Moser—*U. S. 2,556,335*). Products suitable as linoleum bases or similar factice were made by chlorinating rubber-fatty acid mixtures (Sommers—*U. S. 2,536,579*). Drying oil polymers were used as binders for fibers of a newly patented brake lining (Kuzmick—*U. S. 2,539,631*).

The new drier composition inventions comprised mixtures of metal soap driers with *o*-phenanthroline or $\alpha,\alpha'$-dipyridyl (Wheeler—*U. S. 2,565,897*), and with esters of lower alcohols with lactic and tartaric acids (Packer—*U. S. 2,531,460*). Gorbach & Bukowiecki (*Fette u. Seifen 53,* 631) described two micro-methods for evaluating dryers and the amounts necessary. One depended on the distortion of a droplet of drier-containing oil on glass fiber, and the other dealt with using chromotography paper as the holder for the oil sample.

WATER-INSOLUBLE METAL SOAPS AND LUBRICANTS. Among metal soap literature a patent (Kebrich—*Brit. 650,164*) was on reacting lead oxide with fatty acids for paint purposes, and the reviews (Hadert—*Fette u. Seifen 52,* 741; Licata—*Paint Oil & Chem. Rev. 114,* No. 13, 16; Nebbia—*Olearia 5,* 90) contained general information on properties and applications of the soaps, while the other information on the soaps in this subdivision pertained to their use in lubricants.

New confirmations that aluminum soap gels were made of difatty acid salts of aluminum in solution with fatty acids were based on phase equilibrium data between acid solutions and the solid soap (Black & Almin—*Acta Chem. Scand. 4,* 1401), on the heat of reaction of fatty acids and aluminum alkoxides (Alexander & Gray—*Proc. Roy. Soc., London A200,* 162), the degree of association in solution, effect of moisture, and the spreading properties (McRoberts & Schulman—*Ibid.* 136). These publications and two others on gelling characteristics of the aluminum soaps (Parry—*Ibid.* 148, Cheremisinoff & Stumpf—*Am. Paint J. 35,* No. 42, 94) related manufacturing technique, composition of the gel, and solvent to viscosity or plasticity and other properties of interest in lubricant manufacture. An entirely new means of demonstrating that aluminum soap in gels does not exist as the trifatty acid derivative was based on the inability of aluminum trilaurate made from aluminum trimethyl and pure lauric acid to form gels in hydrocarbons unless moisture was present to hydrolyze off some fatty acid (McRoberts *et al.*—*J. Chem. Soc. 1950,* 2082).

Physical data were recorded on various metal soap-hydrocarbon systems which should be technically useful. Banerjee & Palit (*J. Indian Chem. Soc. 27,* 385) determined the dipole moments of oleates of zinc, copper, magnesium, nickel, lead, and calcium in benzene. Cheremisinoff (*J. Am. Oil Chemists' Soc. 28,* 278) recorded the water solubility, acetone solubility, softening point, gel temperature, and gel color of several silver soaps. The gelling, in this work, was observed in xylene. The rheologic properties of aluminum stearate (Rager—*Rev. inst. franc. petrole 5,* 311), and soaps of sodium, lithium, and aluminum (Moses & Puddington—*Can. J. Chem. 29,* 996) dispersed in hydrocarbon oils were determined. These data contained information on the relation of temperature and concentration to viscosity, or shear, and thixotropy. A thermal analysis of the system sodium stearate-cetane was made to ascertain the state of the system at various temperatures and concentrations (Stross & Abrams—*J. Am. Chem. Soc. 73,* 2825). An investigation on the peptisation of zinc soap with organic compounds showed that organic bases were most efficient (Tughan & Pink—*J. Chem. Soc. 1951,* 1804). An x-ray diffraction study of calcium stearate monohydrate-cetane systems led to postulations that the solid soaps consisted of regular micellar layers superimposed with stacking disorder, and that water enhanced the stability of the systems by its effect on the colloid structure rather than by a reaction to form calcium stearate monohydrate (Vold & Smith—*J. Am. Chem. Soc. 73,* 2006).

In an investigation on lubrication of rough steel surfaces, soaps were the most effective lubricant; fatty esters were less effective; and hydrocarbons were poor lubricants (Barwell *et al.*—*Phys. of Lubrication, Brit. J. Applied Phys. Suppl. 1, 1951,* 44). In this work the metallic ion or the acid radical in the soaps had little effect on friction other than that attributed to the physical state of the lubricant. Glass & Rubin (*Inst. Spokesman 14,* No. 11, 7) in a discussion on greases described products suitable within the range of —65 to 250°F. and mentioned that some will function at —100°F. He stated that an immediate objective was a grease suitable up to 400°F. for use by the Air Force. A method for testing high-temperature performance of greases was based on packing into ball bearings and their useful lubricating lives determined by the number of hours the bearing would run before seizure or large power consumption takes place (Finn—*Ibid.* No. 9, 7).

A continuous grease manufacturing plant was designed by Stevens (*U. S. 2,542,159*). Barium soaps were used as the soap constituents of products stable to 200°F. (Carmichael & Armstrong—*U. S. 2,564,561*). Soaps of myristic acid (Puryear & Bray—*U. S. 2,542,570*), isomerized and polymerized acids (Whitney—*U. S. 2,545,126*), dimerized acids (Ashley & Mason—*U. S. 2,555,104*), castor oil acids (Davies & Noad—*U. S. 2,566,793;* N. V. de Bataafsche Petrol. Maatschappij—*Dutch 66,982;* Union Oil Co.—*Fr. 943,251*); fatty acids containing mercaptans (Morway & Smith—*U. S. 2,567,023*), and tall oil fatty acids (Morway & Kolfenbach—*U. S. 2,576,031*) were used in grease manufacture to obtain special properties such as high temperature resistance, water resistance, and desired consistency. Improvement of stability in greases was obtained by adding polymer-like compounds containing four moles of alkylsuccinic acid with two terminal stearate radicals (Knowles, *et al.*—*U. S. 2,528,373*). Sorbitan trioleate (O'Halloran—*U. S. 2,562,814*) and aliphatic alcohol-fatty acid esters (Morway—*U. S. 2,565,981*) were added to greases to improve the physical structure. Other soap greases were patented in which nonfatty compounds were used as modifiers (O'Halloran—*U. S. 2,534,053;* Bondi—*U. S. 2,545,190;* Smith & Cantrell—*U. S. 2,545,114;* Morway, *et al.*—*U. S. 2,576,032-3*).

The fatty compounds added to lubricants to inhibit corrosion were fatty ketone-phosphorus pentasulfide reaction products (Hughes—*U. S. 2,553,588*), sulfured fatty amines or sperm oil (Hughes & Bartleson—*U. S. 2,553,586*), fatty selenomercaptans (Stewart & Clayton—*U. S. 2,543,734-5*), condensation products of castor oil fatty acids and sulfonic acid compounds (Ruedrich—*U. S. 2,556,108*), similar products with pentaerythritol oleate (Zimmer, *et al.*—*U. S. 2,560,202*); zinc dixylylstearate (Zisman, *et al.*—*U. S. 2,539,504*), and zinc diphenylstearate (Zisman, *et al.*—*U. S. 2,539,503*). The fat derivatives patented as pour point depressors for lubricants were a pyrolytic product of fatty acid halides (Mikeska & Lippincott—*U. S. 2,525,076*), polyallyl esters of fatty acids (Butler—*U. S. 2,541,686*), and polymerized fatty acid-fatty alcohol esters (Evans & Whetstone—*U. S. 2,524,563*). The new viscosity improvers were polyvinyl esters of fatty acids (Port, *et al.*—*Ind. Eng. Chem. 43,* 2105), copolymers of allyl fatty acid esters with diallyl or divinyl phthalate (Larsen & Marple—*U. S. 2,541,590*), complex compounds of dicarboxylic acid, fatty acids and alcohols (Mikeska & Smith—*U. S. 2,559,510*), and reaction products of phosphorus pentasulfide on unsaturated fatty materials (Musselman—*U. S. 2,566,241*). Phosphorus containing fatty material was used as an antioxidant additive (McDermott—*U. S. 2,545,158*). Glycol and glycerol esters of oleic acid were patented as extreme pressure additives (Stucker—*U. S. 2,541,789*).

Lubricant oils were derived from fatty oils. Methods of preparing and polymerizing squalene for various lubricant uses were described (Ishikawa, *et al.*—*Repts. Sci. Research Inst., Japan 24,* 244, 398, 401; Yamaguchi, *et al.*—*Rept. Inst. Sci. &*

*Technol. Univ. Tokyo 4,* 16, 83). Catalytic polymerization of non-drying and semi-drying fat oils with the use of antimony trichloride as the catalyst yielded suitable lubricants (Meerburg—*U. S. 2,558,494*). Blown rape oil was mixed with mineral oil lubricant (Sharma, *et al.—Proc. Ann. Convention Oil Technol. Assoc., India 2,* 6). Lubricant hydrocarbons were prepared by hydrogenating (Murata—*Japan 176,128*), and pyrolyzing (Bhasin & Aggarwal—*J. Sci. Ind. Research, India, 9B,* 298; Ishikawa, *et al.—Repts. Sci. Research Inst., Tokyo, 24,* 239; Ueno & Sigeno—*J. Chem. Soc. Japan Ind. Sect. 52,* 164) fatty material. Motor fuel was also produced in these processes. Practical experiences on using castor oil (Mathur *et al.—J. Sci. Ind. Research, India, 9B,* No. 5, 121) and several little known seed oils (Thiagarajan & Srikantan—*J. Indian Chem. Soc. Ind. & News Ed. 13,* 163) as lubricants were published.

Fatty derivatives were prepared for special lubricant purposes. A watch lubricant consisted of the monophenyl and 9- and 10-phenylstearic acid esters of glycol (Martin—*U. S. 2,534,611*). A lubricant for use on the bearings of the dial of telephones consisted of a mixture of aluminum soap, a polycarboxylic acid of at least 16 carbon atoms, and dibutyl phthalate (Bloomenthal & Wood—*U. S. 2,530,804*). One for wire rope contained hydrogenated fish oil acids, metal soaps, petroleum sulfonate, fatty phenyl amine, and wool grease Mowray & Zimmer—*U. S. 2,556,289*).

The literature on textile oils included a review of new information on producing textile olein (Schlenker—*Seifen-Öle-Fette-Wachse 77,* 306), a description of the use of atomizers to distribute oleins on wool in a manner that inhibits oxidation (Vallee—*Bull. mens. ITERG 4,* 513), and a record of results obtained on stabilizing oleins with antioxidants, by aging with lead salts, by removing linoleic acid by solvent segregation and other means (Francois & Juillard—*Ibid. 5,* 173, 186, 238).

The fat additives for mineral oils and oil emulsions used as cutting oils were partial esters of fatty acids and aliphatic hydroxy polycarboxylic acids (Blake—*U. S. 2,531,801*), rosin soaps (Dixon—*U. S. 2,563,588*), sulfured fatty oils (Ishii—*Japan 175,991*), fats sulfured at 50-100°F. (Sperry—*U. S. 2,577,636*), and soap or detergents (Schott & Lang—*U. S. 2,540,795*).

**Preparation of Fatty Acids, Fatty Esters, Fatty Ketones, and Nitrogen and Hydrocarbon Derivatives of Fats.** Linoleic acid and some of its isomers were synthesized to study the properties of the pure compounds (Walborsky, *et al.—J. Am. Chem. Soc. 73,* 2590; Gensler & Thomas—*Ibid.* 4601; Howton & Davis—*J. Org. Chem. 16,* 1405) and because of their physiological interest (Schmid & Lehmann—*Helv. Chim. Acta 33, 1494*). Oleic acid isomers were synthesized to gain information for methods of isolation, purification and determination of the acids in natural fats (Brown, *et al.—J. Am. Oil Chemists' Soc. 28,* 416; Gensler—*J. Am. Chem. Soc. 73,* 1071). The $C_{18}$ to $C_{24}$ saturated acids were synthesized from lower aliphatic chlorides and dicarboxylic acids (Sobotka & Stynler—*Ibid. 72,* 5139). Fatty chlorides were converted to homologous fatty acids containing an additional carbon atom by the Arndt-Eister reaction (Vandenheuvel & Yates—*Can. J. Research 28B,* 556). Arosenius, *et al.* (*Arkiv. Kemi Mineral Geol. 26A,* No. 19, 20 pp.) synthesized various acids and their amides with 13 to 35 carbon atoms and recorded their general properties and crystalline structure as determined by x-rays. A method of reducing the chain length of fatty acids by exactly two carbon atoms involved forming the chloride, α-brominating this, debromination, and saponifying (Hunter & Popjak—*Biochem. J. 50,* 163). The recent literature on fatty acid synthesis was reviewed by Breusch (*Fortschr. Chem. Forsch. 1,* 567) and Seher (*Fette u. Seifen 53,* 692). Many branched chain fatty acids were also synthesized in connection with biological investigations and studies of the properties of the compounds (Dickman—*Rev. faculte sci. univ. Istanbul 15A,* 108; Cason, *et al.—J. Org. Chem. 15,* 850, 1170, 1177, 1181; Moroe—*J. Pharm. Soc. Japan 71,* 116, 121, 123; Weitzel & Wojahn—*Z. Physiol. Chem. 285,* 220). In work on catalyzed esterification of branched-chain acids with methanol, the side chain seemed to increase the polarity of the carboxyl group (Schulte & Kirschner—*Fette u. Seifen 53,* 267).

Specific fatty acids were prepared for technical purposes. Moore (*Paint, Oil & Chem. Rev. 114,* No. 1, 13) published information on the uses of dimer fatty acids in the paint and other industries. The use of esters of dimeric acids as nondrying adhesives was patented (Wingfoot Corp.—*Brit. 585,664*). Frey *(U. S. 2,525,889)* increased the chain length of normal fatty acids by heating with isoparaffins in the presence of hydrogen fluoride. Fatty acids were arylated for the production of germicides (Asano, *et al.—J. Pharm. Soc. Japan 70,* 622; Shinozaki & Ishimoto—*J. Soc. Chem. Ind. Japan 45B,* 81). Peroxides developed in fatty material with enzymes were suitable for bleaching fats and baked food products. Epoxidized oils and fatty acids were patented as intermediates for the manufacture of plastics (Swern & Findley—*2,567,930, 2,569,502*). Hydroperoxide fatty acids were useful for the flotation concentration of minerals (Bishop, *et al.—U. S. 2,535,344-5*). Chlorinated fatty acids were patented as plasticizers for protein colloids (Molteni—*U. S. 2,530,439*). Optimum methods of preparing fatty chlorohydrins by reaction of fatty acids or the esters with chlorine gas or hypochlorites were developed (Naudet—*Bull. soc. chim. France 1950,* 842). Patented polishing (Lupo—*U. S. 2,545,291*), leather softening (Gelinas—*U. S. 2,580,167*), and buffing (Young—*U. S. 2,570,904*) compounds contained fatty acids, and other fatty derivatives.

Specific triglycerides (Baer & Newcombe—*Can. J. Chem. 29,* 812), 1,3-diglycerides (Baur & Lange—*J. Am. Chem. Soc. 73,* 3926) and difatty-L-α-phosphatidic acids (Baer—*J. Biol. Chem. 189,* 235) were prepared to examine those properties which would aid in the study of comparable natural materials. Preparation procedures and properties were also recorded on long chain alcohol esters of fatty acids (Crowe & Smith—*J. Am. Chem. Soc. 73,* 5401), mixed esters of lactic and fatty acids (Fein—*Ibid.* 5870), and vinyl fatty esters (Swern & Jordon—*Org. Syntheses 30,* 106). Optimum conditions for preparation of methyl-fatty acid esters directly from fats by reaction with methyl sulfate were published (Young & Craig—*J. Am. Oil Chemists' Soc. 28,* 521).

Various fatty acid esters were made for technical purposes. Esters of oleic acid with unsaturated alcohols were made for use as intermediates for useful polymerized products (Swern & Dickel—*U. S. 2,527,597*). A continuous process was designed for acylating castor oil (Fisher & Fein—*U. S. 2,562,900*). A mixture of monooricinoleate esters and alkali borates was used in liquid rust-proofers (Burghart—*U. S. 2,566,923-6*). Castor oil orthosilicate gels were used to impregnate paper-wound electric capacitors (Miller & Flowers—*U. S. 2,544,342*). An antibiotic chloromycetin preparation was in the form of chloromycetin palmitate (Larkin—*Proc. Soc. Exptl. Biol. & Med. 78,* 191).

Heptanal and hendecenoic acids were manufactured by heating ricinoleic esters on metal or quartz surfaces (Soc. Organico—*Fr. 952,985*). Lauraldehyde was produced by dehydrogenating dodecyl alcohol at 310-20° in the presence of metal oxide catalysts (Ueno, *et al.—J. Chem. Soc. Japan, Ind. Sect. 52,* 140). Condensation of oleic acid with formaldehyde yielded $C_{19}$ keto-aldo- and keto-hydroxy-acids, semicarbazone and a disemicarbazone (Pigulevskii & Tatarskaya—*Zhur. Obshchei Khim. 20,* 1456).

The descriptions on manufacture of fatty alcohols from fats contained methods based on sodium reduction (Pryde—*J. Am. Oil Chemists' Soc. 28,* 16), on special hydrogenation processes (Ueno—*J. Chem. Soc. Japan, Ind. Sect. 52,* 53; Warren—*Chem. Eng. 58,* No. 6, 117; Peppel—*U. S. 2,538,034*), or a combination of alkali treatment and hydrogenation (Orth—*Ger. 803,832*), by means of using calcium-sodium mixtures, recovered from the electrolytic manufacture of sodium, for the reduction of the fats (Calingaert—*U. S. 2,543,399*), and on extracting the alcohols from reduced fats and saponified sperm oil (Blinoff—*U. S. 2,530,042*).

The new data on characteristics of fatty alcohols included a record of refractive indexes of pure and mixed $C_{12}$ to $C_{18}$ alcohols (Paquot—*Oleagineux 5,* 644), the polymorphism observations of *n*-hexadecanol and *n*-octadecanol (Kolp & Lutton—*J. Am. Chem. Soc. 73,* 5593), and the behavior of ricinoleyl, linolyl, and linolenyl alcohols with regard to viscosity, polymerization and change in unsaturation (Jacini—*Chimica e industria, Milan, 32,* 268).

Decarboxylation of fatty acids by α-particle radiation occurred with greater ease as the size decreased from $C_{22}$ to $C_{2}$ (Whitehead, *et al—J. chim. phys. 48,* 184). Other means of removing the carboxyl groups of fatty acid to produce the hydrocarbon were by hydrogenation with zinc chloride and moisture as catalyst (Wakayama—*J. Soc. Chem. Ind. Japan 50,* 116), by reaction with phthalic anhydride (Petru—*Chem. Listy 43,* 75; Waldmann & Petru—*Chem. Ber. 83,* 287) and by reaction of persulfates on soaps (Kolthoff & Miller—*J. Am. Chem. Soc. 73,* 5118).

Patents assigned to Armour & Company described the process and equipment for manufacture of fatty acid nitriles by reaction with ammonia *(U. S. 2,546,521; 2,555,606)*, refining the nitriles by treatment with phosphoric acid *(U. S. 2,548,369)*, and their hydroxylation by sulfating and hydrolysis of the sulfate radical *(U. S. 2,558,666)*. The products were intermediates for plastics, flotation agents, and detergents. Rubber-like compositions were prepared from the nitriles by vulcanizing with butadiene polymers (Ralston & Corley—*U. S. 2,564,857*). Hydrogenation of fatty amides with metal oxide catalyst yielded alcohols (Ueno, *et al.*—*J. Soc. Chem. Ind. Japan 45B*, 214).

Other nitrogen-fatty derivatives were made for special purposes. Fatty quaternary pyridinium salts were patented as water repellent coating compositions (Green—*U. S. 2,557,653*). Reaction products of fat with polyalkylenepolyamines provided corrosion inhibitors (White *et al.*—*U. S. 2,568,876*). The antiseptics and insecticides prepared by Takahashi & Kondo (*J. Pharm. Soc. Japan 67*, 223) were disubstituted fatty piperidine compounds.

## Deterioration

REVIEWS. The general discussion and review papers on fat spoilage were written on methods for testing for spoilage (Sokolov & Mirkin—*Myasnaya Ind. S.S.S.R. 21*, No. 6, 69; Beadle—*Advances in Chemistry Ser. 3*, 55; Zinov'ev—*Myasnaya Ind. S.S.S.R. 21*, No. 6, 70), determination and inhibiting rancidity in fish oils (Szybalski—*Przemysl Chem. 6*, No. 29, 262), preservation of fats and oils (van der Ley—*Seifen-Öle-Fette-Wachse 77*, 355), oxidative reactions in fatty material (Täufel—*Fette u. Seifen 53*, 558; Sims—*Can. Chem. Process Inds. 35*, 125), determination of the oxidative processes (Fiedler—*Seifen-Öle-Fette-Wachse 77*, 137) and stabilization of fatty materials (Cartwright—*Soap Perfumery & Cosmetics 24*, 47). A report on chemicals in foods to the Association of Food and Drug Officials contained some information on suitability of using antioxidants (Lehman—*Assoc. Food & Drug Officials of U. S. 15*, 82).

TESTING FOR DETERIORATION. Several investigations concerned the measurement of the peroxide value. Three studies involved the use of ferric thiocyanate as the analytical reagent. Golden (*J. Am. Pharm. Assoc. 40*, 119) found the method simple, accurate, and requiring 75-90% less time than the Swift active oxygen method. Devi & Ray (*Current Sci., India, 19*, 243) considered the method more sensitive than the Lea iodometric determination. Kolthoff & Medalia (*Anal. Chem. 23*, 595) considered the method rapid but less accurate than iodometric methods; consequently, they emphasized its usefulness only for control work where relative peroxide values were desired. Of two modifications of the iodometric determination of peroxide value only one was a combination of the Wheeler and Lea procedures (Mukherjee—*J. Indian Chem. Soc. 27*, 87), and the other was on standardization of the procedure used in Russia so that results would be consistent (Drozdov & Starikova—*Myasnaya Ind. S.S.S.R. 22*, No. 3, 52). Cleaning glassware with synthetic detergents rather than with the usual chromate-sulfuric acid cleaner improved reproducibility of stability results by the Swift active oxygen method (Fore *et al.*—*J. Am. Oil Chemists' Soc. 28*, 73). An oxygen-absorption apparatus for measuring the induction periods of fats comprised a syringe which contracted due to a reduction in oxygen thereby opening an electric circuit arranged with a clock for timing (Hunter—*J. Am. Oil Chemists' Soc. 28*, 160).

Several studies were on the aldehyde reactions of spoiled fats. Patton *et al.* (*J. Am. Oil Chemists' Soc. 28*, 391) applied the Kreis color reaction to 31 compounds which they thought were likely products of fatty decomposition due to spoilage. They obtained positive tests with malonic dialdehyde, malonic dialdehyde diacetal, oxidation products of trimethylene glycol, and oxidation products of acrolein. However, only the colors obtained with the first and the last of the above products were spectrally similar to the Kreis colors developed with rancid fats. Pool & Klose (*Ibid.* 215) used a chromatographic method to isolate monoaldehydes from rancid fats. In this method the aldehydes were converted to the hydrozones and observed spectrometrically. A method for detecting deterioration in milk fat depended on the infrared spectrophotometric observations for ketones or aldehydes separated from the fat by steam volatilization (Henick—*Food Tech. 5*, 145). Drozdov & Materranskaya (*Myasnaya Ind. S.S.S.R. 22*, No. 2, 30) modified the Kreis test to obtain quantitative results by standardizing the details of the procedure and preparing color standards for measuring the intensity of the color produced.

Two studies on rancidity were records of objective and subjective tests on various fats (Guimaraes & Pechnik—*Engenharia e quim, Rio de Janeiro 3*, 18; Sudachenkov—*Myasnaya Ind. S.S.S.R. 22*, No. 4, 29). The limitations of the tests with regard to quantitative and comparative aspects were discussed. A similar study was made on the fat of pork products (Naumann *et al.*—*Food Tech. 5*, 496).

Methods of testing in connection with deterioration of fats also included analyses for antioxidants in fatty products. Mahon & Chapman (*Anal. Chem. 23*, 1120) found that 2,6-dichloroquinonchlorimide was a better reagent than ferric chloride for determination of butylated hydroxyanisole antioxidant in fats. A method for determining propyl gallate, butylated hydroxyanisole, nordihydroguaiaretic acid, and tocopherol by the same investigators (*Ibid.* 1116) depended on segregating the first three compounds from tocopherol by extracting a petroleum ether solution with alcohol; removal of the first compound and colorimetric determination with ferrous tartrate, determination of the second and third compounds by differentiation in rate of color development with ferric-chloride-1, 1'-bipyridyl reagent, and determination of the tocopherol in the petroleum ether solution of the fat by any well known procedure.

Peanut oil passed through an absorption column containing sections of activated carbon and filter aid, activated alumina, and anhydrous sodium sulfate, respectively, had a keeping time of two hours in the Swift stability test and was useful for evaluating and distinguishing antioxidants from synergists, and for the preparation of vitamin-free fat diets (Fisher & Bickford—*Am. J. Pharm. 123*, 233).

MECHANISM OF DETERIORATION. Khan, Brown & Deatherage (*J. Am. Oil Chemists' Soc. 28*, 27, 105) studied the mechanism of oxidation of oleates by determining oxygen consumption and products such as water, carbon dioxide, partial oxidation products and double bonds in the residue after autoxidation of synthetic methyl oleate, methyl stearolate, and methyl-9,10-dideuteriooöleate. This work suggested that oxidative attack was initiated at the double bond, progressed to the α-methylenic position, and then involved moisture formation, etc. At least some of the hydrogen in the water formed came from the olefinic hydrogen. Most of the volatile cleavage products arising from the rupture of the carbon-to-carbon bond appeared to be peroxidic in character. The peroxides formed were different from commercially available organic peroxides, for the former oxidized oleate to dihydroxystearic acid whereas the others gave low-melting isomers. In subsequent work (Max & Deatherage—*Ibid.* 110) studied oxidation of 8,8,11,11-tetradeuterio-*cis*-9-octadecene and *cis*-9-octadecene. The results were interpreted to indicate oxidative attack at the α-methylenic position. The hydrogen of the water formed did not come from the α-hyperoxide for it contained very small amounts of deuterium.

The studies on autoxidation of methyl oleate by Skellon & Gordon (*Chemistry & Industry 1951*, 629) and Skellon (*J. Chem. Soc. 1950*, 2020) indicated the following course: formation of hydroperoxide or epoxide; decomposition of these to either epoxy, aldehydic, dihydroxy, or keto hydroxy derivatives; and formation of products of polymer character.

Lemon *et al.* (*Can. J. Tech. 29*, 523) followed the autoxidation of methyl esters of peanut oil fatty acids by observations of infrared absorption spectra. Bands developed which were associated with formation of hydroperoxides, hydroxyl groups, carbonyl groups, diene conjugation, and *cis* and *trans* isomerization.

Mukherjee (*Indian Soap J. 16*, 106, 183) isolated $C_9$ compounds from autoxidation products of methyl oleate. His work (*J. Indian Chem. Soc. 27*, 230, 238) on the kinetics of autoxidation of oleic and linoleic acids contained analyses of the course of the reaction with regard to oxygen consumption and changes in characteristics. These data were discussed in connection with the function of the α-methylene group in the process.

In coupled reactions between methyl linoleate and bixin, or tocopherol, during oxidation by lipoxidase, the presence of bixin, or tocopherol, inhibited conjugation (Kunkel — *Arch. Biochem. 30*, 306).

Keeney & Doan (*J. Dairy Sci. 34*, 713, 719, 728) isolated several ketones from volatile flavor material of oxidized milk fat. These included 2-hydroxypropanal, $C_7$ and $C_9$ unsaturated ketones neither of which was a methyl ketone, and a $C_{12}$ α,β-unsaturated carbonyl compound. The organoleptic character of milk fat during oxidation was attributed to a blending of these various compounds.

The readers are also referred to section C under protective coating of this review, for much of the information on autoxidation in drying oil equally concerns spoilage.

FACTORS AFFECTING STABILITY. Studies were made on the stabilities of various fats and oils. Palm oil from Belgium Congo originally contained 2% free fatty acids which increased to 7-9% during transportation (Vanneck *et al.*—*Bull. Agr. Congo Belge 42*, 57). This was an autocatalytic decomposition rather than an enzymic process. Spanish peanuts were more susceptible to peroxidative deterioration than either Runner or Virginia types based on over 70 storage tests involving peaunts grown in six consecutive seasons. (Pickett & Holley—*J. Am. Oil Chemists' Soc. 28,* 478). Preheating milk to 160-170°F. delayed rancidification in the whole milk powder produced therefrom (*Christensen et al.—J. Dairy Sci. 34,* 404, 412; Bell & Mucha— *Ibid.* 432). Temperatures just sufficiently high to permit destruction of enzymes were unsuitable. In a study on the acceleration of rancidification of butters due to copper and iron proöxidants, it seemed that copper accelerated oxidation of triglycerides while iron catalyzed the rancidity arising from lecithoprotein (Barnicoat—*New Zealand J. Sci. Technol. 32A,* No. 2, 11). The findings were discussed in relation to partition of the proöxidants between the fat and aqueous phases. Similar studies by Mukherjee (*J. Indian Chem. Soc. 27,* 586, 607, 695, 699) involved many metal proöxidants and the effect of the metal was found to be least when it was confined to the aqueous phase. The accelerating effect of the different metallic compounds was rated by means of several deterioration tests. The effects of light, moisture, humidity, and oxygen concentration were also recorded in this work. Poor stability in sesame oils was attributed to proöxidants which could be removed by treatment with alumina (Saletore & Harkare—*Current Sci. India, 20,* 10; *J. Ind. Chem. Soc. Ind. Sect. 13,* 129). Treatment of the oil with charcoal removed antioxidants, thus accelerating rancidification. The naturally rapid rancidification of Mahwa seed oil was attributed to the presence of an easily rancidified highly unsaturated hydrocarbon in the unsaponifiable fraction (Srivastave & Rao—*Soap, Perfumery & Cosmetics 24,* 673).

Feeding tocopherol to turkeys improved the storability of the dressed birds as judged subjectively and by peroxide value for fat rancidity (Criddle & Morgan—*Proc. Soc. Exptl. Biol. & Med. 78,* 41). Similar turkey feeding tests with linseed oil versus coconut oil, showed that the highly unsaturated oils induce fishy flavors in turkey tissue (Klose *et al.—J. Am. Oil Chemists' Soc. 28,* 162).

Studies were made on stabilizing specific fatty foods with antioxidants. In deep fat frying of potato chips, nuts, etc., antioxidants were lost during the cooking, but addition of antioxidants after the process did increase the storage life of these foods (Sair & Hall—*Food Tech. 5,* 69). In dry lard at concentration of 0.005% the effective antioxidants in decreasing order were: nordihydroguaiaretic acid, butylated hydroxyanisol, propyl gallate, and α-tocopherol; whereas, in aqueous solution the order of the first two listed was reversed (Lehmann & Watts—*J. Am. Oil Chemists' Soc. 28,* 475). In this work Manddrell's salt was more effective as a synergist than ascorbic acid or phosphate material. Soybean and cottonseed flours were recommended for stabilizing the fat in pastry mixes (Overman—*Food Res. 16,* 39). Heating such material with lard to improve stability of the fat produced undesirable color, and when this color was removed by bleaching the induced stability was lost (Lips—*J. Am. Oil Chemists' Soc. 28,* 58). Studies for candy making indicated that nordihydroguaiaretic acid with synergists inhibited copper-accelerated deterioration in fondants, whereas, oat flours accelerated the spoilage (Robinson—*Food Technol. 5,* 20). Nordihydroguaiaretic acid protected acid sesame oils better than propyl gallate (Banerjee—*Ind. J. Med. Res. 37,* 433). Antioxidants that were effective in retarding oxidative changes in edible oils were also effective for the same purpose in orange oil (Kenyon & Proctor—*Food Res. 16,* 365).

The antioxidants recorded as effective for stabilizing vitamin A in oils were a combination of isobutyl gallate and tartaric acid (Patel & Sreenivasan—*J. Sci. Ind. Res., India, 9B,* No. 4, 99), vegetable meals (Burns & Quackenbush—*Ind. Eng. Chem. 43,* 1592); a mixture of ascorbyl palmitate and 2,3-dimethyl-1,4-bis(3,4-dihydroxyphenyl)butane (Wodsak—*Fette u. Seifen 53,* 73); and nordihydroguaiaretic acid, pyrogallol or hydroquinone (Katsui & Kuyama—*Vitamins, Japan 4,* 47). Bickoff (*J. Am. Oil Chemists' Soc. 28,* 65) recommended using those antioxidants accepted for use in lard for the stabilization of carotene. In a study of antioxidants for general pharmaceutical practice sodium diethyl dithiocarbamate, hydroquinone, and propyl gallate were considered good (Sandell—*Svensk Farm. Tid. 54,* 473, 501, 525).

Specific antioxidants were the chief concern in some studies. Of the alkyl hydroxyanisoles those with the alkyl group in the meta position with respect to the hydroxyl group had the highest potency (Rosenwald & Chenicek—*J. Am. Oil Chemists' Soc. 28,* 185; Dugan *et al.—Ibid.* 493). The shelf life of salted peanuts was increased by butylated hydroxyanisole with propyl gallate and citric acid as synergists (Cecil & Woodroof—*Georgia Agr. Expt. Sta. Bull. No. 265,* 3). In studies on stabilizing the phospholipid fraction of milk, nordihydroguaiaretic proved to very suitable, and pH and synergists suitable for most effective protection were worked out (Stull *et al.—J. Dairy Sci. 34,* 181, 187). In a study of the relative effectiveness of $C_2$ to $C_{17}$ alkyl esters of gallic acids, the lower esters were superior and their effect was considerably enhanced by citric or phosphoric acids (Kring—*Dansk Tids. Farm. 24,* 211). Improved procedures for preparing the esters of gallic acid with higher alcohols were published by van der Kerk *et al.—Rev. trav. chim. 70,* 277). The mechanism of action of several synergists with tocopherol was explained on the basis of regeneration of tocopherol activity from the oxidized product (Issidorides—*J. Am. Chem. Soc. 73,* 5146). Bixin enhanced the antioxidant capacity of γ-tocopherol to a much greater degree than it did for the α-form (Kunkel—*Arch. Biochem. 30,* 317). In this work the α-tocopherol had greater antioxygenic activity than other forms of tocopherol. Hemoglobin or hemoglobin with ascorbic acid catalyzed the oxidation of linoleic acid; whereas, the system effected antioxidation when it contained tocopherol and ascorbic acid (Watts & Wong—*Arch. Biochem. 30,* 110). Work on the antioxidant effectiveness of nordihydroguaiaretic acid showed that the effectiveness varied with the fat and such effectiveness fails when deterioration was due to bacterial causes (Ulex & Kroger—*Deut. Lebensm. Rundschau 46,* 256). Dihydroquercetin from Douglas fir and Jeffery pine bark, was proposed as an antioxidant and its efficiency in several edible fats and oils was evaluated (Kurth & Chan—*J. Am. Oil Chemists'Soc. 28,* 433). In an evaluation of 68 substances proposed as antioxidants, special emphasis and elaboration of efficiencies of citric acid and derivatives were made (Fennecke—*Fette u. Seifen 53,* 636).

Täufel & Rothe (*Fette u. Seifen 53,* 381) studied antioxygenic activity as related to structure. The aromatic hydroxy compounds were generally more active than corresponding amino-, nitro-, or quinone-compounds. The effect of hydroxyl compounds decreased as these groups increased. Among polynuclear aromatic compounds those with the hydroxyl in α-position were most effective. Antioxidant effect did not appear to be related to solubility or reduction capacity.

Pharmacological studies on alkyl gallates (Allen & DeEds—*J. Am. Oil Chemists' Soc. 28,* 304; van Sluis—*Food Manuf. 26,* 99) and on alkyl citrates (Calbert *et al.—Food Res. 16,* 258, 294) uncovered no evidence to indicate that ingestion in amounts used to protect fats against rancidity would produce harmful effects.

The patented antioxidants were mono-, di-, and/or trialkyl or -alkene esters of citric acid (Vahlteich—*U. S. 2,523,792*); alkyl esters of polycarboxylic acids that also contain hydroxyl groups (Vahlteich—*U. S. 2,578,649*); combinations of thiopropionic acid, citric acid, alkylated hydroxyanisole and a thiodipropionic acid compound (Gribbins & Dittmar—*U. S. 2,563,835*); various combinations of the above, tartaric acid, glycerol, lecithin, and ethyl tyrosine with a β-substituted mercaptopropionic acid (Gribbins & Dittmar—*U. S. 2,564,106*); tetraalkylthiuran disulfide (Ned. Org. Toegepost-Natuur-Wetschap. Onderzoek Voeding—*Dutch 66,584*); mixed triglycerides of butyric acid and cysteine (Nyrop—*Dan. 71,108*); esters of betaine with sugars (Shappirio—*U. S. 2,536,100*); *p*-hydroxycoumarans and *p*-hydroxychromans (Gleim & Chenicek—*U. S. 2,535,058*); *1,2*-dinitroso compounds (Rosenwald—*U. S. 2,555,509*); hexahydroxy-*p*-terphenyl compounds having two hydroxy radicals on each of the phenyl rings (Chenicek & Gleim—*U. S. 2,557,921*). Oleic acid contaminated with linoleic acid was stabilized by reacting the latter with maleic anhydride and distilling off the oleic acid. (Ross—*U. S. 2,567,404;* Trent—*U. S. 2,567,409*).

FLAVOR REVERSION. In one series of papers on flavor reversion of soybean oil, a system of organoleptic identification was developed and used to evaluate the effect of various metals on the process. Linoleic acid was identified as the unstable precursor of the "fishy-painty-grassy-melony" flavors in soybean oils (Evans *et al.—J. Am. Oil Chemists's Soc. 28,* 68, 115, 118).

MICROBIOLOGICAL DECOMPOSITION OF FATS. Silliker & Rittenberg (*J. Bact. 61,* 653, 661) recorded data on aerobic oxidation of $C_9$ and $C_{10}$ acids by bacteria. These data were consistent with either multiple alternate oxidation or a somewhat modified form of beta oxidation. Mukherjee's (*Arch. Biochem. & Biophysics 33,* 364) work on microörganic spoilage of fat was interpreted as suggesting that hydrolysis was the first step, followed by oxidative enzymic action, and then other processes such as desaturation, etc,. but to some extent they occur simultaneously to complicate the studies.