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

Report of the Literature Review Committee*

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Introduction

This year, as in the past, the compilation of new information was made from current original publications and from abstracts of the publications which were not available in the original. A small portion of the references was dated previous to the period under review because they had been too late in coming to our attention for earlier reviews.

STATISTICS. The following information was collected from recent issues of the Bureau of Agricultural Economics' publication, *The Fat and Oil Situation.* The production of fats and oils from domestic material during this season was estimated to be about the same as that of the last season. This is slightly above the 1937-41 crop year average. Consumption per capita (food and nonfood combined) during the season was 10% below the 1937-47 average. No major change in civilian consumption or total inventories of fats and oils is anticipated during the marketing season for the 1946 crop. However, the United States is likely to have a slight net import of fats in 1946-47 compared with a net export of about 180 million pounds in the preceding period.

Among economic factors on fats, the price fluctuated most. This occurred after mid-October when price ceilings were terminated. The fat and oil prices of early November were triple those of prewar years and about one-fifth higher than the previous peak reached in November, 1919. It is expected that these prices will continue high until marketing of the 1947 oilseed crops begins.

Other economic reports treated the fat and oil industry of Netherlands Indies (Canning — *Foreign Commerce Weekly 20,* No. 12, 5, 49), fats, oils, and oil- bearing material trade of Japan (Cragg—*U. S. Tariff Commission Spec. Industry Analysis No. 15,* 16 pp.), production of vegetable oils in the Soviet Union (Goldovskii—*Pishchevaya Prom. 1944,* No. 11, 20), oils and fats in Germany (Langton—*Food 15,* 117), and the drying oils situation during the war [Wood—*Industrial Ref. Service (Pt. 5) 4,* No. 21, 5 pp.]. One report contained a brief summary of the world fat situation (*Rept. FAO Preparatory Commission on World Food Proposals,* p. 40). World production in 1946 was just over 16 million metric tons in terms of oil equivalent or about 75% of the prewar level. In 1946, oils and fats available for export were less than three million metric tone compared with over six million before the war. It was estimated that to restore the prewar per capita fat utilization, total imports of more than seven and one-half million metric tons would be necessary.

FOSTERING INDIVIDUAL SOURCES. The most comprehensive work of this type was that by Woodruff *et al.* (*Georgia Agr. Expt. Sta. Bull. 247,* 24 pp.; *Food Industries 18,* 525) on peanut oil. They described methods of storage and protection against deterioration, comparison of the oil with other cooking oils, and manufacture of peanut butter. Other general publications on peanut oil described briefly the processing and uses (Vizern — *Bull. matières grasses inst. colonial Marseille 30,* 103), and the peanut industry of Senegal (Adam—*Oleagineaux 1,* 61). Similarly, in a symposium on soybeans, the subjects discussed were soybean research at Northern Regional Research Laboratory (Hilbert — *Soybean Digest 6,* No. 11, 33), world trends in major oil crops and their effect on soybean acreage in the United States (Hansen—*Ibid.* 40), soybeans and the world fats and oils situation (Rossiter—*Ibid.* 42), and the future of soybean oil in margarine and related products (Betzold —*Ibid.* 52). Other general descriptive information of limited scope was on the sunflower industry of Costa Rica [Quiros—*Dept. nacl. agr.* (Costa Rica), *Bol. tec. No. 50,* 23 pp.], and the linseed oil industry of Argentina (Tognoni—*Industria y quím. 8,* 67).

TABLE OF CONTENTS

A. INTRODUCTION.
   Statistics, outlook, fostering individual sources, new literature.

B. PRODUCTION PROCESSES.
   Animal fats, vegetable fats, refining, tall oil, medicinal oils, fat acid fractionation, hydrogenation, interesterification.

C. PRODUCTS (except detergents).
   Table and cookery fats, emulsifiers, protective coatings, resins, synthesis of acids, alcohols, ketones and esters, fat derivatives containing nitrogen, soaps of polyvalent metals, lubricants, fuels, miscellaneous products.

D. DETERIORATION.
   Reviews, methods for testing, mechanisms, factors, influencing autoxidation, flavor reversion, biochemical rancidity, radiochemical changes in fats.

E. BIOCHEMISTRY AND PHYSIOLOGY.
   Desirability of fat in the diet, relative dietary values, adsorption, mobilization, fat soluble vitamins.

F. CHARACTERISTICS AND COMPOSITION.
   Methods of testing, new data.

G. DETERGENTS.
   Soap manufacture, testing, list of patents on nonsoap detergents.

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The entrance of tobacco seed oil into the edible oil field during the war was of interest because its acceptance as food is very recent. Since these seeds can be produced and collected without affecting the leaf crop, a new by-product industry should develop in the tobacco business. The nontoxicity and equality of the oil in digestibility and nutritive value with other household oils were confirmed by several investigators (Rapp *et al.—J. Nutr. 31,* 273: *Briquet—Mitt. Lebensm. Hyg. 36,* 206; Rowaan—*Oliën, Vett. Oliezaden 27,* No. 6, 29; Toni—*Boll. chim. farm. 85,* 113). Another possible oil source is the seeds of the wild gourds of southern United States and Mexico (Curtis—*Chemurgic Digest 5,* 221). For further references on new fat and oil sources the reader is referred to the charts in Section F giving the analytical data recorded on new fats and oils.

A patent in connection with producing fat from microorganisms described how to extract it with an alcohol or ketone (Zimmermann—*Ger. 745,633 Cl. 23a*). In working with *Rhodotorula gracilis,* Enebo *et al.* (*Arch. Biochem. 11,* 383) increased production of fat by drastic reduction of nitrogen and phosphorus in the culture. In this work four and one-half grams of glucose was required for the formation of one gram of fat. In similar work with *Fusaria lycoperseci,* Witter & Stotz (*Ibid. 9,* 331) synthesized fat from glucose in a non-nitrogen containing medium, but there was little or no growth of the mycellium. They suggested, therefore, that the process of growth and fat formation were separate.

The communications on the production of fatty acids from paraffins were largely descriptions of the German industry (Kling—*Parfumerie 1,* 185; Rosendahl—*Seifensieder-Ztg. 1944,* 68; Anon.—*Soap, Perfumery Cosmetics 19,* 561; Baldeschwieler—*Chemie & industrie 55,* 329; Bellamy & Nillson—*Ibid. 56,* 18).

NEW LITERATURE. Several new books of interest in the fat and oil industry appeared during the year. The new *Official and Tentative Methods of the American Oil Chemists' Society* (Mehlenbacher—published by the American Oil Chemists' Society, Chicago) is a very complete compilation of methods. The tenth edition of Gardner's paint book is an extensive revision and has been printed in a more convenient size (Gardner & Sward—*Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors,* published by H. A. Gardner Laboratory, Inc., Bethesda, Md.). *The Alkaline-Earth and Heavy-Metal Soaps* was the subject of a 340-page monograph (Elliott—published by Reinhold Publishing Corp., New York). A second edition of a book containing formulas for emulsions was issued (Bennett—*Practical Emulsions,* Chemical Publishing Co., New York). A textbook on emulsions was written by Sutheim (*Introduction to Emulsions,* Chemical Publishing Company). The new fat and oil journals are entitled *Boletim de divulgacão do instituto de óleos* (published by Instituto óleos, Rio de Janeiro) and *Oleagineux* (published by Institut de recherches pour les huiles de palm et oleagineux, Marseille). The latter is a continuation of *Bulletin des matières grasses.*

The comprehensive reviews in the journal literature dealt with the chemistry of the lipides (Brown—*Ann. Rev. Biochem. 15,* 93), recent developments in vegetable oils [Saletore—*J. Sci. & Ind. Research* (India) *4,* 399], and utilization of fats (Ray—*Chimie & industrie 53,* 379).

Production Processes

ANIMAL FATS. The interest among producers of domestic animal fats reflected a desire to use the processing principles developed for fish and marine animal oil production. These included predigestion of the stock with alkali or enzymes, followed by centrifugal separation in equipment designed for continuous or semicontinuous operation. The enzyme method for lard production was considered uneconomical because the increased yield was not worth the extra effort (Anon.—*Natl. Provisioner 114,* No. 1, 15). A process with alkali predigestion was developed to a semi-plant scale (Deatherage—*Oil & Soap 23,* 327). Although not yet a commercial reality, its smoothness of operation and the acceptable quality of the products derived therefrom indicate it may have a promising future for lard production. A semicontinuous process used in a Danish system designed to turn raw pork fat into finished lard in 15 minutes comprised digestion of the ground fatty tissue with superheated steam, centrifuging the liquid portion, and expeller extracting the solids (Anon—*Natl. Provisioner 115,* No. 26, 9). In a patented bone glue or gelatine manufacturing process, rendering without deleterious effect on the stock was carried out by heating to 90-175° F. and applying pressure to release the fat (Mueller—*U. S. 2,395,900*).

In the fish industry the alkali rendering process was improved by precipitating the proteins with electrolysis or acids before the removal of the oil (Torgersen—*Norw. 66,302*). In enzyme rendering with pepsin, the use of pH of approximately 1.5 and temperatures not exceeding 38° was found advantageous from the standpoint of yield and quality of the medicinal oil produced (Parfentjev—*U. S. 2,395,790, 2,406,249*). Expeller pressing at 57-58° provided a simple continuous means of recovering oil from blubber (Hansen—*Norw. 67,042*).

VEGETABLE FATS. The general papers on vegetable oil seed processing included a good treatise on German practices (Goss—*Oil & Soap 23,* 241) and a description of cottonseed oil processing with expellers and continuous refining (Malffei—*Rev. brasil. quim. 21,* 83). Processing investigators included work relative to the storage and handling of the oil-bearing material. Improvement of storage properties of cottonseed with ammonia treatment, which was successful in the laboratory and pilot plant experiments, proved unfeasible for full mill-scale practice (Altschul *et al.*—*Oil Mill Gazetteer,* Feb., 1946). In the same investigation, it was claimed that vapors from a commercial sodium alkyl aryl sulfonate were effective in inhibiting heating and rate of free acid formation in flaxseed. Fundamental data on seed storage by Milner & Geddes (*Cereal Chem. 23,* 225, 449) included the "critical" moisture value for some seed species. This value is at a hydroscopic equilibrium with a relative humidity of 75%; which is minimal for growth of most xerophytic mold species contaminating seeds. The authors also demonstrated that spontaneous heating occurs in sterile seeds in which no microfloral activity takes place.

In connection with pressure extraction of seed oils, investigators found no evidence that so-called invisible oil losses occur in milling peanuts (Dollear *et al.*—*Oil & Soap 23,* 45), and in another report the effect of shell content and storage on oil expelled from tungnuts was evaluated (Holmes & Pack—*Ibid.* 314).

When none of the shell (33%) was removed, processing was satisfactory and the recovery of the oil was higher than from stock containing ⅔ of the original. Bags of nuts with hulls removed but shell intact showed no deterioration after two months' storage in a well ventilated shed. Froth flotation of water-cooked pebble-milled milkweed seed was experimentally successful in producing a concentrate with twice the oil content of the original seed (Grace & Palmer—*Can. J. Research 24F,* 338). The interest here was in connection with the utilization of oil from waste materials such as grain screenings.

Among developments in solvent extraction processes an entirely new method for cottonseeds has advanced to pilot plant testing at the U.S.D.A. Southern Regional Research Laboratory (Boatner & Hall—*Oil & Soap 23,* 123; Editorial—*Ind. Eng. Chem. 38,* No. 12, Suppl. 16; Howard—*U.S.D.A., A.I.C. 118,* 6). In the process, the flaked cottonseed meats were violently agitated in a special mixture of chlorinated and unchlorinated solvents, adjusted so that the mixture finally separated into three fractions, the pigment glands floated to the top, the meats settled, and the oil remained dissolved in the solvent as an intermediate phase. The method was applicable for the preparation of pigment glands and pigment-free oil and meal from cottonseed.

The general literature contributions on solvent extraction included a description of an Allis Chalmers oil milling unit (Gordon—*Southern Power & Ind. 64,* No. 1, 55), a report on the economics of using hexane as a solvent for soybean oil extraction (Greenfield—*Oil Gas J. 44,* No. 30, 101), description of the most common commercial units (Goss—*Oil & Soap 23,* 348), and a discussion of the applicability of continuous extraction of tung oil (Holmes & Pack—*U.S.D.A., A.I.C. 116,* 16 pp.).

Most other investigations on solvent extraction dealt with the solvent and solvent oil solution. Bonotto (*Oil & Soap 23,* 297) emphasized the need of continuously filtering out the fines (or dust) from the miscella so that continuous distilling equipment would function properly. An investigation on the suitability of various solvents for soybean oil extraction indicated that trichlorethylene, methylene chloride, and ethylene dichloride were most suitable. From work on distillation of miscellas, Porchez (*Corps gras, savons 2,* 72) found that evaporation of from 10 to 50% oil by a multiple effect system followed by steam distillation under vacuum was most economical. The multiple effect system was described as one designed to use the heat in the vapors produced under high pressure distillation to evaporate the solvent under low pressure. Vix *et al.* (*Ind. Eng. Chem. 38,* 635) recorded the effects of various temperatures used in evaporating cottonseed and peanut oil miscellas on the color and refining properties of the oils produced. The data supplied engineering information of use in designing, installing, and operating solvent extraction processes. A small scale continuous vegetable oil extraction unit for laboratory study of the process was designed by Beckel *et al.* (*Ind. Eng. Chem., Anal. Ed. 18,* 56).

REFINING. Several improvements were suggested for refining oils. Bush & Lasher (*U. S. 2,410,926*) deslimed oil by treating with aqueous solutions of organic acids to break the dispersion, added water adsorbent filter aid, and filtered out the filter aid, acid, and water with the slime from the purified oil. Lloyd & Keil (*U. S. 2,397,874*) treated fats with proteolytic enzymes to convert the protein impurities into an easily separable gelatinous flocculate. Clayton (*U. S. 2,392,973*) adjusted alkali treatment and the temperature used to permit production of an oil retaining a substantial proportion of the phosphatides. Bradshaw & Meuly (*U. S. 2,398,492*) refined low-grade fats by esterifying the free fat acid components with diethyl sulfate in the presence of an adsorbing agent to neutralize the mineral acid liberated. Modification of the Clayton continuous refining process to permit the use of higher concentrations of the alkali refining agent improved decolorization and reduced the refining losses (Clayton—*U. S. 2,412,251*). The general publications on refining fats were a history of the process for soybean oil (Durkee—*Soybean Digest 6,* No. 4, 8) and a description of the "Solexol" process of refining by solvent extraction of the impurities with propane (Editorial—*Chem. Industries 59,* 1016).

Hinners *et al.* (*Oil & Soap 23,* 22) investigated the possibility of evaluating the adsorptive capacity of bleaching earths of various pH for the chlorophyll of soybean oil. The removal of the chlorophyll followed Freundlich's adsorption equation which relates the color adsorption to an exponential function of the amount left in solution. The quantity of earth required for a definite reduction could be calculated, provided ion adsorption characteristics and bleaching capacity in the oil at any concentration were known. Nomographs prepared by Langston & Rich (*Ibid.* 182) for determining the relative bleaching costs of adsorbents assumed power cost was constant and the relative bleaching cost depended on the cost of adsorbent, handling, and oil lost in the press cake. Newly patented bleaching methods comprised washing the oils with soap (Sullivan—*U. S. 2,408,454*) and treating with oil soluble negatively charged metallic compounds, *e.g.,* aluminum and tin alkyls (Clayton—*Brit. 570,040*). One invention described adsorbent bleaching of solvent extracted oils before recovery of the solvent (Julian & Iveson—*U. S. 2,392,390*). Instructions for bleaching fats with chlorine dioxide were presented in two papers (Tuttle & Woodward—*Chem. Met. Eng. 53,* No. 5, 114; Woodward & Vincent—*Soap Sanit. Chemicals 22,* No. 9, 40). Another general paper contained a picture flowsheet of Armour and Company's continuous deodorizer (Anon.—*Chem. Eng. 53,* No. 9, 134). An improvement for deodorization equipment comprised supplying heat to the vapor zone to reduce reflux condensation (Phelps & Black—*U. S. 2,407,616*).

Several other miscellaneous means of improving oils were patented. Briggs *et al.* (*U. S. 2,393,965*) dehydrated oils by means of a flash distilling system. Brown (*U. S. 2,393,744*) obtained improvements in winterizing salad oils by adding 0.05% phosphatides to the refined oil before crystallization. Desirable flavors, *e.g.,* olive, coconut, etc., were imparted to refined oils by Forkner (*U. S. 2,411,201*) by infusion with by-product materials containing the desired flavor.

TALL OIL. Since tall oil is a mixture of resin and fat acids instead of glyceride oil, the production and refining processes are quite different from those of the usual oils. There were several new means of separating the resin and fat acids. Osterhof (*U. S. 2,396,471*) decarboxylated the resin acids by heat in the presence of a small amount of an organic sulfonic acid, neutralized the fat acids, and separated them. Jennings (*U. S. 2,398,312*) selectively polymerized the resin acids in the presence of sulfuric acid and separated the fat acids by washing. Several methods of separation depended on selective alkylation of the fat acids and fractionating by various means. Dressler *et al.* (*U. S. 2,396,646*) and Lovas & Bruins (*U. S. 2,395,284*) saponified the resin acids and recovered the fat acid alkyls with organic solvents; Hasselstrom (*U. S. 2,396,651*) heated the mixture in the presence of a small amount of iodine and removed the resin acids by crystallization; and Segessemann (*U. S. 2,400,607*) hydrogenated the mixture and, by crystallization from a solvent, precipitated the fat acid esters. In connection with the above processes, Gayer & Fawkes (*U. S. 2,411,536*) patented a selection of temperature and pressure conditions to limit the alkylation to the fat acids. One process of separating resin from the fat acids by Lovas & Bruins (*U. S. 2,395-282-3*) depended on the selective solvent action on some ketone-water mixtures. According to Longley (*U. S. 2,409,137*), a mixture of tall oil and levulinic acid deposited sterol crystals at room temperature; further cooling to —30° F. caused fat acid crystals to separate, and thus producing sterols, resin acids, and fat acids. A process for simple refining of tall oil comprised acidifying with hydrochloric acid and steaming to break the emulsion and remove volatile compounds (Weston & Beall—*U. S. 2,399,588*).

MEDICINAL OILS. The literature on processing medicinal oils described methods for concentrating the vitamins. Among the patents assigned to the National Oil Products Co. were a commercial means of saponifying and extracting the vitamin containing unsaponifiable with ethylene dichloride (*U. S. 2,400,101*), a means of further improving the concentrate by washing out inactive material with methanol (*U. S. 2,404,-*365), and also, separating vitamins A and D by selective saponification (*U. S. 2,404,618*) or selective esterification (*Brit. 564,283*) of vitamin A followed by extracting with selective solvents. A concentrate in dry form assigned to the same concern (*U. S. 2,401,293*) comprised an absorbate of the vitamin oils in finely divided vegetable material. Shantz (*U. S. 2,410,590*) concentrated vitamins by a process of separating the unsaponifiable material wherein amines were used to saponify the glycerides. Van Orden (*U. S. 2,394,968*) applied liquid-liquid fractionation to concentrate the vitamin fractions. A study of the efficiency of recovery of vitamin A in the unsaponifiable of fish liver oil by Black *et al.* (*J. Soc. Chem. Ind. 65,* 249) revealed variations from 93 to 100%; the possible causes for the differences were discussed. Grahm *et al.* (*U. S. 2,408,625*) removed chlorophyll from fat-soluble vitamin concentrates by a dialysis process utilizing a synthetic rubber membrane. The vitamins and pro-vitamins selectively diffused from a solution through the membrane to an organic solvent.

FAT ACID FRACTIONATION. In the new literature on fat splitting, general papers treated the methods in use (Tous & Mendoza—*Ion 5,* 573), the continuous splitting processes (Seaman—*Soap, Perfumery Cosmetics 19,* 821), autoclave splitting (Naumenko—*Pishchevaya Prom. 1945,* No. 2, 39), and details of a catalytic process (Levit—*Ibid.* 42).

Likewise much literature on fat acid fractionation was of descriptive or historical nature. Ristorcelli & Fournier (*Inds. corps gras 1,* 164) reviewed the evolution of the stearin industry. A report on the recovery of sewage grease at Johannesburg (Wilson—*City Eng. Ann. Rept. 1945,* 56) described the local splitting, distillation, and crystallization processes. From a daily yield of 1200-1400 lbs. of wet grease, 150 lbs. of "oleic" acid, 300 lbs. of "stearic" acid, and 50-100 lbs. of still residues were recovered. In another paper on processing of low-grade fats, Trauth (*Oil & Soap 23,* 137) discussed determination of yields and listed the principal causes for loss of glycerol and fat acids. A new process, "Emersol process," for production of stearic acid by a continuous system comprising hydrolysis, crystallization of saturated acids from 90% methanol, and distillation was said to have an operating cost 65% that of the conventional pressing method (Kistler *et al.*—*Ibid.* 146). One report (Ruiz & Munoz—*Mon. farm. 52,* 83) claimed that the saturated acids of linseed oil acid solutions could be removed by adsorption on aluminum oxide.

Very little information appeared on fat acid distillation. A new analytical distillation apparatus was designed and data on the low pressure vapor-liquid equilibrium of fat acids and their methyl esters were obtained (Monick *et al.*—*Oil & Soap 23,* 177). The data were in agreement with Raoult's law at a pressure of 4.0 ± 0.2 mm. of mercury, except for the system lauric acid-myristic acid. The data should be applicable to developing distillation methods and equipment. Seaman (*Soap, Perfumery Cosmetics 19,* 1023) briefly described the general principles of commercial flash and fractional distillation as applied to fat acid processing. Other distillation information which may be connected with fat and oil processing was patented improvement of molecular stills assigned to Distillation Products, Inc. (*U. S. 2,392,124, 2,396,374, 2,403,978, 2,408,639*).

HYDROGENATION. Development of new fundamental information on hydrogenation was afforded by the availability of improved analytical methods. In this connection, Bailey & Fisher (*Oil & Soap 23,* 14) rated the reactivity of fat acids toward hydrogenation under selective conditions by the following whole numbers: oleic 1, iso-oleic 1, isolinoleic 3, linoleic 20, and linolenic 40. The hydrogenation of linoleic acid appeared to proceed in two stages with intermediate desorption of oleic acid from the catalyst; but with linolenic, part might have proceeded to oleic without intermediate desorption of linoleic. Hilditch (*Nature 157,* 586) interpreted the above and several reports of past years to suggest that the ease of hydrogenation appeared to be connected with the presence of a $-CH_2-$ group separating the unsaturated groups, because the selective addition of hydrogen might be influenced by the ready detachment of hydrogen from the central $-CH_2-$ group. A much lessened selective hydrogenation of free acids as compared to the esters was attributed to the competitive action of the strongly polar carboxyl group. Hydrogenation under selective conditions, *i.e.,* hydrogen pressure of 10-15 lbs. and 0.1% nickel catalyst, followed by crystallization to remove saturated acids was used by Swern *et al.* (*Oil & Soap 23,* 128) to prepare oleic acid in good yields from inedible tallow. According to Kentie & Nauta (*Rec. trav. chim. 64,* 159), rapeseed oil dissolved in dioxane was hydrogenated at 35° in the presence of Raney nickel catalyst and ammonium chloroplatinate as a promoter; no reduction of the carboxyl group occurred.

Several hydrogenation reports were primarily of technical interest. Palfray (*Inds. corps gras 1,* 132, 169) plotted the courses of the physical changes occurring in ten common oils during hydrogenation. His work with Delaplanche (*Ibid. 2,* 36) on linseed oil was a graphical illustration of the progressive changes in the fat acid composition during reduction. Joglekar & Jatkar (*J. Indian Inst. Sci. 23A,* 139), in a study of continuous selective hydrogenation, observed that the linolein to stearin reaction predominated when linolein and olein were in about 1:1 ratio, while linolein to olein reaction took place when they were in a ratio of 1:0.25. A newly patented continuous hydrogenation system comprised a group of hydrogenating tubes in a temperature controlled chamber and the necessary means of adding hydrogen, oil, catalyst, etc. (Manderstam & Warner—*U. S. 2,410,670*). A patented stabilizing, bleaching, and hydrogenating process was based on hydrogenation in the presence of catalytic mixtures of heavy metal oxides (Paterson—*U. S. 2,410,102*).

Several other publications were concerned with hydrogenation. These were a method of preparing very active Raney nickel catalyst (Pavlic & Adkins—*J. Am. Chem. Soc. 68,* 1471), two reports on the theory of adsorption and activation of fat acids on catalytic surfaces [Smith & Fuzek—*Ibid.* 229; Balandin— *J. Gen. Chem.* (U.S.S.R.) *15,* 608, 619], and a review of present day hydrogen manufacturing processes (Reed—*Trans. Am. Inst. Chem. Engrs. 42,* 379).

Raymond & Moretti (*Compt. rend. 222,* 893) used Raney nickel catalyst to study the dehydrogenation of saturated fat acids. The production of unstable liquids was submitted as evidence that desaturation took place.

INTERESTERIFICATION. The information on the extent and course of interesterification reactions in fats had until recently been very meager; although it has been long known that such reactions take place under favorable conditions. Desnuelle & Naudet [*Bull. soc. chim.* (France) *Ser. 5, 13,* 90], in what appears to be one of the original detailed analyses of the interesterification process, found that heating a 1:1 mixture of triolein:tristearin for five hours at 135° in the presence of a suitable catalyst yielded: tristearin 30.3, distearomonolein 18.9, stearodiolein 20.6, and triolein 30.2%. The tendency of fat acids to shift to random distribution among the glycerides was pointed out, but was only partially attained. However, when Norris & Mattil (*Oil & Soap 23,* 289) carried out the reaction with tripalmitin:triolein mixture under more appropriate interesterification conditions (temperature of 225°) the change to essentially random distribution was attained as evidenced by a residual wholly saturated glyceride content of 14.3% (the calculated theoretical value is 12.5%). The authors demonstrated some interesterifications between natural and hydrogenated fats and suggested that the process might possibly be one of the mechanisms involved in the digestion and metabolism of fats.

Interesterification reactions were used to prepare mono- and diglycerides. Ross *et al.* (*Oil & Soap 23,* 257) produced α-monostearin and α-monomyristin by the action of glycerol on methyl esters of fat acids and tabulated their characteristics. Feuge & Bailey (*Ibid.* 259), in work on reaction between cottonseed oil and glycerol, found that at temperatures below 200° and at equilibrium the proportions of free glycerol, mono-, di-, and triglycerides conformed closely to a pattern of random distribution. Removal of combined glycerol by means of superheated steam left a mixture with decreased mono- and triglycerides and increased percentage of the diglyceride. The same type of investigation was reported by Ivanoff (*Bull. matières grasses inst. colonial Marseille 29,* 51). He recorded that monoglycerides were first formed, and when these were heated, they yielded diglycerides and glycerol, then triglycerides and glycerol. When monoglycerides were heated in the presence of 0.5% benzenesulfonic acid in phenol solution between 140-250°, there was a change to diglyceride and finally triglyceride.

Products (Except Detergents)

TABLE AND COOKERY FATS. The success attained in the development of continuous butter-making in Germany (Gemmill—*Food Industries 18,* 841) was possibly greater than has been achieved in this country because the European practice has been to churn sweet cream. Progress in such equipment in the United States was slow because it had to be designed to handle either sweet or sour cream. According to these processes (Gemmill—*Ibid.* 1872; Lundal & Robichaux—*U. S. 2,407,612*; Farrall—*U. S. 2,406,819*), the cream was pasteurized and concentrated to practically pure butterfat and was then mixed with salt water in the proper proportion to produce a butter containing the desired amount of fat and salt. One new piece of patented accessory equipment (Horneman *et al.*—*U. S. 2,395,051*) continuously kneaded the butter to impart a texture like that produced in batch churned butter.

During the war large scale production of "hardened butterfat" was developed for use in the tropics. This product contained three per cent hardened peanut oil, four per cent skim milk powder, two per cent salt, some sodium carbonate, and two tenths parts per million of diacetyl (Wiley & Coombs—*J. Council Sci. Ind. Research 19,* 140). The product possessed good keeping quality without refrigeration.

Some other patented developments were also of interest in the dairy field. Buxton (*U. S. 2,404,034-7*) manufactured a "butter concentrate" by selectively dissolving vitamins, flavor-imparting substances, and antioxidants from butter oil with special solvents as isopropanol, heptane, acetone, etc. North & Alton (*U. S. 2,399,565*) added lecithin to powdered cream to improve the mixability and solubility for use in ice cream manufacture. A whipping cream substitute was made from a pasteurized and homogenized emulsion containing soybean flour, salts, gum karaya, and hardened peanut oil (Mason & Justesen—*U. S. 2,407,027*).

The literature on processing of margarine was principally of a review or descriptive nature. It included a plea for more favorable regulations to aid the French industry (Lecomte—*Corps gras savons 2,* 193), a description of modern equipment (Mees—*Ibid.* 194), a description of British equipment (Anon.—*Food Manuf. 21,* 196), and a discussion on laboratory control methods (Feron—*Corps gras savon 2,* 199). A margarine patent dealt with using a mixture of vegetable phosphatides and fat acid monoglycerides as the emulsifier (Stanley—*U. S. 2,402,690*).

The function and qualities desired in shortening were described especially for the bakery technicians (Harder & Muller—*Baker's Digest 20*, 5; Peterson—*Ibid.* 7; Epstein *et al.*—*Trans. Am. Assoc. Cereal Chem. 4*, 117). Pratt (*Food Industries 18*, 16) discussed details and limitations in connection with increasing the effect of shortening in bread by the use of lecithin. Several patents described the manufacture of dry powdered shortening by mixing the fat with milk or soybean protein and an emulsifier such as lecithin and sodium alginate (North *et al.*—*U. S. 2,392, 994-5*; Chapin—*U. S. 2,392,833*).

EMULSIFIERS. The new general purpose emulsifiers included the reaction products of sugar and fat acids (Danilevskaya & Egorova—*U. S. S. R. 64,592*), of sugar and a glycol or glycol ether (Griffin—*U. S. 2,407,002*), and of oleic acid, ethylene oxide, and propylene glycol (Griffin — *U. S. 2,407,003*). One emulsifier was a mixture of cation-active amines and partial glycerol esters of fat acids (Epstein & Katzman—*U. S. 2,398,295-6*). Partial esters of fat acids were also used to restore the emulsifying value of sugared egg yolks (Scott & Parsons—*U. S. 2,395,587*); and as emulsifiers in the gum coating used to impart scroop to textiles (Kaplan—*U. S. 2,410,382*).

Two improved pectin emulsifiers were a product coated with fat acids and fatty amides or fatty alcohols (Nelson—*U. S. 2,412,282*), and a mixture of pectin and skim milk (Rossen—*Dan. 63,636*). A cosmetic lotion was emulsified with a mixture of pectin, boric acid, and cetyl trimethyl ammonium bromide (Manchey & Schneller—*U. S. 2,372,159*). A 1:2 diethanolamine:oleic acid mixture was patented as an emulsifier for petrolatum in the manufacture of ointments (Rosenthall — *U. S. 2,398,254*). Lachampt (*Inds. corps gras 2*, 149) reviewed and classified the various types of cosmetic emulsions.

One class of surface active agents, called petroleum demulsifiers, was used to break the emulsions formed during the treatment of petroleum bearing rock strata with mineral acids to release more oil from the strata. The patents granted to the Petrolite Corp Ltd. (*U. S. 2,384,080-1, 2,394,432, 2,395,400, 2,400,393-5, 2,401,055, 2,403,343-5, 2,406,206, 2,407,-895, 2,411,029, 2,411,957*) for this purpose included such compounds as subresinous amines, diamides, amides or esters usually derived from fat acids, particularly ricinoleic acid. A patented compound for the same purpose assigned to the Standard Oil Development Co. (U. S. 2,401,966) was a reaction product of bodied fatty oils and a polyethylene glycol.

PROTECTIVE COATING PRODUCTS. Many efforts were made to improve the drying qualities of oils. Notable advances along this line were made by catalytic conjugation, particularly at the Northern Regional Research Laboratory (Radlove *et al.*—*U.S.D.A., A.I.C. 101*, 46 pp.: *Ind. Eng. Chem. 38*, 997; Falkenburg *et al.*—*Ibid.* 1002). Here it was discovered that nickel on active carbon or earths could effectively catalyze the isomerization of vegetable oils without splitting them. Soybean and linseed oils treated by the process could be converted into bodied oils of lower acid number and better color than was possible with the original alkali refined oils. Their superiority in time of "cook" and drying, resistance to water and alkali, and hardness of films was also demonstrated. At the same laboratory, Teeter *et al.* (*Oil & Soap 23*, 216) prepared addition products of ethyl crotonate and crotononitrile with conjugated methyl linoleate derived from soybean oil and indicated their utility as plasticizers by tabulating their compatibilities with ester gum and modified rosin maleic acid resins. Other patented means of conjugating fats or fat acids included heating with iodide compounds (Ralston & Turinsky—*U. S. 2,411,111-13*) or with magnesium silicate (Turk & Boone—*U. S. 2,405,380*). Terry & Wheeler (*Oil & Soap 23, 88*) were successful in concentrating conjugated methyl linoleate to 75% by fractional distillation. A review on isomerized oils was compiled by Touchin (*Paint Manuf. 16, 237*).

Several reports contained descriptions of treatments for converting castor oil to an efficient drying oil. Mukherjee & Mukherjee's (*J. Indian Chem. Soc. 22*, 305) process comprised a polymerization during which dehydroxylation and conjugation occurred. Da Rosa [*Bol. divulgacão inst. óleos* (Rio de Janeiro) *1944*, No. 2, 2] recommended iron as the catalyst and a temperature of 265° as most favorable. Several Russians (Osnos & Golovistikov—*Khimicheskaya Prom. 1945*, No. 2, 19; Ivanova & Bespalko—*Ibid.* No. 12, 11) investigated the influence of catalyst, temperature, and pressure on the process. They were particularly interested in improving the rapidity of the reaction with minimum pyrogenic action and hydrolysis of the oil. Among the many catalysts tried, maleic anhydride and sodium bisulfate were considered most suitable. Two new patented processes for dehydroxylating and conjugating comprised heating the oil in thin layers (Colbeth—*U. S. 2,392,119*) and the use of ammonium compounds as catalyst for the process (The Distillers Co. Ltd.—*Brit. 559,887*).

Several other methods of improving the drying qualities of oils or preparing synthetic drying oils were treated in communications. In one discussion on modern drying products, the pentaerythritol esters of fat acids was the main topic (Greaves—*Oil, Colour Trades J. 109*, 506; *Chim. peintures 9*, 38). The newer trend seems to be to utilize the tall oil and natural resin acids to make synthetic drying oils or resins. A patented composition was prepared by first partially esterifying rosin with some glycerol and then completing the esterification with pentaerythritol (Woodruff—*U. S. 2,409,332*). Oswald (*Official Digest Federation Paint & Varnish Production Clubs 254*, 122) described preparation of one-, five-, and 110-gallon batches of varnish from pentaerythritol-rosin esters. No significant differences were recorded for the different scale runs. A series of tests on variously prepared pentaerythritol-tall oil esters in varnish formulas by Widegren (*Tek. Tid. 74*, 153) indicated that with higher resin content, the viscosity of the esterified oils was higher and the drying better, but the resistance to water decreased. Savary (*Bull. matières grasses inst. colonial Marseille 30*, 84) recorded that monoesters were formed by reactions of fat acids with excess pentaerythritol in boiling phenol. Other methods of modifying an oil to improve its drying characteristics included heating with 30% fluorescein (Auer — *U. S. 2,396,670*) or resorcinol (Auer—*U. S. 2,406,337*), or furylethylene (Mighton —*U. S. 2,401,769*), polymerizing with diene hydrocarbons in the presence of soluble resins (Gerhart—*U. S. 2,399,179*), and chlorinating with nascent chlorine followed by treatment with nascent oxygen (Stark & Slack—*U. S. 2,399,697*).

Several general papers pertained to the drying oil industries. The subjects treated in reviews were: heat bodying (van Loon—*Verfkroniek 17/18,* 103; Touchin—*Paint Incorp. Paint Manuf. 16, 186*; Feinberg—*Official Digest Federation Paint & Varnish Production Clubs 254,* 112), cooking varnishes to obtain low zinc reactivity (Singer— *Am. Paint J. 30,* No. 15, 9), cooking procedures for tall oil surface coatings (Golden Gate Paint & Varnish Production Club—*Paint Oil Chem. Rev. 108,* 144), heat bodying equipment (Russell—*Paint Ind. Mag. 61,* 16), synthetic drying oils (Williams—*Paint Incorp. Paint Manuf. 16,* 193), physical chemistry of lacquer (Schäfer—*Fette u. Seifen 51,* 12), and storage of tung oil (Eisenschiml—*Am. Paint J. 30,* No. 28, 76).

Drying oils and varnish bases were modified to produce wrinkle finishes. These included treatment at temperatures below bodying with various natural and synthetic resins (Luaces—*Brit.—566,000*; New Wrinkle, Inc. — *Brit. 566,056-7*; *U. S. 2,389,794-5, 2,392,346, 2,394,498-500, 2,395,360-1, 2,407,623, 2,411,-767*). A bodying method specifically for oiticica oil comprised blowing it with air for 0.5-2 hours at 350° F. Patented means of improving bodied oils included deacidification by esterifying the free fat acids with alcohols (Edel—*Ger. 742,271 Cl. 22h*) and removing non-drying constituents by solvent extraction with mixtures of ethanol and ethyl acetate (Ransom & Zucker—*U. S. 2,403,458*).

Some papers contained discussions of the theoretical aspects of bodying oils with laboratory data on the physical changes during treatment. Several types of linseed oils (Terrill—*Oil & Soap 23,* 339), several fish oils (Carrière & Arnoux—*Compt. rend, faculté sci. Marseille 1,* 124), peanut oil (Carrière—*Inds. corps gras 1,* 140), and ethyl linoleate (Carrière & Pellero—*Bull. matières grasses inst. colonial Marseille 30,* 18) were treated in these reports. In similar work Adams & Powers (*J. Applied Phys. 17,* 325) derived equations which predicted the amount of specific polymer present as a function of the extent of the reaction and the original oil composition. Petit (*Peintures, pigments, vernis 22,* 3) analyzed the volatile, polymerized, and nonpolymerized constituents of bodied oils and concluded that during bodying of linseed oil, the linoleic and linolenic acid radicals dimerize to form a network of connected glycerides; and the two acid groups form a six-carbon ring which turns aromatic by double bond shifts. Tollenaar & Bolthof—*Ind. Eng. Chem. 38,* 851) suggested that the decrease of viscosity with increasing shearing stress in heated linseed oil resulted from the deformation and consequent alignment of colloid particles.

Some new analytical methods were applicable to fundamental study of drying of oils. A new semimicro titration method for measuring acidity of drying oil films was used (Frilette—*Ind. Eng. Chem. 38,* 493) to determine wrinkling and alkali resistance of films. These were related to the acid values. An analytical study of blown oils by Carrière (*Ind. corps gras 1,* 76) contained recommendations for molecular weight, and iodine, thiocyanogen, and diene value determinations with discussion of reactions that affect these. The work of Miller (*J. Phys. Chem. 50,* 300) should serve in selecting proper oils for paints used as rust proofing coatings. He found that contact-angle values measured a more fundamental property than adhesion values, since contact-angle apparently determined the ability of a paint to displace adsorbed air or moisture films from steel.

RESINS. Among the literature on fat derived resins, that on alkyd resins was most abundant. One inventor patented the rate of proportioning the ingredients into a reaction chamber of a continuous system (Haines—*U. S. 2,396,698*). Co-reacting alkyd resins with partial alkyl esters of polysilicic acid was said to improve hardness and decrease tackiness (Iler *et al.—U. S. 2,395,550*). Alkyds made from mono- and diglycerides had improved bodying properties (Schwarcman—*U. S. 2,412,176-7*). Clear gels which yielded infusible and insoluble resins were made by copolymerization of alkyd resins with triallyl phosphate (Kropa—*U. S. 2,409,633*). A copolymerization product of dicyclopentadiene and alkyd resin had a high resistance to weathering and to alkalies (Gerhart & Adams—*U. S. 2,404,836*). Mono-nitro-paraffin (Bogin —*U. S. 2,389,837*) and *p*-toluene sulfonyl chloride (Auer—*U. S. 2,410,418*) were added to alkyd resins to improve the varnishes made thereof. Formulas for using a combination of guanazole aldehyde and alkyd resins in varnishes were patented (D'Alelio & Underwood—*U. S. 2,389,896*). An alkyd prepared for use in soap wrapper inks contained coumarone and indene resins to improve alkali resistance (Bernstein —*U. S. 2,401,898*). Pigmented bodied oils were used to obtain colored alkyd resins (Waldie—*U. S. 2,388,-301*). The resins made from polymerized rosin in place of oil had high melting points (Peterson—*U. S. 2,399,692*). Two pressure sensitive adhesives for making adhesive tape were a reaction product of castor oil and a polybasic acid (Brinker & Gehrenbeck—*U. S. 2,392,639*; Priepke *et al.—U. S. 2,405,-926*). Other patents on the manufacture of alkyd resins from castor oil contained methods for preparing and purifying the product (Bent & Ryan—*U. S. 2,-394,742;* Ullmann—*U. S. 2,396,763;* Agens & Nordlander—*U. S. 2,404,204*). Lynas-Gray (*Paint Tech. 11,* No. 124, 129) published general methods for making several types of oil modified alkyd resins, and Drinberg & Grinevich [*J. Applied Chem.* (U.S.S.R.) *17,* 606] issued instructions for making a product using polymerized glycol maleate. According to Karasev (*Khimicheskaya Prom. 1944,* No. 12, 5), alkyds made by the use of ammonium salts of fat acids were particularly suited for making water dispersed varnishes. Moore's (*Oil & Soap 23,* 69) review on alkyds correlated the properties with raw material used. Nedey (*Peintures, pigments, vernis 22,* 109) tabulated information which illustrated the acceleration caused by ultra-violet light upon the rate on drying of resin coatings and also the effect of pigment on this rate. In similar tests infrared rays acted only like a heat source.

Fat products were also used in the manufacture of non-alkyd type resinous material. Phenol aldehyde resins were modified with fatty oils (Mazzucchelli—*U. S. 2,413,412*). Adhesives and coatings were made by subjecting emulsified solutions of polymerized drying oils and polyethylene oxide-castor oil condensation products to oxidation with hydrogen peroxide (Stamberger — *U. S. 2,391,041-2, 2,403,408*). Another adhesive contained polyvinyl acetyl acetal resin and a complex of the Werner type in which a trivalent chromium atom was co-ordinated with a fatty acid (Johnson—*U. S. 2,410,414*). Fat acid cellulose ester plastics were improved in regard to clarity when the unreacted fat acids and impurities were removed with ethanol (Fisher—*U. S. 2,400,494*). Shellac was made compatible with drying oils by reacting it with glycol and then with fat acids (Gidvani & Kamath—*London Shellac Research Bur. Tech. Paper No. 28*, 19 pp.). Partially vulcanized bodied fatty oils containing nine per cent sulfur were suited for varnish bases (Auer—*U. S. 2,413,281*). Cowan *et al.* (*Ind. Eng. Chem. 38*, 1138) sulfured polyesters of polymeric fat acids with ethylene glycol in a similar process to prepare rubber-like adhesives and coatings. Other elastomers described by Powers (*Ibid.* 837) were copolymers of dimethylstyrene and vinyl fat esters with butadiene.

The resinous products made for waterproofing textiles were special thiocyanate quaternary compounds (Pikl—*U. S. 2,402,526*), substitution products of benzoic acid and fat acid carbamyl or fat acid sulfamyl (Aelony—*U. S. 2,398,272*), reaction products of fat acids with organic nitro hydroxy compounds (Robinette—*U. S. 2,402,776*), reaction products of fatty alcohol, phthalic acid, pyridine hydrochloride, and dimethoxydimethylurea (West—*U. S. 2,397,451*), and gelled rape oil and white factice mixture (Ioco Rubber & Waterproofing Co. Ltd. *et al.*—*Brit. 564,422*). A textile size contained polyvinyl acetate, boric acid, and polydioxolane stearate (Dittmar—*U. S. 2,406,749*).

Many of the patented plasticizers were derivatives of fats. These were described as esters of higher alcohols and fat acid polymers (Eckey & Taylor—*U. S. 2,413,612-13*), alkyl esters of ricinoleic acid (Savage—*U. S. 2,407,179*), halo alkoxy derivatives of fat acids (Price & Griffith—*U. S. 2,392,100*), semi-drying oils lightly heat treated with organic acid anhydrides (Rodman—*U. S. 2,396,129*), and alkyl and alkoxy derivatives of fat acids (Blades—*U. S. 2,397,592*).

SYNTHESIS OF ACIDS, ALCOHOLS, KETONES, AND ESTERS. Breusch & Keskin (*Rev. faculté sci. univ. Istanbul 11A*, 24; *Enzymologia 11*, 356) described the procedure they used to prepare the C_{10} to C_{13} β-keto fatty acids and the C_7 to C_{13} and C_{15} α, γ-diketo fatty acids which they required for fundamental research on metabolism of fats. For similar reasons Lehninger (*J. Biol. Chem. 162*, 333) synthesized the acyl phosphates of some higher fat acids. Baudart (*Compt. rend. 221*, 205; *Bull. soc. chim. 11*, 336) synthesized 9,10,16-trihydroxyhexadecanoic, 16-hydroxy-7-hexadecenoic, and one linoleic acid in work on confirming the respective structures to aleuritic, ambrettolic, and elaidinized natural linoleic acids. In an investigation on synthesis of triolein, Desnuelle & Naudet (*Ibid. 12*, 998) observed that methods in which heating was at about 180°, up to 11.1% isoöleic acid formation occurred.

Some of the work on synthesis was for the manufacture of intermediates for plastics, detergents, and other products. The syntheses of hydroxystearic from oleic acid (Milas—U. S. *2,402,566*) and epoxyoleyl alcohol from oleyl alcohol (Swern—*U.S.2,411,762*) were by means of controlled oxidation processes. Unsaturated fat acids were converted into α-halogenated keto acids by treatment with a hypohalous acid to produce the halo hydrin and these were then oxidized (Price & Sprules—*U. S. 2,396,969*). Two publications on manufacture of fat acid chlorides were reviews on the subject (Bauer—*Oil & Soap 23*, 1; Bouquet—*Inds. corps gras 2, 247*). An investigation by Ackley and Tesoro (*Ind. Eng. Chem., Anal. Ed. 18*, 444) on preparation of lauryl chloride showed that best yields (90-92%) were obtained with 1.1-1.5 moles of thionyl chloride per mole of acid. This report contained an original analytical procedure for estimating yields.

The communications on synthetic esters showed varied interests. Swern *et al.* (*J. Am. Chem. Soc. 68*, 1673) prepared several alcohol esters of 9,10-dihydroxystearic acid and recorded their melting points. They suggested that some may be good plasticizers for cellulose plastics. Gordon *et al.* (*Ind. Eng. Chem. 38*, 1239) pointed out that proteins could be acylated by fat acid chlorides and suggested this means for reducing the affinity of industrial proteins for water. Desai and Waravdekar (*Proc. Indian Acad. Sci. 23A*, 341) prepared and recorded the physical characteristics of stearic, palmitic, and lauric esters of 2-naphthol. Various alkyl esters of hydroxystearic acid were patented for use as mold lubricants (Hunter—*U. S. 2,390,027*; Hunter & Fenn—*U. S. 2,397,008*). Decarboxylated half esters of hydroxylated fat acids and unsaturated polycarboxylic acids were new intermediates for the manufacture of rubbery or rigid resins (Agens & Nordlander—*U. S. 2,404,204*). The preparation of the fat acid ester of *d*-ascorbic acid containing an unsubstituted ene-diol group was described (Wells & Swern—*U. S. 2,408,182*). During synthesis of pure esters, unsaturated fat acids were protected against polymerization or oxidation by halogenation and after esterification unsaturation was restored by dehalogenation (Black & Overley—*U. S. 2,408,905*). The use of an amide as a catalyst for esterification was patented (Tucker—*U. S. 2,399,959*).

FAT DERIVATIVES CONTAINING NITROGEN. Reviews on the subject contained information on manufacture, composition, and properties of fatty amines (Johnson—*Chem. Industries 59, 838*), fatty phthalimides (Hatt & Reid—*Australian Chem. Inst. J. & Proc. 13*, 204), and fatty amides (Bouquet—*Inds. corps gras 2*, 220). A general review on fat derivatives also contained information on the nitrogen compounds (Ripert & Sisley—*Ibid.* 41). In a modification of Ralston's method of laboratory preparation of nitriles, Reutenauer & Paquot (*Ibid.* 336) used glass beads in place of alumina as the catalyst. The new methods of hydrogenating nitriles to amines were described in the same paper; a "neutral" method comprised hydrogenation while in acetic anhydride solution; and in a "basic" method the fat nitrile was dissolved in a 1:1 water:alcohol solution containing six per cent sodium carbonate. New manufacturing technics relating to these compounds were patented. The secondary product formed in hydrogenation was converted to primary amine by returning this residue to succeeding batches of nitrile to be hydrogenated (Stegemeyer—*U. S. 2,408,959*). A process for refining fat acid nitriles comprised treating with maleic anhydride and washing with water (Ralston *et al.*—*U. S. 2,401,772*). A new insecticide, N-isobutylhendecylenamide, was derived by simultaneous amidation and pyrolysis of castor oil (Bousquet—U. S. 2,402,530). Hendecylenamide was patented as an intermediate for the manufacture of insecticides (Farlow & Lazier—*U. S. 2,402,541*). Amino isobutyric acid esters of fat acid monoglycerides were found useful as antiseptics, germicides, and preservatives (Harris—*U. S. 2,406,329*). Defoaming of foaming compositions was possible with basic fat acid polyamino alcohols (Monson—*U. S. 2,408,527*). Fatty derivatives of pyridine imparted scratch resistance to cellulose nitrate coatings (E. I. du Pont de Nemours & Co.—*Brit. 566,068*). Films of fat acid salts of primary amines (Rust—*U. S. 2,400,784*), of guanidine (Rust—*U. S. 2,400,786*), or of polyethylene polyamine (Rust—*U. S. 2,400,785*) protected silverware from tarnishing. Some fatty amidoamines had anticorrosive properties (Miskel—*U. S. 2,403,293*). Fat acid derivatives of aminocarboxylic acids (Hintzman—*Ger. 745,015 Cl. 22g*). and of monoaminobiphenyl (Aelony—*U. S. 2,404,896*), and reaction products of fat acid amide and formaldehyde (Stegemeyer—*U. S. 2,393,202*) were used in polishing wax formulas. A fat acid ester of hydroxy-alkyl nontertiary amine salt proved useful as a flotation reagent (Cahn—*U. S. 2,389,763*). For magnetic concentration, a fatty amine, "Lorol Amine," was found most efficient among several reagents tested (Scott *et al.*—*Am. Inst. Mining Met. Engrs. Tech. Bull. No. 1902*, 10 pp.).

Some physical chemistry studies of fat acid amines were recorded. A study on the freezing point, conductivity, viscosity, and transport data on aqueous solutions of hexanolamine oleate, by Gonick and McBain (*J. Colloid Sci. 1,* 127) indicated the existence of small micelles or particles and hexanolammonium ions. Hoerr *et al.* (*J. Org. Chem. 11,* 199) recorded the freezing and melting points of a series of fat acid secondary amines. The data indicated that those below ditetradecylamine presented dimorphic tendencies except in very highly purified condition. A spectrophotometric study of bisdodecylamino-cupric acetate by Broome *et al.* (*J. Am. Chem. Soc. 68,* 849) disclosed that it dissociated in trichloromethane solution.

SOAPS OF POLYVALENT METALS. An interest in developing continuous manufacturing methods was reflected in a patent on making lead soaps (Weber & Hamblet—*U. S. 2,395,307*). In this system hydroquinone was used as a catalyst to reduce decomposition (Hamblet — *U. S. 2,409,678*). Another patent claimed that advantages in operations were realized when the glycerides were split and then rapidly saponified with the polyvalent metal prior to separation of glycerol, water, and fat acids (Thurman—*U. S. 2,403,413*). A copper soap prepared by Taylor (*U. S. 2,397,767*) was submitted to oxidation with air during the manufacture. Aluminium chloride catalyst spent in petroleum conversion processes was found suitable for making aluminum soaps (Morway—*U. S. 2,396,744*).

The metallic soaps had a very wide variety of uses. A polishing wax contained 25% magnesium, zinc, or aluminum soap (Akt. Junckers Savvaerk—*Dan. 60,378*). A blend of fat acids, paraffin, and metallic soaps waterproofed textiles, paper, and wood (Berliney *et al.*—*U. S. 2,401,217*). A mixture of inorganic oxides and zinc soap was fused on flame resistant asbestos fabric to render it water repellent (Kurlychek—*U. S. 2,406,779*). The thickening agent used for preparation of gelled gasoline fuels, and incendiary bomb and flame thrower fuel was aluminum soap (Fieser *et al*—*Ind. Eng. Chem. 38,* 768; Minich—*U. S. 2,390,609*). A patented smokeless powder had a calcium stearate glaze (Holmes—*U. S. 2,395,135*). A compilation of the many new uses for these soaps was prepared by Downie *Paint Manuf. 16,* 167). One communication, describing research on determination of free acid in lead soap, recorded the discovery that the soap underwent double-decomposition with sodium iodide (Burnett—*Ind. Eng. Chem., Anal. Ed. 18,* 333). The major portion of literature on metallic soaps involved lubricant grease manufacture and is taken up under lubricants.

LUBRICANTS. Two x-ray diffraction powder diagram studies on metallic soaps were connected with investigating the course of the reactions taking place during grease manufacture. Smith & Ross (*Oil & Soap 23,* 77) used this technic to demonstrate that neither basic metallic soaps nor acid soaps were formed in the process as was the concept in several patented manufacturing processes. In the other study Ross & McBain (*Ibid.* 214) found that aluminum di-soaps appeared to have crystal structures analogous to those of sodium soaps. The reviews on greases contained information on their manufacture (Baouman—*Ind. chim. 33,* 55), types (Van Gundy—*Steel 118, No. 12,* 92), and analyses [Webber—*Petroleum* (London) 7, 18].

In analytical work on greases, several modifications were made in the American Society for Testing Materials method of determination of soap, fat, and mineral oil (Kaufman *et al.*—*ASTM Bull. No. 141,* 54). A test machine for determining the best greases for aircraft generators approximately duplicated the conditions encountered in service (Macphearson—*Ibid. No. 140,* 63). Gallay and Puddington (*Can. J. Research 24B,* 73) determined the flow-pressure relations and viscosities under pressure, for suspensions of calcium soaps in mineral oils of various viscosities. The outstanding results of the work were the increases obtained by the addition of water. The data and technic were applicable to the control of grease manufacture.

A new method of grease manufacture comprised dissolving the fat in a portion of the mineral oil, dispersing the saponifying agent in another portion, and mechanically mixing and comminuting (Gallay & Puddington—*U. S. 2,394,907*). The consistencies of patented greases were improved with sodium and zinc soaps) Morway & Beerbower—*U. S. 2,411,587*), nonsoap detergents (Brunstrum & Leihe—*U. S. 2,398,075;* Leihe—*U. S. 2,394,790*), phenolic compounds (Sproule & Zimmer—*U. S. 2,394,567*), and organic hydroxy amines (Standard Oil Development Co.—*Brit. 563,429*). A grease for bearings of plastic rolling mills contained lead and soda soap, a sulfur compound, fat acids, and mineral oil (Hilliker—*U. S. 2,386,553*). The syneresis tendency of greases was controlled by alkali salts of aromatic acids (Meyer—*U. S. 2,409,950*). The compounding and manufacturing of lithium soap greases, which are particularly efficient at high temperatures, were the subject of several patents (Morgan—*U. S. 2,393,797*; Fraser—*U. S. 2,397,956*; Standard Oil Development Co.—*Brit. 560,885*; *U. S. 2,398,173*; Lien—*U. S. 2,403,104*; Bax *et al.* — *U. S. 2,406,655; Luckenbach — U. S. 2,388,166*). A research report on the lithium greases by Luckenbach and Meyer (*Foote-Prints 17,* No. 2, 3; *Inst. Spokesman 10,* No. 4, 2) showed that fat acids with a molecular weight above and below that of stearic acid unfavorably affected penetration, bleeding, and stability of consistency of the grease. A new grease that was stable and plastic over a relatively wide temperature range contained silver soaps (Morgan—*U. S. 2,391,842*).

Many fat derivatives were added to lubricating oil to improve certain characteristics. The purpose, active agent, patentee, and patent number are most conveniently listed:

Viscosity-index improvers: copolymer of oleyl ketone and butadene, Meyer—*U. S. 2,399,817*; condensation product of a fatty alcohol with a γ, β-unsaturated acid, Blair—*U. S. 2,384,595*; phosphatides, Julian & Meyer—*U. S. 2,400,120.*

Pour-point depressants: esterification products of phthaleins and fat acid chlorides, Lieber—*U. S. 2,382,730.*

General improvers: calcium salts of sulfurized oleic acid, Lincoln & Byrkit—*U. S. 2,395,889*; product obtained by distillation of castor oil in the presence of alumina, Paluszek—*U. S. 2,401,369*; reaction products of fat acid esters of lower alcohols and phosphorous pentasulfide, Musselman—*U. S. 2,399,243*; reaction product of lauryl alcohol and phosphorous pentasulfide, Musselman & Lankelma — *U. S. 2,396,719;* cetyl *α-methacrylate*, Fenske & Cummings—*U. S. 2,407,954.*

Lubricant defoamers: dimethylaniline, quinoline, pyridine, and nicotine compounds of isoamyl cetyl phosphate, Smith & Cantrell—*U. S. 2,397,377-81*; calcium soap and a sodium fat acid sulfate, Barton *et al.*—*Brit. 564,281*; acetyl and butyl esters of sulfonated ricinoleic acid, Bennett & Marshall—*U. S. 2,390,491-2.*

Stabilizers against oxidation and sludge formation: monooctadecylphosphoric acid, monooctadecenylphosphoric acid, and like compounds, Farrington *et al.*—*U. S. 2,382,043*; fat acid selenide compounds, Denison & Condit—*U. S. 2,398,414, 2,398,416, 2,400,106*; sulfurized lanolin, Musselman—*U. S. 2,385,832*; sulfurized secondary fat acid amines, Bartleson & Veatch—*U. S. 2,403,474*; reaction product of lauryl alcohol with a condensation product of turpentine and phosphorous pentasulfide, May—*U. S. 2,392,253*; sulfurized nitriles from tall oil, Jolly—*U. S. 2,380,531*; sulfurized oleyl ketone, Otto & Meyer *U. S. 2,383,497*; vanadyl oleyl phthalate, Frank *et al.*—*U. S. 2,388,400*; phosphatides and sulfurized mononuclear aromatic compounds, Musher—*U. S. 2,408,090.*

Corrosion inhibitors: fat acid ester of anhydroalkitol, Sharp—*U. S. 2,398,193*; fat acid substituted thiophosphoric acid, Nelson & Mikesla—*U. S. 2,391,184*; fat acids linked with sulfur at the β-position, Zublin *et al.*—*U. S. 2,398,202*; fatty amine salts of various compounds, Smith & Cantrell—*U. S. 2,387,537, 2,400,611, 2,403,762*; imido esters, imides, and amidines containing fat acid radicals, Fischer & Jenkins—*U. S. 2,388,132*; phenolic compounds and cyclohexylamine oleate, Rocchini—*U. S. 2,399,510.*

Several of the latter additives were especially recommended for turbine lubricants. A valve lubricant contained stearamide and glyceryl monoricinoleate (Morgan & Lowe—*U. S. 2,393,800*). A lubricant designed especially for clocks contained 10% polymerized mixture of octyl and decyl esters of methacrylic acid (Morgan & Lowe—*U. S. 2,396,191*).

The patented textile lubricants containing fat derivatives were mixtures as listed: mahogany soap, oleic acid, soap, water, and diethylene glycol (Moscowitz—*U. S. 2,396,718*); mineral oil, peanut oil, diamyl phenol, butyl acetyl ricinoleate, oleic acid, and triethanolamine (Seymour & Brooks—*U. S. 2,385,423*); mineral oil and an amine wetting agent (Haussmann *et al.*—*Ger. 748,836 Cl. 29b*). Moscowitz (*Am. Dyestuff Reptr. 35,* 310) discussed the special characteristics desired in wool lubricants.

Similarly the new cutting oil formulas contained: mineral oil and sulfurized fats (Standard Oil Development Co.—*Brit. 559,167*; Hughes—*U. S. 2,386,952*); lecithin and chlorinated sulfurized sperm and petroleum oils (Culmer—*U. S. 2,412,131*); lard oil and sulfochlorinated and phosphorized fat (Yule—*U. S. 2,394,734-5*); sulfurized mineral oil and an oil soluble detergent (Hughes—*U. S. 2,398,429*); lard oil, sulfur, and pine oil (Gabriel—*U. S. 2,412,082*). A cutting base contained rosin soap and a monoglyceride of a fat acid (Myers & Muckerheide— *U. S. 2,393,927*). Difat acid silicones were patented as cutting oil defoamers (Diamond—*U. S. 2,406,671*). A refining method for used cutting oils comprised treatment with adsorbent under vacuum and steaming to remove volatile matter (Dunmire — *U. S. 2,401,338-41*).

Fuels. Fats and oils are used as Diesel engine fuels or are converted into hydrocarbon motor fuels in some countries where the supply of petroleum is limited. Chinese workers published their experiences in making motor fuels and lubricants by pyrolysis of many vegetable oil soaps and polymerization of the pyrolytic products (Suen *et al* — *J. Chinese Inst. Engrs. 4,* No. 1, 15; Lo & Tsai—*J. Chem. Eng. China 9,* 22). The tarry still residues from the process were suitable for roofing and road paving material (Suen *et al.*—*Ibid.* 6). In similar work on fish oils by a French worker (Arnoux—*Ann. musée colonial Marseille 9,* No. 1, 1), best yields of light hydrocarbons were obtained by pyrolysis of the soaps of dried lime. Pascal & Lilia (*Compt. rend. 221,* 44) obtained additional yields by hydrogenating the residue tars.

The suitability of fatty oils as Diesel fuels was characterized by Otto (*Bol. divulgacão, inst. óleas* (Rio de Janeiro) *1944,* No. 2, 12) according to their behavior in contact with hot metallic walls. Thus when cottonseed oil was projected on a metal surface of 440-475° temperature, it ignited and adhered until consumed, depending on its viscosity and the catalytic action of the metal. Mineral oil remained globular with small area of contact. Cottonseed oil on iron formed a varnish; with copper it remained liquid for a longer time and left a removable varnish. The results also had bearing on design of Diesel engines to be fueled by vegetable oils.

Miscellaneous Products Containing Fat Derivatives. A rust preventive composition contained wool fat partially saponified with lime, wax, and hydrocarbons (Ruedrich—*U. S. 2,392,102*). A similar composition containing, in addition, phosphatides was made for protecting guns (Shields—*U. S. 2,397,904*). In evaluating these oils Pilz and Farley (*Ind. Eng. Chem. 38,* 601) found that contact angles formed by a drop of water resting on oil-coated steel panels was related to the rust preventive ability of the oil. Their findings were in agreement with the theory of rust prevention which postulated orientation of the polar additives at the oil-metal interface and establishment thereby of a barrier to normal mode of entry of the causative agents of rusting, oxygen, and water.

The communications on oil treating of leather were brief treatises on essential factors for water repellency of chrome leather (Pressley—*J. Intern. Soc. Leather Trades' Chem. 30,* 94), fat-liquoring side leather (Meyers—*J. Am. Leather Chem. Assoc. 41,* 427), and uses of fatty materials in the tannery (Meunier—*Bull. assoc, francaise ind. cuir 1943,* No. 17, 321). A patented leather preservative contained fatty oils or fat acids and triaryl phosphates (Benischek—*Ger. 741,056*). A paper on leather polishes gave the analyses of 13 oil types, eight oil-in-water emulsions, three water-in-oil emulsions, two solid without oil, and three solid with oil (Herfeld *et al.*—*Fette u. Seifen 50,* 576). A general service polishing wax contained wax, oleic acid, morpholine, and a nonsoap detergent (Wassell—*U. S. 2,395,025*).

A miscellaneous group of unrelated fat products was difficult to classify in the preceding paragraphs. A composition for dielectric usage comprised hydrogenated castor oil and an aromatic sulfone (Clark—*U. S. 2,410,715*). Fat acids, recovered from sulfuric acid treated vegetable oil refining foots, served as defoamers in the sugar industry (Larsen—*U. S. 2,412,276*). Cottonseed oil phosphatides were used as spreaders for insecticides (Thurman—*U. S. 2,407,041*). The active ingredient of an insecticide was 2-ethyl-*n*-caproic acid (Jones & Travis—*U. S. 2,396,012*). A flushing liquid for cleansing internal-combustion engines contained light spindle oil, a detergent, fat acids, and sulfurized wool fat (Burk—*U. S. 2,403,169*); another product for the same purpose contained various organic solvents, mineral oil, water, morpholine oleate, and oleic acid (Skinner—*U. S. 2,403,618-9*). A cloth for metal polishing was impregnated with oleic acid, triethanolamine, and powdered abrasive (Morgan & Lowe—*U. S. 2,403,821*).

The Rates of Oxidation of Unsaturated Fatty Acids and Esters[*]

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ALTHOUGH several studies of the rates of oxidation of fatty acids and their esters have been reported (1), most of these studies concern themselves with small groups of purified substrates or even a single substance. Moreover, data from these studies cannot be directly compared because of the widely different conditions under which they were made. Inasmuch as several fatty acids and esters were available to us and many of these substances have not been studied in this regard, it was thought that a comparative study of the rates of oxidation of a series of pure acids and esters would be of sufficient interest to merit attention. It is to be regretted that some acids and esters were not available, making certain comparisons difficult, and that time did not permit the preparation of missing isomers or homologs before the fatty acid research program was terminated at this laboratory. However, the information gained from the present study throws some light upon the effects of fatty acid composition upon the rate of oxidation.

Experimental

The oleic acid and ethyl oleate used in this study were prepared by F. Greenwood by low-temperature crystallization methods. The linoleic acid, ethyl linoleate, linolenic acid, ethyl linolenate, and methyl arachidonate were prepared through their respective bromides. Trilinolein, trilinolenin, pentaerythritol linoleate, and dipentaerythritol linoleate were prepared by a modification of Wheeler's method (2). The preparation and properties of these latter substances is reported elsewhere (3). Elaidolinolenic acid was prepared by J. P. Kass (4).

The 10,12-linoleic acid was prepared by alkaline isomerization of ethyl linoleate (5). To 300 ml. ethylene glycol containing 50 g. potassium hydroxide at 180° 27 g. of ethyl linoleate was added with stirring. The temperature was maintained at 170-180° for 30 minutes when the mixture was poured into about five volumes of ice and water. The soaps were acidified and the mixture chilled to yield a solid cake of fatty acids which was removed and recrystallized twice from alcohol and twice from petroleum ether at —40°. The resulting product melted at 7.0-7.5° (uncorrected) and had a molar extinction coefficient of 28,600 at 2330 Å in methanol.

The properties of the substances used in this study are presented in Table I.

The autoxidation of the acids and esters was carried out in air at 37° upon small samples in Warburg respirometer vessels of 10-12 sq. cm. bottom area as described previously (6). The rates of enzymatic oxidation of ethyl linoleate, ethyl linolenate, and methyl arachidonate were determined in systems described elsewhere (7). The temperature 13° was chosen be-

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