

# Review of Literature on Fats, Oils and Soaps for 1942\*—Part 1

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## General

Notable features of the past year in oil and fat commerce were a record domestic production, a change from net importation to net exportation, control of prices and orders restricting use.

According to U. S. Department of Agriculture Bureau of Agricultural Economics monthly reviews of the fat and oil situation, production from domestic materials in the year 1943 is expected to be 11.7 billion pounds as compared to 10.1 billion pounds for the last year. The supplies for 1943 are estimated as follows: production from domestic materials 11.7, imports 0.8, factory and warehouse stock January 1, 2; total, 14.5 billion pounds. Disposition of these is estimated as follows: military use, Lend-Lease export, commercial exports and shipments to U. S. territories 2.6, civilian nonfood use limited to 3.2, civilian food use limited to 6, factory working stock for end of year 2 and government contingency reserve at end of year 0.7 billion pounds. In addition, 18 to 20 million bushels of soybeans will be withheld from crushing for foreign and domestic contingency needs.

Requirements for fats will be greater than allotted, particularly for civilian consumption and for contingency reserve. The Food Requirements Committee placed the goal for reserve at 1.5 billion pounds. To achieve this goal it would be necessary to institute direct consumer rationing of food fats and oils at levels below present manufacturers' limitation order. The food fat per capita estimated supply is 48.2 pounds for 1943. This is practically equal to past consumption; the averages were 48.9 for 1935-9 and 50.9 for 1940-2. However, the Bureau of Agricultural Economics estimated on the basis of past relationship between consumption, price, industrial workers' income and prices of competing products that consumer demand at the present controlled price will be for 57 pounds per capita in 1943.

To achieve the desired supply there will be an increase of hog and beef fats and an increased acreage for flaxseed, peanuts and soybeans. Cotton acreage will be reduced. Production of butter will decrease slightly.

The change from net importation to net exportation was due to war conditions, lack of transportation, Lend-Lease needs and military use.

The average price of domestic oils during 1942 rose about 27%. Prices of imported oils were held practically unchanged. Most oils are now at the ceiling price

at which they have been pegged by governmental orders. Linseed oil was a little less than ceiling price at the end of the year, probably because of the large production and the decreased demand due to restricted building activity. Toward the end of the year, on announcement of a support price for the 1943 flaxseeds, the price of the oil began to rise.

One of the first fat and oil restrictions was that which forbade the use of coconut oil for edible purposes. This high glycerin and high lauric acid oil was held for use in soap. In the food field this oil was used for the manufacture of margarine, candy and spray coatings for candy, biscuits and crackers.

Substitutes for this product in the confectionery industry have been suggested by O'Malley and Price (*Manufg. Confectioner* 22, No. 3, 13) and Sheuring and Tracy (*Ice Cream Field* 39, No. 6, 28).

Soap makers in the latter part of 1942 were limited to 88% of the fat and oil raw material and 150% of the fat acids that they used during 1940-1, with exemption of restriction for soap made for Lend-Lease and military governmental departments. For 1943, the fat limit was lowered

to 84%. Since soap has been at record production during the last few years no shortage is expected. The production for the last 3 years approximates 30% higher than for the previous 3 years. The production of glycerin is of paramount importance in the soap industry and adequate regulations on soap manufacture have been promulgated so that maximum economical recovery occurs. Soap makers are not receiving as much of the coconut oils as they desire. The status of this problem has been discussed in several editorials and communications (*Soap* 18, No. 1, 31; No. 3, 21; No. 11, 28; No. 12, 29; Lee—*Ibid.* No. 6, 23; Kemp—*Ibid.* No. 12, 25; *Perfumery & Essential Oil Record* 33, 260). Substitution with South American oils and use of rosin and synthetic detergents were the outstanding suggestions. Lack of transportation and of good substitutes precludes full replacement by South American oils. Rosin is being used but must be limited because of objection to the color. According to Pohle (*Soap* 18, No. 2, 29, 69) this objection can be overcome by hydrogenating where white products result.

During the latter part of 1942 shortening manufacturers and other industries using edible oils were limited to the use of 88% of the average fat and oil used during 1940-1, with exemption for fats and oils used in the manufacture of products for Lend-Lease or military use. This limit has been reduced to 84% for 1943. The quantity of fats and oils that may be

## OUTLINE

- A. General
- B. Technical Treatment
- C. Products (except Detergents)
- D. Deterioration
- E. Biochemical
- F. Characteristics and Composition
- G. Detergents

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used in the manufacture of margarine for domestic civilian consumption was increased January 1, 1943, from 110 to 180% of the 1940-1 average use.

Several writers and editors prepared analyses on the fat and oil situation under present war conditions (Murphy—*Chem. Industries* 50, 476, 618, 768; McBride—*Food Industries* 14, No. 2, 57; Eisenschiml and Eisenschiml—*Am. Paint J.* 26, No. 27, 22; 27, No. 1, 7; Newell—*Am. Baker* 10, No. 10, 40; Editorials—*Chem. Met. Eng.* 49, No. 2, 98; *Chem. Industries* 51, 528). Production, consumption, stocks, interchange, commerce, new sources and like subjects were treated. The Allies have divided their import market so that the United States will obtain the export fats and oils of the Americas except the animal fats of Argentina and Uruguay and the copra of Tahiti, Free French Islands, Portuguese and Spanish Africa and Liberia; Britain will have the exported animal fats of Argentina and Uruguay and the oil seeds of the British Empire, except her American possessions, the oil seeds of Free French Africa and Belgian Congo. In the United States, the development during the war period of an association of fat and oil importers was fostered by the Commodity Credit Corporation of the Department of Agriculture.

Several communications discussed the South American countries as sources of fat and oil, especially of those that can not be produced in the United States (Gordon—*Soap* 8, No. 8, 19; Markley—*Oil, Paint & Drug Repr.* 142, No. 4, 7; U.S.D.A., ACE-173; Singer—*Chem. Industries* 51, 243). The Brazilian Ministry of Agriculture invited a mission of United States technicians to visit Brazil for the purpose of studying the vegetable oil industry. The report of this mission (Lund, Jamieson, Mood, Gordon, Wood and Vahlteich—June, 1942) contains a very good description of the industry, its equipment, processes used, statistics and untapped supplies. The extent of supplies in relation to production equipment and to means of transport were analyzed and recommendations were made as to the most economical facilities necessary for the exploitation of these supplies.

If our supplies of fat products prove too inadequate during 1943, conservation in the distribution and utilization of waste may be necessary. As a background for this purpose Bernstein (*U. S. Dept. Labor Hist. Study Nos. 43 and 45*) reviewed these activities during the war of 1917-8. In the present war the first step to prevent waste of fat was a well publicized fat salvage plan (*Soap* 18, No. 9, 28). It was estimated that about 2 billion pounds of cooking fat and fat trimmings were wasted annually by the American housewife. The immediate response was good, but it soon began to dwindle. Plans are now being made for another publicity campaign through radio, civilian defense organizations and newspapers. The War Production Board recommends that fat from pork chops, steaks and other meats left on dinner plates in homes and restaurants should not be wasted (*Oil, Paint & Drug Repr.* 141, No. 20, 5). Their experts believe that 300,000 to 500,000 tons of edible fat could be saved by trimming meat carcasses a little closer. There are now rumors of issuing instructions to this effect. Stewart and Mussehl (*Poultry Sci.* 20, 450) pointed out that a good soap stock fat can be recovered from the waste offal of poultry evisceration plants. Dry rendering yielded 4.6 to 8.1% fatty oil.

Several reports on substitution appeared. Over half of the fish oil vitamin has recently been derived from shark liver oils (Harrison and Samson—*Fishery Market News* 4, No. 2, 3). A new tinning oil was derived from petroleum (*Chem. Eng. News* 20, 181), and was said to compare favorably with palm oil and tallow, now in most common use. Davies (*Wool Record Textile World* 57, 392) recommended the use of stabilized peanut oil as a substitute for olive oil in textile manufacture. Hardy (*Perfumery & Essential Oil Record* 33, 203) reviewed the plants containing saponins which might be used as suitable substitutes for soap. Jojoba oil, a liquid seed wax, was proposed for nonedible use where stability was important (Markwood—*Chemurgic Digest* 1, 174).

Each year there are publications describing new or little known oils or oils from new sources. Some of these were:

Aleurites oils of India. Imp. Institute—*Ann. Rept. Imp. Inst.* 1941, 15.

An algae seashore fat from Piaui. Rolin—*Rev. quim. ind.* 11, No. 118, 13.

Stone fruit fat. D'yachenko—*Obshchestvennoe Pitanie* 8, No. 11/12, 39.

Madol oil. Child and Nathanael—*Trop. Agr. Ceylon* 97, 78.

Grape seed oil. Mir—*Ion, Madrid* 1, No. 1, 17; Fiedler—*Die Chemie* 55, 137.

Blue shark and mackerel (*Germo alalunga*) oils. Legendre and Lormand—*Bull. sci. pharmacol.* 48, 224.

Wild and cultivated oil bearing plants of Europe. Regel—*Angew. Botan.* 22, 400.

Development of gurjun oil industry in Bengal. Karium, Azam and Waliullah—*Govt. Bengal Dept. Ind. Bull.* No. 90, 11 pp.

Processing cadavers. Anon.—*Allgem. Oel- u. Fett-Ztg.* 38, 86.

Citrus-seed oil. Stambovsky—*Drug Cosmetic Ind.* 51, 156.

Minor oil producing crops of the United States. Kester and van Atta—*Oil & Soap* 19, 119.

Macadamia nut oil. Jones—*Hawaii Agr. Expt. Sta. Ann. Rept.* 1940, 52.

Those publications containing sufficient information for tabulation will be charted in the section of this review on composition and analysis.

The publications on bacterial production of fat covered the use of *Mucor mucedo* (Bline and Bojce—*Arch. Mikrobiol.* 12, 41), *Endomyces vernalis* (Bichkovskaya—*Microbiol. U.S.S.R.* 8, 1170) and *Oöspora lactis* (Fredholm—*Kgl. Lantbruksakad. Tid.* 80, 341). Optimum temperature and pH, and choice of substrate for the respective microorganisms were the main contributions. Munin (*Fette u. Seifen* 49, 123) reviewed the work of the Swedish investigators on this subject. Barker and Taha (*J. Bact.* 43, 347) isolated 9 strains of an anaerobic spore-forming bacterium, *Clostridium kluyverii*, from fresh water and

marine muds, that forms caproic acid from ethyl alcohol, particularly when growing with methane-producing bacteria.

The fat and oil situation in European Axis countries is most acute. According to a special correspondence section of *Chemical & Metallurgical Engineering* (49, No. 12, 130) most of the German soaps contain less than 3% fat in the form of soap powder. The hand soaps contain 80 to 90% abrasives and fillers as pumice powder, clay and like material. Saponin is added to most of the substitute soap to form a lather. The limitations in the use of saponins were reviewed by Ruemele (*Seifensieder-Ztg.* 68, 278). They are mild washing agents, useful only in washing the more easily damaged fabrics. Addition of saponin to soap lowers the sudsing ability of the latter. It can not be used to replace toilet and shaving soaps because of its possible irritating action. Instructions for white-laundering with available Axis products were issued by Chwala (*Fette u. Seifen* 49, 253). Rape growing is being fostered with publications on cultivation and effect of fertilization (Nicolaissen—*Ibid.* 1; Kaufmann—*Ibid.* 169). The literature also encouraged sewage fat recovery (Anon.—*Allgem. Oel- u. Fett-Ztg.* 38, 83; Gläss—*Seifensieder-Ztg.* 68, 277). Another salvage publication dealt with industrial removal of unsaponifiable contents of fat recovered from sewage, and from waste water from tanning, wool wash, felting and synthetic fat manufacture (Lindner—*Fette u. Seifen* 49, 179). The manufacture of fat supplements containing synthetic and natural fats for livestock feeds has been patented (Skraup—*Ger. 681,670 Cl. 53g*). In Italy an increase in peanut cultivation was fostered (Wittka—*Allgem. Oel- u. Fett-Ztg.* 38, 7). The climate is unsuitable for the production of soybeans.

### Technical Treatment

A comprehensive monograph of the chemistry and technology of soybeans and their derived products was prepared by Markley and Goss (*U.S.D.A. Bureau Agr. Chem. and Eng. ACE* 142, pts. 1 & 2, 69 & 112 pp.). Brief monographs containing information on processing, refining uses and statistics appeared on cottonseed (Markley and Lynch—*Cotton Research Congr. Proc.* 1, 211, 231; Halcomb—*Chem. Eng. News* 20, 440); soybean (Engles—*Allgem. Oel- u. Fett-Ztg.* 38, 119), Turkish olive (Esat-Kadaster—*Fette u. Seifen* 49, 561, 634), fish liver (Wood—*J. Council Sci. Ind. Research* 14, 311), poppy seed (Redgrove—*Intern. Export Chemist* 22, No. 11, 358) and rosin (Edwards—*Chem. and Ind.* 61, 233) oils, and wool fat (Wontner-Smith and Campbell—*Manufg. Chemist* 13, 135). Another review presented a chronological list of important dates in the history of processing fats and waxes (Blank—*Oil & Soap* 19, 110).

The patents on rendering dealt with the processing of whale meat and bones (Southern Whaling and Sealing Co.—*Brit. 521,521*; Aktiebolaget Septr., Lever Bros. and Unilever—*Brit. 533,300, 536,328, 543,047*). These featured such improvements in continuous systems as the use of special rotary digesters, rotating strainers to remove the bulk of the suspended matter and centrifuges for oil separation. Some features of rendering had entered the vegetable oil industry. According to a patent assigned to Duchscher &

Co. (*Fr. 852,387*) palm fruit or fiber press residues could be further deoiled by boiling with water and separating the oil from the decanted liquids.

Rozanova (*Proc. Sci. Inst. Vitamin Res. U.S.S.R.* 3, No. 1, 355) investigated the loss in the production of Russian fish liver oils. The greatest losses were the incomplete recovery due to inefficient pressing and to non-utilization of the cake. The loss of vitamin A was smaller when the livers were pressed on trawlers than when pressed in rendering plants. Methods suggested for preserving fish livers before pressing included treatment with sodium sulfite (Hickman—*U. S. 2,289,780-1*) and addition of alkali to a pH in excess of 9 (Bedford—*U. S. 2,280,024*). Wentworth (*Can. 401,447*) used alkali to disintegrate the livers for extraction by pressing. Sterner (*Fr. 852,879*) designed a press especially for extracting herring oil. The liquor from fish oil pressing could be separated into aqueous and oil fractions by treatment with alkaline buffer such as trisodium phosphate (Hempel—*U. S. 2,266,036*). Other methods of extracting vitamin oils dealt with the use of other oils such as cottonseed and soybean oils as solvents (Musher—*U. S. 2,282,795-6*; Hickman—*Brit. 539,089*; *U. S. 2,256,392*). According to the Hickman patents the vitamins were concentrated from the solvent oil by short-path distillation. The Lava process for production of coconut oil from fresh copra (*Oil, Paint & Drug Reprtr.* 141, No. 4, 7; Torres—*Coconut J.* 1, No. 3, 7) featured ideas similar to those used in the fish oil industry. A comminuted coconut meats-water mixture (2:1) was pressed in a special press and the oil removed from the liquid by adjusting the pH or by dehydrating to release it from the emulsion. The advantages of the process were the avoidance of bacterial decomposition or pest infestation of the raw material before manufacture, the elimination of drying to the copra stage and the production of edible oil and residue.

In the seed oil field Weigle (*U. S. 2,288,662*) designed a new cooker; Anderson (*U. S. 2,269,898, 2,275,337*) and Upton (*U. S. 2,262,566*) patented improvements on expeller presses; and Lüthi and Winger (*Ger. 682,032 Cl. 23a*) designed an expeller for olive oil production.

Improvements in pressing oleaginous material were claimed by Silberstein (*Brit. 543,424*) for treatment with surface tension lowering materials at elevated temperature. For the same purpose Musher (*U. S. 2,278,942, 2,280,046*) froze the raw materials, reduced moisture, then subjected to steam and pressure, and suddenly released the pressure. McKinney and Halbrook (*Oil & Soap* 19, 182) related some of the experiences and developments of the personnel of the U. S. Tung Oil Laboratory. Among the activities were development of maximum tung oil yields, improvement of the product by research and by disseminating advice to the producers and processors regarding production, pressing conditions, etc. Koo (*Ind. Eng. Chem.* 34, 342; *J. Chem. Eng. China* 7, 1; 8, 1) developed empirical equations on the effect of pressure, temperature and pressing time for the pressing operation of several oils. Constants for use in the equation were ascertained for several common oils.

A fat trap for factory waste water contained 2 zones, in the first the flow was turbulent and in the

second quiescent flow was obtained (Hirshstein—*U. S. 2,284,737*). This second zone contained baffling means to continuously skim off the floating oil or fat.

One research report on solvent extraction contained data on semi-batch and continuous countercurrent extractions of porous plates saturated with soybean oil (Boucher, Brier and Osburn—*Trans. Am. Inst. Chem. Engrs. 38, 967*). The extraction process was found to be one of pure molecular diffusion, the diffusion coefficients being substantially constant for any one temperature and system, and independent of liquid concentration, even though there was a large difference in the viscosities of solute and solvent. Data on continuous extraction of soybean flakes indicated that the process likewise was one of a molecular diffusion. Rose, Freeman and McKinney (*Ind. Eng. Chem. 34, 612*) proposed recovery of the residual oil from tung oil press cake. The extracted oil solidified through isomerization to solid  $\beta$ -eleostearin, but was rendered permanently liquid by heating at 200° for 30 minutes. Powell and Cameron (*Ibid. 358*) showed that solvent recovery of suitable oil from the whole cotton plant was possible if the raw material was first treated with sulfides or sulfites. After bleaching the oil with standard adsorbents it met standard specifications.

Several patents described new improvements in solvent extraction equipment. Truax (*U. S. 2,306,655*) designed a new soybean flaking machine. Reichert's (*Ger. 682,912 Cl. 12c*) continuous extraction system included repeated grinding in the presence of solvent during extraction. Other continuous system improvements were on the mechanical details for countercurrently flowing raw material and solvent (Frazier—*U. S. 2,276,298*; Bonotto—*U. S. 2,273,557*; Lawrence—*Brit. 526,047*). Several patents were on handling the solvent. In a cacao bean extraction system the solvent was recovered by injecting steam and separating the solvent from the condensate (Rockwood & Co.—*U. S. 2,278,647*). Hickman (*U. S. 2,277,401*) recovered solvent by vaporizing and then absorbing vapors in a new charge. Schoch (*U. S. 2,280,723*) recovered fat acids from starch by extracting with methyl alcohol, ethyl alcohol or dioxane. Arnold (*Soybean Digest 1, No. 2, 4*) described the progress that has been made in the development of a small community soybean oil solvent extraction plant. Although the experimental plants built were considered not quite efficient enough for small scale work, the author believes that such a unit will soon appear.

Tall oil proved to be a good source of fat acids. Segessemann (*U. S. 2,273,186, 2,275,075, 2,278,674, 2,305,498*) refines the oil by treatment in petroleum hydrocarbon solvents with ethylene chlorohydrin under conditions such that ethylene chlorohydrin is immiscible in the tall oil solution, or refining by acid treatment followed by removing sterols with alcohol. His methods of separating the fat acids comprised (1) hydrogenation, followed by crystallization of the fat acids or their soaps from organic solvents and (2) esterifying the fat and resin acids with alcohol, transesterifying the fat acids with an alcohol boiling lower than the first and then distilling the fat acid esters thus formed. Oliver and Palmer (*U. S. 2,280,842*) substantially completely hydrogenated tall oil and separated the stearic acid by fractional distillation. Miller (*U. S. 2,291,824*) esterified the fat

acid constituents with crude methanol, refined with water and fractionally distilled the fat acid esters. Gayer and Fawkes (*U. S. 2,288,946-7*) converted the fat acids to alcoholates, the resin acids to their aluminum or zinc salts and then extracted the fat acid esters with organic solvents. Christmann and Houpt (*U. S. 2,285,902*) separated the fat acids as soaps from tall oil by the use of selective solvents. A communication on tall oil contained nomenclature suggestions (Avelius—*Svenk Papperstidn. 44, 203*). As examples, the products of refining and processing tall oil could be named: tall resin acids, tall resinates, tall fatty acids, tall oleates, etc.

Oxidation of hydrocarbons is an active source of fat products. In order to determine the optimum air addition for their manufacture by the Fischer-Tropsch-Gatsch process data were plotted (Pardun and Kuchinka—*Fette u. Seifen 49, 441*) for temperatures of 100-160° with 0.05 to 1 liter of air per gram per hour and oxidation to acid number of 50. At each temperature oxidation increased logarithmically with increase in air. The uses of synthetic fat acids in the soap and cosmetic industry were discussed by Foulon (*Allgem. Oel- u. Fett-Ztg. 38, 159*). The Standard Oil Development Co. patented a method of manufacture of synthetic fat acids (*U. S. 2,274,057, 2,274,632*) which comprised subjecting paraffin wax to temperatures of 100-160° in the presence of potassium permanganate and soda ash, separating the unsaponified by solvent extraction, adding a small amount of sodium thiosulfite and recovering the acids by acidification. In such processes, according to Dreyfuss and Groombridge (*Brit. 521,202*), the acids can be recovered from the soaps or salts by warm treatment with carbon dioxide in ethyl alcohol solution.

Recent patents issued to Refining Inc. (*Brit. 538,155-6*; *U. S. 2,268,567, 2,292,822, 2,301,109-10*; Matikow—*Oil & Soap 19, 83*) indicated the successful development of a refining method using soda ash as the refining agent. The oils were first treated with double the amount of soda ash necessary for neutralization, dehydrated, rehydrated with 6-20° Bé soda ash solution and the foots was separated by means of centrifuges. A new centrifuge designed for like purposes separated the material into 3 fluid components, i.e., oil, soap and aqueous solution. Lachle (*U. S. 2,281,884*) and van Dijek (*U. S. 2,268,786*) invented refining procedures containing 2 neutralization treatments. The latter used ammonia as the neutralizing agent and removed the impurities by extraction with isopropyl alcohol. A method of injecting the alkaline refining agent as a mist was assigned to Anderson, Clayton Co. (*Brit. 531,749*). In a continuous system, where the oil was flowed upward through a refining solution, the oil was held in a state of subdivision by a zone of nails above the oil inlet (Colbeth—*Brit. 534,338*).

Fish oils were refined by Buxton (*U. S. 2,258,671-3*) by heating to 100-200° with sugar, formaldehyde vapors, or edible gums. This inventor (*Ind. Eng. Chem. 34, 1486*) showed that refining medicinal fish oils with carbon removed the antioxidant thus rendering the vitamin A therein unstable. The freshly carbon treated fish oils had essentially the same vitamin A value as the respective crudes.

The assignors of patents to Anderson, Clayton & Co. (*Brit. 537,682, 537,704*), under the assumption

that the suspensions in oils were electrically charged, added an oppositely charged suspension or subjected the oil to the action of radiant energy of 0.535 micron wave lengths to reduce the dispersion of the impurities and then they alkali refined the oil. Highly acid oils may be neutralized by esterifying the free fat acids with monoglycerides (*Ludvik-Spirk Chem. Listy 35, 45*).

Liquid-liquid extraction entered the fat refining field. McDonald (*U. S. 2,279,408*) treated with alcohol the oils containing soap and extracted the oil with chlorinated hydrocarbons. Gummy material (Ewing—*U. S. 2,288,441*) and fat acids (Hixon and Bockelmann—*Trans. Am. Inst. Chem. Eng. 38, 891*) were removed from oils by liquid propane at critical solution temperatures. Dissolving a crude oil in hydrocarbon solvent and liquid-liquid extracting with polar solvents removed the coloring and odoriferous compounds from the oil solution (National Oil Products Co.—*U. S. 2,265,020*). Kaufmann (*Fr. 853,066*) removed impurities and free fat acids from oils by passing them through columns of special selective adsorbents.

A few publications on refining dealt with individual oils. The odor and taste of colza oil was reduced by heating with starch, charcoal, dried elm bark or bread (Lefevre—*Compt. rend. acad. agr. France 26, 1044*). Congo palm oil can be refined and decolorized by heating with finely divided nickel, cobalt, zinc, manganese or copper and then treating with adsorbents under vacuum (Kellens—*U. S. 2,260,910*). Petroleum ether solvent-extracted tung oil can be clarified by heating at 200° for 30 minutes (McKinney *et al.*—*U. S. 2,277,342*). Wool fat extracted from lime-lanolin precipitate was improved by treatment with sulfuric acid while still in benzene solution (Vod-sinkaya *et al.*—*Sherstyanoe Delo 19, No. 3/4, 12*). Brown (*U. S. 2,271,621*) refined wool grease by washing with an aqueous solution of an abietic acid salt.

Two chemical methods of bleaching and deodorizing oils, respectively, made use of chlorine dioxide for the former (Kauffmann—*U. S. 2,269,667*) and washing with sodium sulfite and solutions of lead acetate for the latter (Gruenwald and Reider—*U. S. 2,276,233*). This deodorizing method was especially applicable to tung oil. The patents on adsorbent bleaching dealt with improving this process by addition of diatomaceous earth to aid filtering (Harrison—*U. S. 2,296,850*), following the process with the removal of residual suspended matter from the treated oil by electrostatic precipitation (J. Bibby & Sons, Ltd.—*Brit. 520,233*), and subsequently heat-treating the oil in vacuum (Glenn—*U. S. 2,292,027*). Erdheim (*Allgem. Oel- u. Fett-Ztg. 38, 99*) recorded that bleaching capacity of earths increased with fineness while adsorption of oil remained approximately the same. His (*Ibid.* 162) investigation on recovery of bleaching earths showed that extraction with benzene and drying at 110° gave the most active recovered earth. Fluorescence in certain bleached fats was attributed to substances absorbed from the earth (Schloemer—*Z. Fleisch- u. Milchhyg. 50, 176*). Improvements were made in the location and in the heating elements of the Foster Wheeler Corp.'s (*U. S. 2,280,896*) continuous fat and oil deodorizing system.

Mitchell and Kraybill (*J. Am. Chem. Soc. 64, 988*) discovered that oils containing linoleic acid developed

absorption bands at 2680 A. and oils containing both linoleic and linolenic acid develop bands at 2680, 3000 and 3160 A. during bleaching. The band at 2680 was due to a tetraene conjugated system formed by both acids and the other two bands were due to the same phenomenon from linolenic acid. Bleached oils yielded 0.1-0.2% conjugated materials. This was lowered on deodorization due to polymerization.

With some oils valuable by-products are separated during the refining procedures. Thornton and Kraybill (*Ind. Eng. Chem. 34, 625*) described the separation of phosphatides, sterols and sterol glucosides from vegetable oils by means of adsorbents. Stanley (*Food Industries 14, No. 7, 59*) pointed out that soybean phosphatides could be employed to replace scarce fats in the confectionery, baking and ice cream industries. To facilitate separation of phosphatides from dry solvent extracted vegetable oils, Krause (*U. S. 2,269,772*) added a crude oil-phosphatide mixture of low oil content and containing 3-10% moisture. An emulsifier prepared by Kraybill *et al.* (*U. S. 2,276,316*) was the phosphatide fraction of soybean oil in alkali solution. Products developed by Thurman (*U. S. 2,271,127, 2,271,409-10, 2,272,616*) were sodium phosphate-phosphatidic compounds, phosphatides containing hydroxy acids and phosphatides containing alkali metals. Some of the preparations could be used in soap to prevent calcium precipitation. Dziengel (*Ger. 721,002 Cl. 120*) increased the water solubility of phosphatides by heating them with acid sulfides; for the same purpose Jordan (*U. S. 2,296,933*) first dissolved them in a mixture of mono- and di-ethyl ethers of diethylene glycol. A baking constituent patented by Niescher (*Ger. 719,268 Cl. 2c*) was soybean phosphatides containing 10% finely powdered sodium bicarbonate or other alkali reacting salt.

Sterols were recovered from oils by extraction with ketones followed by crystallization from acetic acid (Julian and Cole—*U. S. 2,273,045-6*), and by preparing soap stock, hydrolyzing with acid, distilling the fat acids and extracting the sterols from the still residues with isopropyl alcohol. Phytosterol glucosides separate on standing as a middle layer from acidified oil foots (Langlois—*U. S. 2,306,547*). A vitamin concentrate of fish oils was the unsaponified portion prepared by extracting the fish oil soap with methyl chloride and separating the product from the solvent (Atlantic Coast Fisheries Co.—*U. S. 2,266,830*). To produce vitamin E concentrate and antioxidant, Andrews (*U. S. 2,263,550*) alcoholized wheat germ oil and distilled the ester, glycerol and sterol fractions. The latter was the desired product.

The patent literature indicated a strong trend towards fractionating fat acids by crystallization from solvent solutions or by liquid-liquid extraction. Myers and Muckerheide (*U. S. 2,293,676, 2,298,501*) separated stearic and palmitic acids from unsaturated acids by crystallization from methyl alcohol containing a small amount of water. Formation of crystals having good filtering characteristics was improved by adding 0.2-3.5% neutral fat to the fat acid stock. Dreyer (*Brit. 540,220*) halogenated the unsaturated acids before crystallization from organic solvents. In this process the saturated acids remained in the solvent. Among those using liquid-liquid extraction, Goss and Johnstone (*U. S. 2,290,609*) converted the fat acids to their alcohol esters before extraction.

Patents by Batcholder (*U. S. 2,285,795*) and Freeman (*U. S. 2,278,309*) covered arrangement of apparatus and procedure for liquid-liquid fractionation of acids to obtain predominately unsaturated and saturated portions. Freeman (*U. S. 2,291,461*) used amino and amido type compounds as solvents to separate short chain from long chain acids. Hixon and Bockelmann (*Trans. Am. Inst. Chem. Eng. 38, 891*) pointed out that hydrocarbon solvents could be used for liquid-liquid fractionation of fat acids at their critical solvent temperatures. For example, unconjugated double bonds in fat acids lowered the critical solution temperature of liquid propane 10° and an additional methyl group to a long chain acid gave a 3° lowering. Kaufmann (*Fr. 853,065*) used adsorbents for fractionating from organic solution of the fat acids. Separation of pure myristic acid from a myristic-stearic acid mixture was claimed by the inventor.

Stingley (*Soybean Digest 1, No. 7, 2*) fostered fractional distillation because it has widened the soybean oil market by dividing the product into glycerol, drying acids, nondrying acids, stearin, pitch and derivatives of these products. Several distillation patents were improvements on apparatus parts and technic (Lee—*Brit. 536,333, 536,366*; Cloyd—*U. S. 2,286,786*; Morlock—*U. S. 2,261,939*; Armour & Co.—*Brit. 533,844, 533,847*; Larsen—*U. S. 2,256,438*; Mills—*U. S. 2,274,801-2*). High-vacuum short-path stills were improved by the use of aluminum powder for coating, condensing and evaporating surfaces (Hecker—*U. S. 2,269,153*) or by use of scraping equipment (Hickman—*Brit. 532,770*) to lessen deposition of solid material on the vaporizing surfaces. Brief discussions on preparation of medicinals from oils by short-path distillation were prepared by Hickman (*Chem. & Eng. News 20, 1561*; *Ind. Eng. Chem. Anal. Ed. 14, 250*).

Only a small amount of research activity was reported in the hydrogenation field. Escourrou and Lustyger (*Bull. soc. chim. 7, 445*) claimed that hydrogenation of sardine oils under vacuum eliminated odor. Their report contains data on hydrogenating oils at temperatures up to 600° at various pressures and with the use of several catalysts. McKee and Graziani (*U. S. 2,304,842*) removed natural inhibitors from fat acids by distillation before subjecting to hydrogenation. Gwynn (*U. S. 2,302,994*) regulated the hydrogenation of oils in a continuous system by a manner of distributing the catalyst and by an ascending series of temperatures in the reaction chambers. Joglekar and Jatkar (*J. Indian Chem. Soc. 18, 631*) calculated velocity coefficients for hydrogenation of safflower, sesame, cottonseed and peanut oils in a continuous process. The publications of the Russian writers dealt principally with the experiences of various plants using different catalysts (*Khim. Referat. Zhur., 1940, No. 3, 118-20; No. 4, 109-10*). A process for improving the keeping qualities of butter comprised dehydration, followed by hydrogenation at 35-60°. In an investigation on production of oleic acid, Bailey, Feuge and Smith (*Oil & Soap 19, 169*) developed data on the effects of temperature, concentration of catalyst, hydrogen pressure and nature of catalyst on hydrogenation of cottonseed and peanut oils. The formation of stearic acid was found to be suppressed and the formation of "iso-oleic" acid simultaneously favored by increasing the temperature,

increasing the catalyst concentration, decreasing the pressure and decreasing agitation. Peanut oil was more suitable than cottonseed oil for the production of oleic acid.

Van Vlodrop *et al.* (*Chem. Weekblad 38, 150, 326, 338, 370; Chemie & Industrie 44, 285*) proposed hardening food oils and increasing the viscosity of drying oils by isomerization using sulfur dioxide as the catalyst. Recorded data showed that the food fats have satisfactory color, odor and taste. The improved drying oils, *i.e.*, tung, linseed, herring, etc., underwent isomerization without polymerization and acquired improved drying properties.

One communication recorded information on coatings for fat processing equipment (*Fette u. Seifen 49, 189*). Best stability against alkali, warm fat acids and boiling soda solutions was obtained with coatings based on special hardened phenol resin and on urea resin-nitrocellulose.

Several reviews covered various phases of the chemistry of drying oils. Morrell and Phillips (*Paint Tech. 7, 130, 169*) reviewed autoxidation of drying oils. A review on the physical chemistry of lacquers included 622 literature references (Schäfer—*Fette u. Seifen 49, 481, 585, 653*). One entitled "Molecular Growth of Coating Materials" contained 168 references (Kaufmann—*Ibid. 102, 321*). Linder's review (*Ibid. 428*) treated mainly the conjugated double bond as a factor in both paint and rubber chemistry.

Inducing conjugation in drying oils seems to be a new activity. Undoubtedly this phenomenon occurred in van Vlodrop's drying oils as mentioned above. Spitzer *et al.* (*Am. Paint J. 26, 18, Dec. 15*) recorded that conjugated soybean oil outstripped a bodied linseed oil in fast drying. A conjugated linseed oil dried more rapidly than a bodied natural linseed oil, but the conjugated product dries to a frosted film. The induction of conjugation to produce wrinkled films was patented (Drummond—*U. S. 2,268,022*). Bradley and Richardson (*Ind. Eng. Chem. 34, 237*) determined the degree of conjugation of the artificially conjugated fat acids of 13 oils. The oils were hydrolyzed and isomerized in one operation. The reesterified isomerized acids displayed frosting, dried faster and their films were more water resistant than those of the original oil. In an investigation on the rates of polymerization of conjugated esters, Ault *et al.* (*Ibid. 1120*) added additional evidence to conform with the Scheiber theory of isomerization and the Kappelmeier theory of polymerization.

Recently patented polymerization catalysts included boron halides (Whitely and Turner—*U. S. 2,260,417*), diphenyl disulfide (Parkin—*U. S. 2,263,887*), polar organic compounds (Auer—*U. S. 2,298,270-1*) organic halogen, nitro-, sulfonic or cyclic compounds (Auer—*U. S. 2,298,914-9*), special halogen salts (Auer—*U. S. 2,300,090*) and benzoyl peroxide (Patterson—*U. S. 2,280,256*). Bryson (*Oil Colour Trades J. 101, 126*) recorded that the a.c. discharge of 500-600 cycles at 700 volts suitably polymerized linseed oil. Downie (*Ibid. 924*) described experiences on boiling linseed oil by submerged combustion. The oil froths up considerably during the boiling but satisfactory products result from the process. Asser (*Ger. 705,023 Cl. 22h*) prepared stand oils from marine oils by heating to incipient polymerization and then air blowing. The

extraction of nondrying oil fractions from polymerized oils with ketone and higher alcohol solvents was patented (Vegetable Oil Products Co. Inc.—*Brit. 530,727*). Hassard (*Brit. 534,520*) claimed that the drying qualities of oils were improved by treatment with aqueous solutions of potassium permanganate.

For mixing phenol-aldehyde resin with drying oil in preparing coatings, Seebach (*U. S. 2,279,499*) dissolved them in a solvent for both components and thereafter removed the solvent. Sorenson's (*U. S. 2,280,862*) patented coating composition contained a drying oil, an ester of maleic acid and an unsaturated alcohol. An aminotriazine resin modified oil composition for paint and varnish purposes was prepared by West and Layman (*U. S. 2,259,980*). Experiences on varnishes made from several oils and ester gum were published by the Chicago Paint & Varnish Production Club (*Natl. Paint Varnish Lacquer Assoc. Sci. Sect. Circ. No. 629, 323*).

Tabular and graphical information on the drying of films of triglycerides, of oleic, linoleic and linolenic acids, giving the chemical and physical characteristics during aging, was prepared by Carrick *et al.*—*Am. Paint J.* 26, No. 34, 58; No. 36, 50; No. 38, 50; No. 40, 55). A similar study on raw linseed oil containing zinc oxide was made by the same group (*Ibid.* in 5 Nos. between Jan. 5 and Mar. 2).

The Cleveland Paint & Varnish Production Club report (*Natl. Paint Varnish Lacquer Assoc. Sci. Sect. Circ. No. 629, 315*) showed that drying of drying oil films due to differences in humidity and temperature were not affected by drier concentration when at least a minimum quantity was used; drying was slower at higher humidity and temperature than at intermediate humidity and temperature and retardation of drying by excess drier was more pronounced with heat-bodied than with blown oils. Weber and Rac (*Ber. 74B, 1332*) prepared data on the inhibiting action of several dyes and antioxidants on the autoxidation of linseed oil containing lead compounds.

Pigmented oil gels for use in paint were prepared by saponification of the oil, mixing the white lead and pigment therewith, acidifying, removing water and reesterifying with glycerol (Waldie—*U. S. 2,283,518-20*). Information on water uptake of coatings in relation to pigment content was compiled by Hintze (*Fette u. Seifen 49, 332*). The infra-red radiation drying of paint films was described by Maxted (*Paint Tech. 6, 254*).

A monograph on tung oil was prepared by Hrabe (*Chem. Obzor 16, 7*). A varnish composition containing tung oil, phenol-formaldehyde resin and terpinolene was patented by Engle (*U. S. 2,293,428*). A tung oil substitute was a reaction product of maleic acid, linseed oil, glycerol and linseed fat acids (Swain—*U. S. 2,304,288*).

Monographs on dehydrating or converting castor oil into drying oil were prepared by Worsdall (*J. Oil Colour Chem. Assoc. 25, 104*), Greaves (*Oil Colour Trades J. 100, 485*), Mundy (*Ibid. 101, 305*) and Itihara (*Sci. & Ind. Japan 16, 420*). The catalysts in some of the new patented processes were China clay (Cherry—*U. S. 2,290,165*), sulfuric acid (Schwarzman—*U. S. 2,282,898*), yellow tungstic acid (Rheineck and Crecelius—*U. S. 2,261,663*), polybasic carbonates

and polyhydroxy alcohols (Firma Louis Blumer—*Ger. 715,231 Cl. 39c*) and metal, alkali or alkaline earth chlorides (Rizzi—*Swiss 211,310, 214,100 Cl. 38a*). Colbeth's (*U. S. 2,278,425-7*) drying oil was prepared by borating the castor oil acids and then destructively distilling. Cherry (*U. S. 2,304,074*) extracted the bodied dehydrated oil with low boiling alcohol to improve its drying qualities. A coating composition patented by Colbeth (*U. S. 2,291,794*) was a substantially solid oxidized castor oil emulsified in water with diethylene glycol ethyl ether. The polymerized castor oil derivatives of Gleason's patent (*U. S. 2,284,570*) were claimed to have a molecular weight of over 5,000.

A review on the use of wool fat principally in blackout and water emulsion paints was prepared by Wontner-Smith and Campbell (*Paint Manuf. 12, 40*). Polymers were prepared from coffee oil by halogenation followed by heating with alkalis, polybasic acids and aldehydes. Oiticica oil was improved by treatment with a semicarbazide (I. G. Farbenind. A. G.—*Ger. 711,718 Cl. 22h*). Semidrying oils were converted into drying products by addition of 20% isano oil (Priester—*U. S. 2,280,082*).

### Products (Except Detergents)

It is general knowledge that the use of shortening in bread making produces a change in flavor, a more tender crumb and usually an improvement in quality as judged by texture and loaf volume. The mechanism of this action has not been adequately explained. An investigation by Baker and Mize (*Cereal Chem. 19, 84*) suggested that the effect was not one of lubrication as heretofore believed. Semi-solid fats and even very hard fats that were ground and mixed with the dough induced the improved texture and greater volume in the finished bread, whereas liquid fats did not. Bread dough tested with coconut oil below and above the melting point of the oil corresponded, respectively, to semi-solid and liquid fat doughs. High viscosity fats such as castor oil also yielded baking improvements. It was suggested that semi-solid and hard fats do not blend or emulsify with the natural fats in the dough and remain in masses which weaken the dough film in many spots, thus producing a bread texture that is highly permeable to air.

A newly patented shortening mixture contained 80-95% liquid vegetable oil and 5-20% hard fat having a titer not less than 65° (Gudheim—*U. S. 2,304,452*). Such a fat was said to retain its plasticity over a wide temperature range. Musher (*U. S. 2,282,819*) improved the flavor, odor and baking characteristics of shortening by addition of a small amount of salt-cured macerated peanuts or soybeans. A solid shortening prepared by Gurwitsch (*Brit. 534,223, 535,248*) contained malt or malt extract. Improvements in a shortening cooler and agitator were patented by DeHaven *et al.* (*U. S. 2,281,944*).

Daum, Halliday and Hinman (*Oil & Soap 19, 39*) reported that the most obvious distinguishing effect of glycerol monostearate on the baking properties of cakes was an increase in volume. The addition of partial esters of mannitan and fat acids (Brown—*U. S. 2,303,432*), a dispersed saccharide solution (Schou—*Austrian 156,804 Cl. 2c*), egg yolk (Lever Bros.—*U. S. 2,285,478*) or phosphatides (Thurman—

*U. S. 2,280,427*) to shortening also was for the purpose of improving the texture and increasing volume of baked products. Foaming in the latter patented shortening was inhibited by heating with adsorbents and filtering.

A lard developed for the Army had a melting point of 45° (Wiley), contained 4% hydrogenated lard flakes of 57-61° titer and required plasticizing to a smooth texture (*Natl. Prov. 117*, No. 10, 20). For overseas use .05 to 0.1% lecithin must be added and it must be packed in hermetically sealed containers. A patented meat coating (Hoy—*U. S. 2,290,854*) comprised a mixture of lard and ground pork skin that was plumped by cooking.

Three patents described methods of manufacturing bread spreads. One relating to margarine manufacture contained a de-aerating step while the fat was in a flaky condition (Lübecker Metalg. & Maschinenfabrik—*Brit. 521,394*). Another spread was fat flavored with cheese, peanut butter or other suitable material and emulsified with an equal weight of water (Komarik—*U. S. 2,288,244*). A special nut butter was prepared by finely grinding nuts in the presence of fats (Richardson and Hoffman—*U. S. 2,302,574*).

A few new ointment and cosmetic cream bases were suggested. In Germany one preparation contained by-products of synthetic gasoline manufacture, stearic acid and potassium carbonate (Hübscher—*Seifensieder-Ztg. 68*, 285). Procedures for manufacturing creams containing sodium alginate were given by Musick (*J. Am. Pharm. Assoc. Pract. Pharm. Ed. 3*, 264). A patented product was hydrogenated castor oil having a melting point above 40° and an iodine value less than 70 (Fiero—*U. S. 2,294,229*). Partial esters of organic polyhydroxy compounds and fat acids were recommended as emulsifiers for the products (Müklemann—*Pharm. Acta Helv. 15*, 1; Harris—*U. S. 2,294,233*).

Among the patents on emulsifiers a large portion was on partial esters of polyhydroxy compounds and fat acids (Bennett—*U. S. 2,275,494*; Bruson—*U. S. 2,284,127*; Epstein and Harris—*U. S. 2,285,422*; Epstein—*U. S. 2,299,743*; Goldsmith—*U. S. 2,269,529*; Harris—*U. S. 2,302,121*; Schou—*Brit. 537,275*). Novelty in these was the use of new polyhydroxy compounds, new catalysts, compounding with other material as phosphatides, resins, etc. and procedures for reacting the substances. The preparation of such compounds by exchange esterification of vegetable oils and glycerol or pentaerythritol with lime as the catalyst was studied by Blagonravova *et al.* (*J. Applied Chem., U.S.S.R. 14*, 192). Increased temperature resulted in fuller alcoholysis, while longer reaction time gave products with lower acetyl values, indicating some anhydridization of the polyhydroxy compounds. Characteristics of the products formed under varied reaction conditions were presented. Ralston (*U. S. 2,298,162*) patented the use of mono-glycerides of fat acids as softening agents for films and plastic masses.

Bryan (*Inst. Am. Ice Cream Mfgs. Lab. Council Proc. 1941*, 29) investigated the action of emulsifiers in ice cream. Lecithin and lecithin-protein improved body and texture but retarded overrun (air) incorpo-

ration. Glycerol monostearate improved the whipping ability but slightly weakened the body. Addition of a mixture of lecithin-protein and glycerol monostearate to a mix yielded the most satisfactory ice cream. A casein and alkali metal caseinate mixture was used as an emulsifier for fat soluble vitamins (Ferrari—*U. S. 2,300,410*). The use of fat acid salts of monohydric aminoalcohols as emulsifiers was also patented (Vanderbilt—*U. S. 2,281,177*).

One concern was particularly interested in breaking or clarifying emulsions (Petrolite Corp.—*U. S. 2,260,757*, *2,270,681*, *2,273,181*, *2,278,163-4*, *2,278,170-1*, *2,281,316*, *2,283,646*, *2,290,154*, *2,290,411-7*, *2,295,163-70*, *2,296,600*, *2,300,103*, *2,300,554-6*, *2,305,067*, *2,306,329*, *2,306,718*, *2,306,775*). The products are used in recovery of mineral oils from emulsions in calcareous petroleum oil-bearing strata, and are principally organic and inorganic derivatives of ricinoleic acid or castor oil. One of the patents included the clarification of emulsions such as "ballast water" on ships with ammonium or sodium soaps of sulfonated castor oil.

Many fat derivatives were prepared for use as intermediates in the compounding or preparation of other products. Dicarboxylic acids were prepared from semidrying hydroxylated fat acids by oxidation with air at 110-170° in the presence of cobalt acetate as a catalyst (Loder and Salzberg—*U. S. 2,292,950*). In a similar process, in which sebacic acid was prepared from castor oil, the residue after removal of both the acid and the products that distill at 270° and 4 mm. pressure, could be used for soap manufacture (Cheetham and Rothrock—*U. S. 2,267,269*). Simple vacuum pyrolysis at 550° of methyl ricinoleate from castor oil and methanol yielded 17-18% enanthaldehyde and 25-27% hendeconic acid based on the castor oil used. Unsaturated fat acids were produced by heating halogen substituted fat acids with alkaline compounds (Dreger *et al.*—*Brit. 540,221*). Branch chain fat acids were synthesized from normal acids and the characteristic of these and their amide esters were recorded (Cason—*J. Am. Chem. Soc. 64*, 1106; Schneider and Spielman—*J. Biol. Chem. 142*, 345). Milas (*U. S. 2,267,248*) hydroxylated the unsaturated acids of cottonseed oil by treatment with hydrogen peroxide in tertiary butyl alcohol solvent in the presence of several metal oxides. Chromium and copper containing up to 10% iron were used as catalysts in the hydrogenation of fat acids to alcohols (Sandoz A.-G.—*Ger. 711,180 Cl. 120*). Unsaturated alcohols of this type were converted to aldehydes by hydroxylating at the double bond and then warming the product with red lead and glacial acetic acid (Scanlan and Swern—*U. S. 2,304,064*); or the aldehydes could be prepared from the fat acids by heating with glacial acetic acid, hydrogen peroxide and red lead (*Ibid.*—*U. S. 2,285,059*). Preparation of ketenes by reaction of tertiary amines and fat acid halides was also patented (Deutsche Hydrierwerke A.-G.—*Brit. 522,033*). Fat acid halides were prepared by reaction of the fat acid with phosphorus trihalide (Cahn—*U. S. 2,282,320*). These are used as intermediates particularly for Friedel-Craft reactions. Ralston *et al.* (*J. Org. Chem. 7*, 457) recorded that in the Friedel-Craft acylation of phenols with the use of fat acid halides, nitrobenzene solvents exerted a greater *p*-position directing influence than carbon



disulfide. The length of the fat acid did not influence the ratio of *p*- to *o*- isomers. A subsequent publication by Ralston *et al.* (*Ibid.* 522) dealt with activity of several metal halides for the rearrangement of phenyl caprylate.

Ralston's (*Oil & Soap* 19, 212) discussion on fat derivatives covered information on the manufacture of the nitriles and amines, their uses and reactions. The same investigator with coworkers (*J. Am. Chem. Soc.* 64, 498, 1516, 2067, 2824) has recorded most of the solubility and surface chemistry data of these compounds. Data on pressure, area, temperature and energy of monolayers of stearyl nitrile were determined by Copeland and Harkins (*Ibid.* 1600). The melting points of many fat acid sulfides, sulfoxides, sulfones and fat acid amides of dodecylamine and octadecylamine were tabulated by Hunter (*Iowa State Coll. J. Sci.* 15, 215). New developments in fat acid nitrile manufacture were the use of special bauxite or titanium oxide catalyst for reacting ammonia with fat acids (I. G. Farbenind. A. G.—*Ger.* 704,494 Cl. 120) and the manufacture of the nitriles by reaction of trichloromethylchloroformate with the fat acid amide (Hentrich and Engelbrecht—*U. S.* 2,269,105). Amines could be prepared from the nitriles by hydrogenating the corresponding nitriles in aqueous solution containing an alkaline reacting material (Armour & Co.—*U. S.* 2,287,219). The nitrogen containing preparations of Katzman and Epstein (*U. S.* 2,290,880) were reaction products of alkylolamines and fat acid halides. Pool (*U. S.* 2,304,475) patented the manufacture of fat acid diamides of sebacic acid. A method of polymerizing fat acid amides to yield products that could be spun into threads was patented by Schlack (*U. S.* 2,277,152). Amino fat acid preparations were removed from the crude reaction mixture by treatment with organic acid, filtering and precipitating the desired compounds from the filtrate by neutralization with alkalies (Martin—*U. S.* 2,283,683).

The reaction products of a fat acid amine and cyclic dicarboxylic acids or amidated oxalic ester containing only short aliphatic radicals varied from waxy to resinous products (General Aniline & Film Corp.—*U. S.* 2,272,466, 2,294,878). These were useful for impregnating paper or textile materials and for use in shoe creams. The reaction products of ketonized fat acids and aromatic aldehydes in the presence of alkali metals also yielded compounds suitable in the above uses (*Ibid.*—*U. S.* 2,271,708). A mixture of stearin or palmitin and coumarone-indene resin of melting point above 100° was claimed to be a good substitute for carnauba wax (Corkery—*U. S.* 2,255,242). A general purpose wax was prepared by condensing tall oil acids with aromatic sulfonic acids of the benzene series (McKee and Blengli—*U. S.* 2,280,247). A cheese wax coating composition contained paraffin and small portions of palmitic and propionic acids (Ingle—*U. S.* 2,293,323).

The most numerous patents on resin manufacture from oils were on the polybasic acid condensation products of fats, oil's, glycerol and like material, and their compounding into coating products (Nagel and Koenig—*U. S.* 2,270,889; Cheetham—*U. S.* 2,272,057; Clocker—*U. S.* 2,275,843, 2,286,466; West—*U. S.* 2,276,243; Potts and McKee—*U. S.* 2,297,716; Rust—

*U. S.* 2,306,281). A product suitable for varnish bases was prepared by condensing acylated methylol phenols with rosin acids or fatty oils (Bruson—*U. S.* 2,260,556, 2,282,557). Another coating resin was a water dispersible hydrated straight chain alkyl amine higher fat acid soap (Atwood—*U. S.* 2,298,269). A 3:1 tall oil and red lead mixture resinified on heating (Burrell—*U. S.* 2,306,352). The interpolymerization products of glycol divinyl ethers and esters of saturated alcohols with tall oil were similar to linoxyn and factice (Wolff—*U. S.* 2,298,078). A plastic for manufacture of artificial leather comprised a pigmented composition consisting of 40 parts of nitrocellulose, 30 parts of butyl acetyl ricinoleate and 30 parts of a mixture of castor oil and polymerized rapeseed oil (Medl—*U. S.* 2,273,973). Pentaerythritol esters of drying oil fat acids were used in certain cellulose lacquers to increase the strength of the films (Bowlby—*U. S.* 2,279,438). Dispersions of starch and a small amount of nonhardening alkyl resin modified with nondrying oil were used to impart softness to fabrics (Thackston—*U. S.* 2,303,773).

Press literature has on several occasions announced the invention of rubber substitutes from soybean oil by workers in the U. S. Regional Laboratories. A patent or publication on the process has not yet come to the writer's attention.

In the field of waterproofing fabrics the Bakelite Building Products Co. (*Brit.* 528,308, 540,831) described the method of agitating and mixing to disperse soap and paraffin in water in preparation for applying. Gröner's (*U. S.* 2,285,579) waterproofing compound contained paraffin, soap, sodium polyacrylate and water soluble aluminum salts. Condensation products of octadecyl chloromethyl ether and potassium diglycolate or sodium chloroacetate were also suitable for waterproofing fabrics (Rosenbach and Balle—*U. S.* 2,283,764). Other patented compounds for this purpose were special quaternary ammonium compounds containing fat acid radicals (Waltmann—*U. S.* 2,288,868; E. I. duPont de Nemours Co.—*U. S.* 2,291,519; *Brit.* 537,297; Wolf—*U. S.* 2,301,352; Balle *et al.*—*U. S.* 2,301,676; Linnhoff—*U. S.* 2,270,658; Rust—*U. S.* 2,285,948).

Several new textile, metal cutting and leather oils were patented. Huttenlocker's (*U. S.* 2,297,221) textile oil was an emulsion containing a quaternary ammonium fat acid derivative. The use of butyl oleyl ketone for conditioning cellulose acetate yarns for spinning was patented (McNally and Dekey—*U. S.* 2,279,377). Fife's (*Brit.* 522,151) textile oil was a mixture of mineral oil, fat acid sulfonates and fat alcohols or ketones. A mixture of kerosene, rosin soap and free fat acids was used as a cutting oil (Perkins—*U. S.* 2,303,136). The use of *Laurentii* and *Gentiana raphia* palm oils for stuffing skins and leather was patented (Koppenhoefer and Roehner—*U. S.* 2,280,310). Koppenhoefer (*J. Am. Leather Chem. Assoc.* 37, 118) reviewed the role of fats in the manufacture of leather. Sulfonated marine animal and fish oils were recommended as nonfoaming compounds for textile, cutting and leather oils (Nörring—*U. S.* 2,285,940).

Fat acid derivatives patented as parasiticides were fat acid nitriles (Ralston and Barrett—*U. S.* 2,280,850), and special halogenated fat acid amides (Ep-

stein and Harris—*U. S. 2,268,206, 2,273,849*). Those patented as bactericides and antiseptics were esters of fat alcohols and aminocarboxylic acids (Epstein and Harris—*U. S. 2,290,173-4*) and mercurated ketones, alcohols or nitriles that were prepared from fats (Ralston *et al.*—*U. S. 2,284,067, 2,286,226, 2,289,590*). The germicidal properties of decyl to octadecyl amine acetates first increased with the number of carbon atoms and then decreased; the highest germicidal value occurred with the middle compounds (Harri-man *et al.*—*J. Bact. Proc. 43, 53*).

A miscellaneous group of uses for fat derivatives was found. Cement was waterproofed and cured with the addition of small amounts of stearic acid or metallic soap (Pierce—*U. S. 2,283,573*); Scripture—*U. S. 2,284,023*; Sorem—*U. S. 2,293,410*. A solution of wool fat in trichloroethylene was used as an anticorrosive dip (Rogers—*U. S. 2,298,513*). The  $C_{22}$  fat acids of marine oils (Sheely—*U. S. 2,272,483*) and the glycerine esters of tall oil (Hough—*U. S. 2,270,947*) were suitable core oil substitutes. Mixtures of hydrogenated castor oil, chlorinated naphthalene, *m*-dinitrobenzene and benzoic acid were made into balls of various specific gravity for use in hydrometric units (Chaslyn Co.—*U. S. 2,273,650*). The properties of castor oil solutions in various solvents used for hydraulic fluids were tabulated by Shough (*Ind. Eng. Chem. 34, 628*). The recorded data of Evans (*U. S. Egg & Poultry Mag. 48, 596*) showed that in the preservation of eggs by oiling, the use of 50% volatile solvent in the dip oil was as effective as the oil alone. The patented ore flotation agents were special fat acid amines (Armour & Co.—*U. S. 2,278,020, 2,287,274, 2,289,996*; Am. Cyanamid Co.—*U. S. 2,278,060*), mixtures of amines and nitriles (Armour & Co.—*U. S. 2,298,281*), sulfonated salts of amino alcohol fat acid compounds (Jayne *et al.*—*U. S. 2,278,107*), a mixture of mahogany soap, fat acids, resin acids and fuel oil (Greene and Head—*U. S. 2,303,931*) and acylated (fat acid) protein decomposition products.

The manufacture of aluminum soaps for use in lubricating greases could be hastened by the use of alkali hydroxides or carbonates as catalysts (Boner—*U. S. 2,267,148*). Aluminum stearate prepared by adding aluminum isobutylate to benzene solutions of the acid contained 6.5 to 14.5% aluminum (Eigenberger—*Fette u. Seifen 49, 505*). Zinc soaps were made soluble in many organic nonpolar liquids by addition of amines such as morpholine, pyridine and alkylamines (U. S. Rubber Co.—*Brit. 540,090*). A non-gelatinous solution of aluminum stearate contained aluminum caprylphenoxyacetate and a liquid water-immiscible organic solvent for the above components (Myers—*U. S. 2,289,316*). General publications on the uses for metallic soaps were prepared by Elliott (*Soap 18, No. 7, 26*; *Am. Paint J. 26, No. 35, 50*) and Monsaroff (*Can. Chem. Process Ind. 26, 193*).

Castor oil was modified sufficiently to make it miscible with mineral lubricating oils by heating with a small amount of camphor sulfonic acid (Schwareman

—*U. S. 2,292,902*). The fat derived lubricating oil improvers patented were halogenated foots oil (Lincoln and Byrkit—*U. S. 2,264,319*), special sulfurized or phosphorized fat acid esters (Knowles and McCoy—*U. S. 2,289,437-8*; Pure Oil Co.—*U. S. 2,274,022, 2,274,025*), calcium salts of halogenated fat acids (Prutton—*U. S. 2,272,923*), condensation products of halogenated tall oil with a cyclic compound (Lieber—*U. S. 2,262,809*), tall oil (Lieber—*U. S. 2,270,319*), condensation products of phenyl hepta-decyl ketone with ethylene dichloride (Lieber—*U. S. 2,287,110*) and copolymers of eleostearin and an olefin (Sparks and Field—*U. S. 2,296,315*). The fat derived pour point depressors for lubricants were fat acid (acylated) coumarones (Armour & Co.—*Brit. 537,122*), phenolic esters of fat acids or chlorinated fat acids (Mikeska—*U. S. 2,300,131*), condensation products of polyalkylene polyamines with fat acids (Lieber—*U. S. 2,291,396*) and acetyl stearyl naphthalene or like compounds (Lieber—*U. S. 2,268,049*). A communication on lubrication of clocks and watches contained a discourse on the advantages and disadvantages of beef neatsfoot, mutton neatsfoot, olive, tsubaki and dolphin head oils for that purpose (Cuypers—*Fette u. Seifen 49, 27*).

Various fat derivatives were used in new mineral lubricant greases. One contained the mineral product, metallic soap and an anticorrosion amino ester which could contain a fat acid radical (Standard Oil Co.—*U. S. 2,270,113*). Metallic soap, saturated fat acids and hydrogenated castor oil were used in one patented by Fiero (*U. S. 2,283,602*). Glycol fat acid esters (Schott—*U. S. 2,281,623*) and polymerized fat acid acrylate (Zimmer and Morway—*U. S. 2,275,123*) improved greases made of mineral oil and metallic soaps. Several grease patents were on the type of soap used in the formula. Earle (*U. S. 2,274,673, 2,293,052*) used lithium soaps. Alkali fat acid sulfonates and fatty oil mixtures improved greases (Standard Oil Development Co.—*Brit. 537,615*). An extreme pressure grease contained triethanolamine soap of palm oil fat acids and a phosphorus compound (Waugh—*U. S. 2,291,066*). Rapeseed oil and rapeseed soap were also added to greases (Standard Oil Co.—*U. S. 2,265,791*). A sodium lead fish oil soap complex improved greases (Swenson—*U. S. 2,295,189*). One mineral oil grease contained both magnesium and aluminum soaps (Freuler—*U. S. 2,266,544*). A rubber to metal grease comprised triethanolamine soap, starch and sufficient water to form a non-flowing aqueous solution (Grafton—*U. S. 2,299,139*). A wire drawing lubricant comprised acid prepared by oxidation of petroleum oils, fat acids, soap and lime hydrate (Burwell—*U. S. 2,294,535*).

Raw peanut, refined peanut and cottonseed oils were tested for motor lubrication (Aggarwal and Verman—*Indian Ind. Research Bull. 18, Pt. 1, 5*). The oils gave higher Conradson carbon residue and became more acid than mineral oils. Some stabilizers were effective with the refined peanut oil but not with

the others. Phenols and aromatic amines were the most effective stabilizers. Raw peanut oil produced a heavy shellac-like deposit when used in aero-engines.

Gas oil, heated gas oil, peanut oil, palm oil and cottonseed oil were tested as fuels in a Diesel engine equipped with a Perkins P6 compression-ignition (Seddon—*Gas Oil Power* 37, 136). Peanut oil was equal to cold Diesel fuel and superior to palm oil. Cottonseed oil was fair. Similar work (Chowbury *et al.*—*Ibid.* 80) with a Lister Diesel engine equipped with a Bosch fuel pump and injector supplied the following comparison:

Fuel	Startability	Operation	Exhaust	Power (h.p.) output at 1,200 r.p.m.
Diesel	easy	smooth	colorless	7.83
Peanut oil	easy	smooth	colorless	7.6
Karanj oil	medium	smooth	colorless	7.3
Castor oil	difficult	unsteady	smoky	6.8
Kapok oil	difficult	smooth	colorless	6.9
Cottonseed oil	medium	smooth	colorless	7.8
Rapeseed oil	medium	smooth	colorless	7.7
Coconut oil	medium	unsteady	colorless	7.6

Information on lesser known oils and condition of motors, nature of carbon deposit and like information was also recorded.

## The Saturated Fatty Acids of Elderberry Seed Oil\*

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In an earlier communication (1) were presented data showing the relation of yield of oil from the seeds of the elderberry (*Sambucus canadensis* L.) to the nature of the menstruum employed in its extraction, a few of the simple constants of the oils so recovered, and a comparative tabulation of the reported characteristics of the oils of different species of the plant. Additional data on this oil have since been obtained in the examination of a later crop. They are herein presented as an illustration of the application of the solidification-point technique (2). A report on the nature and constitution of its unsaturated fraction, wherein probably lies the source of a potential technical interest in elderberry seed oil, is reserved for a future time when more material shall have been made available for study.

The clear, greenish-yellow oil used in this investigation was obtained in approximately 30-per cent yield by petroleum ether (40-60°C.) extraction of seeds recovered from the fruit which had matured in the summer of 1938. Its constants (Table 1) sug-

TABLE 1  
Characteristics of Elderberry Seed Oil

Saponification number.....	188.5
Iodine number (Wijs).....	184.1
Thiocyanogen number of acids.....	104.7
Reichert-Meißl number.....	1.4
Polenske number.....	0.4
Hydroxyl number.....	20.0
Saturated acids (pct.).....	8.5
Insoluble acids (pct.).....	92.1
Unsaponifiable matter (pct.).....	2.94

gested the following conclusions as to the type and nature of the constituent acids of elderberry seed oil: very little, if any, of the low-molecular weight acids are present; practically all of the acids would be found to lie in the C<sub>16</sub>-C<sub>18</sub> range, and unsaturation is due, to a large extent, to the multiple type.

The saturated fatty-acid fraction in approximately 70-gram yield and of low iodine number (less than 4) was separated from the unsaturated by a modified Twitchell lead salt-alcohol procedure. Its mean molecular weight was 271, or roughly midway between that of palmitic and stearic acids.

After esterification with methanol and then treatment with bromine for the purpose of holding back the unsaturated esters it was fractionally distilled in a Widmer column at 0.2 mm. Hg. pressure. Four fractions plus a residue containing bromo-stearic esters were obtained. The latter were removed by crystallization.

For the purpose of making qualitative and quantitative examinations of these fractions, the fatty acids were regenerated, purification being effected through the medium of their barium salts (3). Fractional distillation had been so carried out that the mixtures of fatty acids obtained by this regeneration were binary ones. For the identification of each fraction the method of using solidification point curves was used (3). The molecular weight and solidification point of each fraction was determined. The composition of the individual fraction was then found both by calculation from mean molecular weight and by reading it off from the binary solidification point curve. In each case good agreement between the two values was obtained.

Each of the first four, or the distilled, fractions was composed of varying amounts of palmitic and stearic acids, while the small residual fraction was made up of stearic and arachidic acid. The distribution of these three acids is as follows: palmitic, 62 pct., stearic, 31 pct., and arachidic, 7 pct.

The absence of myristic acid was clearly indicated by the fact that the first distilled fraction could be shown to fall on to the palmitic-stearic acid curve, thus precluding the possibility of myristic acid being present since the fraction was definitely a binary mixture of the other two acids. The absence of acids higher than arachidic is indicated by the same method of approach in that the distillation residue showed itself to be a binary mixture of stearic and arachidic acids.

In conclusion, it was found that the oil investigated contained the following percentages of saturated fatty acids: palmitic, 5.3 pct., stearic, 2.6 pct., and arachidic, 0.6 pct.

### LITERATURE CITED

- (1) Schuette, H. A., and Brooks, John W., *Oil and Soap*, 13, 314 (1936).
- (2) Schuette, H. A., and Vogel, H. A., *ibid.*, 18, 246 (1941).
- (3) Schuette, H. A., and Vogel, H. A., *ibid.*, 16, 209 (1934).

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