

Review of Literature on Fats, Oils, And Soap for 1940*—Part I

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GENERAL

THE progress in production, processing and chemical knowledge of fats, oils and soaps seemed to have taken an accelerated pace. This was the result of political encouragement induced after the first World War in countries poor in supplies. In some cases production of oil seeds was stimulated to replace those agricultural products for which the demand and consumption has decreased. In the United States soybeans are now grown on land which formerly produced corn, wheat and oats as the principal crops. In Germany and Russia new plant sources of fats and oils have been developed.

Outstanding processing developments, although invented and reported in years past, have been put to greater commercial use. Synthetic fats for soaps and other technical uses were prepared from mineral oils and coal by-products. Many substitute paints were on the market, as well as paints made from oils not much used previously. Dehydrated castor oil was prominent in the paint field. The uses of tall oil were increased. Fats have been distilled to yield drying and non-drying fractions, vitamin concentrates, antioxidant concentrates and sterols. Commercial lards have been improved both in consistency and stability. Synthetic glycerine from petroleum and glycerine produced by fermentation have assured sufficient supply for present demands. Continuous refining of oils and continuous soap manufacture are supplanting the batch processes.

Chemical knowledge of new fats was reported. Discoveries in separation of fat constituents by adsorption and fractionation have added new analytical technics which may develop into new research, analytical and commercial processes. Such methods for production of sterols have already been patented.

Several lines of research have not yielded commercial processes although they have been under investigation for years. Production of fat from microorganisms, recovery of fat from municipal sewage and collection and extraction of coffee grounds were still reported as uneconomical. The appearance of a German patent a few years ago for the manufacture of edible fats from mineral oils led to persistent rumors that such fats were being marketed for human consumption.

However, the literature did not confirm the rumors.

The prices of domestic fats and oils were lower than in the previous year. This situation was discussed in a government bulletin (*U.S.D.A. Bureau Agr. Ec. FOS. 44*), which also gave information on production and per capita consumption of various fats. The data on wholesale prices of fats and oils in United States for 1910 and 1940 were presented in both tabular and graphical form by Walsh (*U.S.D.A. Tech. Bull. 737*). In an editorial (*Chem. & Met. Eng. 48, 107*) discussing progress in the fat field, the long range outlook was said to be toward lower prices.

Abnormal conditions had detrimental effects on the commerce in certain fats. Our main sources of supply of olive and medicinal vitamin oils were closed. The domestic price therefore rose. The main market for coconut and palm oils in Europe was closed by blockade. However, more than 500,000,000 pounds of these oils entered the United States even though tariffs were high.

The domestic production of fats and oils was higher than that of any preceding year. The following statistics (*U.S. Dept. Com. Ind. Reference Service No. 22, pt.*

3, 4) give a comparison for years 1939 and 1940:

PRODUCTION AND CONSUMPTION OF FATS AND OILS
(In millions of pounds)

Kind		Stocks Jan. 1	Imports	Production from domestic and imported raw materials	Exports	Stocks Dec. 31	Apparent Disappearance
Vegetable oils	1939	1,563	1,001	3,078	150	1,485	4,007
	1940	1,484	873	3,192	168	1,545	3,836
Fish oils	1939	259	87	272	17	245	356
	1940	245	42	174	5	199	257
Animal fats and greases	1939	514	11	5,588	300	544	5,269
	1940	544	8	6,168	215	786	5,719
Total	1939	2,336	1,099	8,938	467	2,274	9,632
	1940	2,273	923	9,534	388	2,530	9,812

* This review is the report of the American Oil Chemists' Society Committee for Review of Literature on Fats, Oils and Soaps. G. R. Greenbank, Geo. S. Jamieson, H. A. Mattill, R. C. Newton, M. M. Piskur, Chairman.

Technical developments in fats and oils were reviewed by Wittka (*Seifensieder-Ztg.* 67, 51, 61, 71, 81, 91, 101, 111, 121, 131, 141, 151, 182, 191, 201, 211, 222). Chemical progress was reviewed by Smith (*Ann. Rev. Biochem.* 9, 93). A review by Greene and Richards (*Oil & Soap* 17, 191) treated animal and vegetable waxes.

War economy items included: possible new fat sources (*Engel—Allgem. Oel- u. Fett-Ztg.* 37, 101; Sessions—*Fette u. Seifen* 47, 10); coffee ground oil (*Heller—Seifensieder-Ztg.* 67, 192); microorganism fat (Haesler and Fink—*Z. Spiritus ind.* 63, 89, 94, 96); soap uses, raw materials, regulations, etc. (Modest—*Seifensieder-Ztg.* 67, 1, 11; Steuer—*ibid.* 21, editorial—*News Ed. A.C.S.* 17, 769, Atkins—*Soap, Perfumery Cosmetics* 12, 892 and Walter—*Fette u. Seifen* 46, 688); and fats from waste (Dean—*Soap, Perfumery Cosmetics* 13, 99; Martinenghi—*Olii, minerali, grassi, e saponi* 19, 100).

Books that appeared during the year were as follows:

- Hilditch. The Chemical Constituents of Natural Fats. Chapman and Hall Ltd. 438 pp.
- Brandt. Whale Oil. An Economic Analysis. Food Research Institute. 264 pp.
- Wigner. Soap Manufacture. Chemical Publishing Co. 162 pp.
- Wittka. Moderne fettchemische Technologie 2. Gewinnung der hohen Fettsauren durch oxydation der Kohlenwasserstoffe. J. A. Barth. 167 pp.
- Burton and Robertshaw. Sulphated Oils and Allied Products. Their Chemistry and Analysis. Chemical Publishing Co. 163 pp.

PRIMARY TECHNICAL TREATMENT

The use of ceramic linings of acid resistant cement for hydrogenation vessels and other apparatus of the fat industry was again fostered (Dymshits—*Masloboino Zhir. Delo* 16, #1, 32). Special non-rusting and acid resisting steel equipment for the dairy and margarine industries was illustrated and described by Tofaute (*Fette u. Seifen* 47, 419).

Technological progress reports were prepared on marine animal oil (Brocklesby—*Fisheries Res. Board Can., Prog. Repts. Pacific Stas.* #44, 4), on recent work of the U. S. Regional Soybean Industrial Products Laboratory (Milner—*Am. Soybean Assoc. Proc. Ann. Mtg.* 19, 56), on soybean processing (McBride—*Chem. & Met. Eng.* 47, 614) and on cottonseed technology from 1607 through 1939 (*Bass and Olcott—News Ed., A.C.S.* 18, 139). Literature on fat from microorganisms was reviewed by Reichel (*Angew. Chem.* 53, 577) and Haesler and Fink (*Z. Spiritus Ind.* 63, 89). *Oidium lactis* (*Ooporo lactia*) yielded the best results; one strain, A, gave optimum results at 24-29° in 5-6 days. With wood sugar a 6:4 sugar: whey ratio was recommended. A fermentation process for fat production on a medium of carbohydrates and fresh animal albuminous pulp was patented by Brandt (*Brit.* 509,755).

Several suggestions for rendering were made. Haneschka (*Brit.* 505,844) heated animal offal, garbage and other fat-containing products with ammonium hydroxide and mono-ammonium phosphate under pressure to form an aqueous protein broth and a fat layer. Stein-

mann (*Ger.* 686,158 Cl. 23a) first crushed glue stock containing bones, dried it at 58° and removed the fat therefrom by means of centrifuges. A new apparatus designed by Lowry (*U.S.* 2,199,670) was used first for rendering animal and fish material and after separation of fat was used to extract the glue stock residue. Codling (*Nature* 146, 9) encouraged the use of rendering equipment for reducing waste in packinghouses. Cracklings from wet rendered animal trimmings could be pressed, dried and smoked for food purposes (Hinko—*Ger.* 681,669). A combined rendering and refining process for oleo fat (Anderson-Orris—*Brit.* 506,968) comprised heating to 75°, titrating the free fatty acids, removing soap by brine spray and separating the fat. The patents on production of fish and marine animal oils (DeLaval Separator Co.—*U.S.* 2,179,941, 2,193,871; Akt. Separator, Lever Bros. and Unilever Ltd.—*Brit.* 511,264) involved the use of centrifuges to give continuous or rapid processing features to the systems. These types of processes in the menhaden industry produced greater yields, improved products and solved the waste disposal problem (Smith—*Chem. & Met. Eng.* 47, 99). A description and flow sheets of a German factory using centrifuges for the production of lanolin were prepared by Steinacker (*Fette u. Seifen* 47, 535).

A report on five years' work on yields in oil milling was compiled by Sethne (*Kgl. Norske Videnskab. Selskaba Skrifter* 1939, # 3, 150 pp). Equations were developed for factory losses, oil yields and cake yields. His results on factory losses were less than others reported in the literature partly because an indirect method for moisture determination was used. The difference between the oil extracted plus the residue and the original sample weight was taken as the moisture content. Figures obtained in this manner were higher on the raw products and lower on the cake than those of direct methods. Equations were developed for the effect of the difference in phosphorus and nitrogen in analytical extracted oil and pressed oil, the effect of water balance and of analytical error, on factory yield calculations.

The Skipin process (Skipin—*Masloboino Zhir. Delo* 16, #1, 8; #2, 5; Filinovich—*ibid.* #2, 8) was reported to be superior to hydraulic methods for sunflower seeds because less oil remained in the cake. Sadomskii and Rodina (*ibid* 15, #2, 3) recommended hulling the sunflower seeds to reduce hull content of cakes and increase oil yields. Expeller type processes were fostered for production of oil from castor beans (Skipin et al.—*ibid.* 15, #4, 6) seeds of *Lallemantia iberica* (Lesyius—*ibid.* 9) copra, palm kernels and cottonseed (Leont'evskii and Morozov—*ibid.* #2, 34; #5, 7). Two methods of pressing without cloths were described. Kuckerov (*ibid.* #2, 9; #6, 4) described special wooden and iron frames for use with a process in which the pressing was done in several stages. Pitkevitsch (*ibid.* #5, 11) heated sunflower meats to form a ball and placed these balls between the press plates. Better oil yields were claimed.

Koo (*J. Chem. Eng. China* 5, 47, 69) developed processing equations for rape seed and tung nuts which represented the effect of pressure, temperature and time on the yield of oil by pressure. Expression of tung oil at temperatures above 80° did not yield products which fulfill usual specification requirements.

A pilot plant for investigating cottonseed processing was in operation at the University of Tennessee (Morton—*Mech. Eng.* 62, 731). The latest efforts were a study and a design of more efficient seed cookers. It

was revealed that cottonseeds may be decorticated by means of steam explosions similar in some respects to the process used in "puffing" wheat and rice kernels.

In Germany a dry method of removing the germ from feed corn was developed to improve the fat supply (Grandel—*Fette u. Seifen* 47, 185). Briefly the method involved centrifuging or beating the corn against a smooth, hard wall to split the corn and loosen the germ and then removing the released germs from the mixture. Another method of waste prevention was to remove the oil from distillery slop. This was accomplished by heating to 250° F., filtering and pressing the oil from the filter cake (Brown—*U.S.* 2,216,904-5).

The pressing equipment inventions of the year were a cake molder (N. V. Oliefabrieken Het Hart en de Zwaan—*Brit.* 509,017) and improvements in a press container and its pistons (Duchscher—*Brit.* 508,909).

Erwin (*Wisconsin Engr.* 44, 55) reviewed the solvent extraction methods for vegetable oils. A new soybean crushing apparatus (Ford Motor Co.—*U.S.* 2,186,066) featured only two rolls especially designed to give efficient crushing for solvent extraction. A solvent method for lanolin production (Pentek—*Hung.*—123,509) comprised removing it from wool with a scouring solution containing a small amount of alkali, evaporating the scouring liquid and solvent extracting the residue.

Among the new apparatus for solvent extraction of fats and oils, Süß (*U.S.* 2,223,747) featured counter-current equipment which took advantage of gravity to give freedom from interior mechanical devices and simplicity of operation. The apparatus of Pattee (*U.S.* 2,187,890) made use of a bucket-like conveyance in a continuous system. Bonotto's (*U.S.* 2,206,595) apparatus contained a series of screw conveyors. Robinson (*U.S.* 2,225,799) drew the oil-bearing material through moving solvents via a series of moving containers. The solvent extraction equipment of Hamilton and Perkins (*U.S.* 2,183,837) contained pulsating presses. The innovations by Dinley (*U.S.* 2,200,983) consisted of improved means of continuously feeding the oil material and continuously withdrawing the solvent, purifying it from extracted matter and returning the purified solvent to the extraction chambers. New patents have been issued on the Hansa Mühle method (*Ger.* 679,708 *Cl.* 12; *Brit.* 507,467). This method (Schmid—*Fette u. Seifen* 46, 464) involved passing the material in bronze mesh bottom baskets through solvent sprays; the amount of solvent supplied by the sprays exceeded that passing through the bottom so that the containers were filled with solvent during a substantial part of the cycle.

Novel work on solvents used for extraction was reported. McDonald (*U.S.* 2,198,412-3) added special absorbents to oil-bearing solvents to remove suspended material before recovering the solvent. He (*U.S.* 2,187,208-9) extracted oil from garbage by drying in an oil bath, extracting with trichloroethylene and distilling the solvent from the oil by passing it into the oil bath. Davis and Bartlett (*U.S.* 2,191,455) preferred low boiling solvents so that the greater portion of the coloring matter was retained by the residue. Simplicity was realized with the use of furfural (Freeman—*U.S.* 2,200,390-1) because the oil was extracted on warming, the solvent-oil mixture was separated and when cooled released the oil. With temperature control this solvent can fractionally extract oil or the oil may be precipitated from the solvent in fractions of different melting points. Owing to the similar properties of ethyl alcohol

and to lack of the solvents commonly used for oil extraction, investigators of the Orient have been promoting the use of industrial alcohol for oil production (Chatterjee—*J. Indian Chem. Soc. Ind. Ed.* 2, 171; 3, 23). The oil can also be released from the solvent by addition of water. Rosenthal and Trevithick (*Oil & Soap* 17, 264) proved that liquid carbon dioxide will not extract oil from seeds as claimed by an old patent.

The removal and production of phosphatides from oil was accomplished by adding water (Thurman—*U.S.* 2,206,210), hydrogen peroxide (Thurman—*U.S.* 2,204,109) or tricalcium phosphate (Beck and Klein—*U.S.* 2,214,520) and either settling out or centrifuging out the precipitated phosphatides. The uses for soybean phosphatides in the textile industry were reviewed by Schwarz (*Am. Dyestuff Repr.* 29, 220). The applications were in spinning, kierboiling, as a leveling agent in drying, in printing pastes and in special finishes. A review of recent research on phosphatides was compiled by Halden (*Fette u. Seifen* 47, 6, 52).

Two methods for recovery of sterols from oils were described. The Glidden Co. (*U.S.* 2,218,971) added lime to the saponified oil to form a porous mass and extracted with organic solvents. Kraybill and Thornton (*U.S.* 2,225,375; *Ind. Eng. Chem.* 32, 1138) passed the oil through a column of aluminum silicate which adsorbed the sterols, phosphatides and mucilage-like materials; the sterols were then concentrated from the mixture by the use of selective solvents. For this process an adsorbent material (Kraybill *et al.*—*U.S.* 2,174,177) may be prepared by mixing aqueous sodium silicate solution with solutions of aluminum salts, filtering and drying the precipitate. New patents on concentrating vitamins (Fawcett and Burrows—*U.S.* 2,186,669; Smith—*U.S.* 2,207,385) and antioxidants (Hickman *et al.*—*U.S.* 2,205,925; 2,221,692) by short-path distillation methods were obtained. Detwiler (*Oil & Soap* 17, 241) supplemented his series of bibliographies on short-path distillation with recent references on the subject.

Several treatments for oils before alkali refining were suggested. Alum was reported more effective than common salt in facilitating the settling and separation of moisture (Matrozova—*Mvasnaya Ind. U.S.S.R.* 10, #8, 32). Strezynski (*U.S.* 2,215,624) clarified freshly pressed oil with special centrifuges. The preliminary acid treatments for removal of colloidal materials were reviewed by Hetzer (*Seifensieder-Ztg.* 67, 201). Colloidal or dissolved metals such as iron, aluminum, magnesium and calcium were removed by treatment with concentrated acid followed by adding water and a settling step (Jakobsen—*U.S.* 2,210,548). Before alkali refining, Duvall (*U.S.* 2,225,557) degummed a portion of the crude oil, added undegummed oil to bring the gums to a certain optimum amount that helped to separate soap stock.

In alkali refining considerable activity was displayed toward improving continuous processes. The improvements in the Refining, Inc. methods (*U.S.* 2,190,588-95; 2,199,041; 2,205,971; 2,216,104; 2,216,680; 2,219,088; 2,219,968; 2,223,077; 2,225,557; 2,225,575; 2,226,211) included methods of preliminary degumming, emulsifying, use of de-emulsifiers, temperature control and means of suitably controlling the moisture. A continuous method described by Colbeth (*U.S.* 2,183,486-7) involved the countercurrent passing of the oil through a column of refining agent. Continuous refining was the subject of 2 reviews (Silman—*Soap* 16, #3, 23; #4, 27; Tovbin—*Masloboino Zhir. Delo* 15, #3, 5).

Directions and results on refining rice oil (Ueno—*J. Soc. Chem. Ind. Japan* 43B, 74), tallow, rice bran oil (Dressler—*Oil & Soap* 17, 124), linseed oil (Osnos *et al.*—*Khim Referat Zhur.* 1939, #7, 112) and hemp oil (*ibid.* 111; Boricheva—*Masloboino Zhir. Delo* 15, #6, 10) were reported. The directions for rice oil included alkali refining, reesterification with glycerine and vacuum distillation methods. The tallow and rice bran oil descriptions fostered the use of lye, sodium carbonate and sodium silicate. A method recommended for linseed oil and one for hempseed oil dealt with acid treatment and neutralization with alkali. Another method for hempseed oil recommended neutralization in two steps with a weaker caustic solution for the final neutralization.

Potassium permanganate and magnesium hydrosilicate mixture (Hussard—*Can.* 384,364), alkali carbonate and bittern mixture (Nemoto—*Japan* 129,041) and blast furnace slag (Belani—*Montan. Rundschau* 31, 303) were recommended as alkali refining agents. Dissolving the oil in water-immiscible solvent before alkali refining has been patented for woolfat (Friedrich—*Ger.* 672,720).

Two methods for treating tall oil were proposed. Coloring matter and phytosterols were precipitated therefrom with sulfuric acid (Gayer and Fawkes—*U.S.* 2,223,850). Segesseman (*U.S.* 2,199,653) first esterified the fat acids with a low boiling alcohol and subsequently esterified the resin acids with higher boiling alcohol. The treatment yielded a mixture that was easily separated. Fatty acids were separated from tar-like residues by extraction with normally gaseous hydrocarbons.

Present technic for bleaching fatty oils was reviewed (Anon.—*Ontario Res. Foundation Bull.* 7, #10, 2). New bleaching processes comprised use of oxidizing agents in acid emulsions followed by bleaching with hydrogen peroxide at pH 8.5 (Scheller—*U.S.* 2,221,559); also the use of emulsions containing per-compounds and albumins (Mahler—*Fr.* 845,020), use of special mixtures of diatomaceous earth, carbon black and glue (Schmidt—*U.S.* 2,219,581), use of calcined alumite (Bierce—*U.S.* 2,211,489) and filtering through activated clays and materials of the class consisting of pyrophyllite, talc, silica, fire clay, etc. (Alton—*U.S.* 2,202,806). A bleaching method for palm oil (Sullivan—*Can.* 390,928) comprised decomposition of the dye-stuff by heating to 200-350°, followed by the usual refining, bleaching and deodorization.

Steele (*U.S.* 2,206,337) described a method of bleaching with a means of collecting, reviving, classifying and reusing adsorbent material. Hagan (*U.S.* 2,214,671) realized economies in the bleaching process by giving the oil a pretreatment with used earth. The bleaching capacity of 3 Jodhpur earths was evaluated at different concentrations on safflower seed oil (Kulkarni and Jatkar—*Kolloid-Z.* 89, 54). Erdheim (*Przemysl Naftowy* 13, 634, 656) pointed out that a mixture of 2 bleaching earths was more efficient than theoretical calculation of results obtained on each separately.

Operation data, diagrams and illustrations of the Foster-Wheeler Corp.'s continuous deodorizer were presented (*Oil & Soap* 17, 217; *Brit.* 505,852). The oil was passed through 2 zones countercurrently to steam. The deodorizing zone comprised a series of trays. The steam passed successively through the bottom tray and upward through each succeeding one, thus first contacting the tray containing the purest oil. A new development (*Brit.* 505,810) in connection with this process

comprised a preliminary vacuum deaeration of the oil to reduce oxidation. Ullmann (*U.S.* 2,203,373) recommended radiation with x-rays for deodorizing neat's-foot oil. Improvements in deodorization apparatus were also designed by Huzimoto (*Japan* 129,040).

For a special process of making soap, lubricants and fat acid derivatives, some consumers prefer fat in the form of fat acids. McBride (*Chem. & Met. Eng.* 47, 830) reviewed the preparation of fat acids and their uses. Ono (*J. Agr. Chem. Soc. Japan* 15, 1085, 1161; 16, 43, 147, 197) investigated the enzyme method of splitting fats. Hydrolysis by pancreatic lipase with ammonium buffer (pH 8.9) in the presence of 10% acetone was favored. Esters of lower fatty acids and highly unsaturated acids were first split. The activity of the enzyme decreased with increasing glycerol concentration. The hydrolysis of the glycerides of stearic and oleic acids increased in the order of tri-, di- and mono-glycerides. It was suggested that mixed glycerides hydrolyzed more rapidly than simple triglycerides because of the difference in emulsification. Ueno and co-workers (*J. Soc. Chem. Ind. Japan* 43B, 101) recommended splitting hardened fish oil with lime by a method in which the operation was interrupted 6 times and the sweet water was separated each time. Morlock (*Ger.* 679,723 Cl. 23d), Ittner (*U.S.* 2,221,799) and Thurman (*U.S.* 2,190,616) designed apparatus for continuously splitting fats and oils.

A distilling apparatus as designed by Lee (*U.S.* 2,177,664) comprised a means of atomizing the fat acids with an inert gas into a distilling zone at sub-atmospheric pressure. The apparatus of Ittner (*U.S.* 2,202,007-8) included special high vacuum and high pressure steam developing equipment. The inventions of Potts and McKee (*U.S.* 2,212,127; 2,224,925-6, 2,224,984-8) were improvements on a fractionating column used to fractionally steam distill fat acids and a procedure for certain oil.

Papers presented on hydrogenation of various organic materials at the Midwest Regional Meeting of the American Chemical Society summarized and illustrated modern practice in the industry. These were entitled, role of catalyst (Adkins—*Ind. Eng. Chem.* 32, 1189), hydrogenation of fats (Wurster—*ibid.* 1193), catalysts from alloys (Raney—*ibid.* 1199), hydrogenation of petroleum (Murphree *et al.*—*ibid.* 1203), economic aspects (Shreve—*ibid.* 1212) and hydrogenation of aniline (Winans—*ibid.* 1215). Other reviews included a historical treatise (Armstrong and Williams—*Chem. & Ind.* 59, 3) and a survey of modern methods (Sethne—*Tids. Kjemi Bergvesen* 20, 28).

In an investigation by Escourrov and Savary (*Bull. soc. chim.* 7, 180) olive oil was hydrogenated at 180° at various pressures. At 20 mm. pressure hydrogenation stopped after selective saturation of the most highly unsaturated constituents. At higher pressure a change in hydrogenation speed was observed at this point. At 760 mm. and 95° isoölein formation appeared at iodine value 82, while at 18° the process occurred at iodine value 78-79. Optimum conditions for hydrogenation according to Dobyichin and Roginskii (*Masloboino Zhir. Delo* 15, #6, 13) were a temperature range of 200 to 240°, a hydrogen rate of 300 to 500 liters per minute per kilogram of nickel and an increase in stirring rate considerably greater than is normally practiced. Changes of physical and chemical characteristics of cotton seed and sunflower oils were tabulated by Ravich (*J. Tech. Phys. U.S.S.R.* 7, 2249; *Klim. Referat Zhur.* 1939, #8, 124). Similar data with the use of

Raney catalyst on coconut, pilinut, peanut and mixtures of these oils were prepared by de Leon and Agdeppa (*Philippine Agr.* 28, 225). For the production of soap fat acids Kaufman (*U.S.* 2,220,279) split and hydrogenated simultaneously in the same apparatus. The hydrogenation of sunflower oil by the conjugated system using methyl, ethyl, propyl, isobutyl and isomyl alcohols yielded a product that had approximately the composition of olive oil (Rush and Dvinyaninova—*J. Applied Chem. U.S.S.R.* 12, 1060). Aldehydes corresponding up to 33.9% of the alcohol were obtained. With isopropyl alcohol 72.5% were recovered as acetone, another 0.9% was accounted for by decomposition of acetone; the authors could not account for the remainder.

Work by Ueno and Suzukawa (*J. Chem. Ind. Japan* 42B, 350) revealed that with a nickel-copper-cobalt-manganese catalyst the activity was increased by chromium, magnesium, zinc or lead as a fifth metal; iron retarded it. With a nickel-copper-cobalt-zinc catalyst the activity was increased by lead, calcium or iron and retarded by manganese. A catalyst containing nickel, copper, magnesium and cobalt was not improved by the addition of a fifth metal. A platinum oxide catalyst for hydrogenating vegetable oils can be prepared by impregnating diatomaceous earth with chloroplatinic acid and alkali metal nitrate and heating to 300-450° (Martin—*U.S.* 2,207,868). Lenth and Newell (*U.S.* 2,201,235) patented the use of a copper-aluminum mixture for use as a catalyst. According to Arnold (*U.S.* 2,205,552) hydrogenation catalysts may be stored in solutions of lower alkyl amines and ammonia. A method for reactivating spent catalyst comprised anodically oxidizing in strong alkaline solution, washing and reducing with hydrogen at elevated temperatures (B. F. Goodrich Co.—*U.S.* 2,208,616).

Several new improvements appeared for separating fats and oils into high and low melting fractions. Dedlow (*U.S.* 2,200,982) and Eckey and Folzenlogen (*U.S.* 2,205,382) described special temperature manipulation and rate of cooling to yield optimum results. Drinberg and Zhebrovskii (*Org. Chem. Ind. U.S.S.R.* 6, 327) described a method of fractionating by freezing naphtha solutions of oils. Cottonseed, sunflower and soybean oils were converted into soap-making and alkyl lacquer-making fractions. A new method comprised selectively extracting the oil constituents with solvents such as furfural and hydrocarbons (Freeman—*U.S.* 2,200,391). An apparatus in which such a process could be carried out was designed by Bottaro (*U.S.* 2,218,080).

Bradley and co-workers (*Ind. Eng. Chem.* 32, 694, 802, 963) accumulated new data on drying oils. A gelled mixture of 89% oiticica oil and 11% sardine oil obtained at 250-60° gave a 70% fraction insoluble in acetone which contained polymers averaging 8 molecules of glycerides. From the data on polymerizing methyl esters of olive, dehydroxylated castor, soybean, linseed and tung oil fat acids, it was shown that the products were principally dimers and had bicyclic structure in the case of tung oil fat acid esters and monocyclic with those of linseed oil. Ultraviolet absorption data on oils during heat bodying suggested that considerable amounts of unreacted acids were present at the gel point. The increase in conjugated acids in linseed oil at the first stages of heating followed by a gradual decrease was followed by ultraviolet absorption technic. Gamble and Barnett (*ibid.* 375) also pointed out the value of absorption spectra technic in studying drying oils. Morrel and Phillips (*J. Soc.*

Chem. Ind. 59, 144) continued their series of investigations on the study of the oxidative reaction by means of hydrogen iodide. Their earlier work on the reactivity of various groups, *i.e.*, enol, ketol, etc., were confirmed. Structures and compounds formed in the treatment of hydrobenzoin, various oils, rosin and resins were suggested.

Reviews on heat bodying oils were prepared by Rheineck (*Paint, Oil Chem. Rev.* 102, #15, 10), Kaufman and Kirsch (*Fette u. Seifen* 47, 108), Carrick *et al.* (*Am. Paint J.* 23, in 10 issues May 1 to Sept. 11) and Huff (*ibid.* 24, in 5 issues Dec. 1939 to March 10, 1940). The latter 2 series of reviews contained tabulated data on the effect of heat, driers, resins, etc., on oxygen consumption and on the characteristics of various oils. Tatimori (*J. Soc. Chem. Ind. Japan* 43B, 163) tabulated the changes in iodine value and viscosity of linseed oil with temperature of treatment. Overholt and Elm (*Ind. Eng. Chem.* 32, 378) studied the changes in drying oil fat acids when in the form of a paint film exposed to ultraviolet light at 25° and 65% relative humidity. The molecular weights indicated that eleostearates passed through a maximum shortly before its maximum peroxide concentration was observed. There was little change in the molecular weights of the methyl esters of oleic, linoleic, linolenic acids although viscosity increased to 100 times the original value.

New improvements in the drying properties of oils were made. Hodgins (*U.S.* 2,196,796) removed anti-oxidants by treatment with nitric acid. Strauss (*U.S.* 2,197,813) mixed the fat acids of drying and semidrying oils and esterified them with polyglycerols having free hydroxyl groups. Malikov *et al.* (*Russ.* 53,401) suggested adding 5-10% unsaturated organic compounds such as isoprene, undecylic acid, styrene or divinylacetylene to the polymerization charge. Auer (*U.S.* 2,189,772) incorporated sodium oxalate during polymerization. McKinney (*U.S.* 2,185,414) improved the drying properties of semidrying oils by heating with 0.1% alkali hydroxide or soap such as calcium hydroxide or calcium linolenate. Hubbuch (*U.S.* 2,190,789) prepared a polymerizable oil by reacting methacrylic anhydride with polyhydric alcohol incompletely esterified with fat acids. The new polymerization catalysts patented during the year were anthroquinone (Sorensen and Konen—*U.S.* 2,213,935), β -naphthol mercaptan (Bradley and Johnston—*U.S.* 2,219,862), special inorganic metal salts (Auer—*U.S.* 2,213,944) and gaseous sulfur dioxide (Waterman and von Vlodrop—*U.S.* 2,188,273). The characteristics of the products, the course of the reaction and the details for use of gaseous sulfur dioxide on several drying and semidrying oils were compiled by Waterman and van Vlodrop (*Verfkronek* 13, 130). Tamamusi and Tohtatu (*Bull. Chem. Soc.* 15, 223) reported that chloriron-copper- and magnesium phthalocyanines displayed activity toward promoting oxidation of drying oils. However, these were less effective than most of the driers commonly used in the industry.

Skin formation in paints could be retarded by adding alkylated, halogenated or aralkylated polyhydric phenols to the oils used in the paints (Martin—*U.S.* 2,225,918-20). Paints dried quickly on being radiated with wave lengths of 0.6-1.6 microns (Groven—*U.S.* 2,186,067). This was accomplished with a carbon filament lamp bulb and a reflecting surface of gold or other suitable metal.

New information on various phases of linseed oil appeared. The drying time of oil from flaxseed decreased with successive stages of maturity (Ruchkin—

Masloboino Zhir. Delo 15, #6, 6). It was suggested that this effect was due to the anti-catalyzing action of chlorophyll which was more abundant in the oil from the greener seeds. Varlamov (*ibid.*, #5, 30) found films of polymerized raw linseed oil considerably stronger than those of polymerized refined oil. Films of polymerized oil had a greater strength and elongation than those prepared by other methods (Shikher—*J. Applied Chem. U.S.S.R.* 12, 1884). Rossetti (*Olii minerali, grassi e saponi* 20, #1, 9; #2, 9) tabulated the characteristics of stand oils, lithographic varnishes and blown oils prepared from linseed oil. Partial solubility in petroleum ether, content of oxidized acids and viscosity were most valuable for distinguishing the products. According to Payne (*Ind. Eng. Chem.* 32, 737) a short heat treatment of linseed oil decreased the solubility, permeability and water absorption of its films. Oils of high acid number absorbed most water. High acidity shortened the induction period and increased oxygen absorption with titanium oxide and zinc sulfide pigments according to Nicholson (*Ind. Eng. Chem.* 32, 1259). The reverse was true with zinc oxide pigment. The addition of terpene-phenolic resin during the bodying of linseed oil made it possible to produce a paler bodied oil without materially altering the drying time (Byrnes—*Paint, Oil Chem. Rev.* 102, #12, 32). Gussman (*Am. Paint J.* 24, Nov. 1, 16) pointed out that the acid number versus the logarithm viscosity curve for any one charge was a straight line. The information and data was of practical value to the ink and paint industry in planning living technic. Change in weight, iodine value and thiocyanagen value of linseed oil films during aging were plotted by Carrick and Christensen (*ibid.*, Sept. 23, 54; Oct. 7, 63). A historical summary of the published reactions between oxides of lead and linseed oil was prepared by Chatfield (*Oil Colour Trades J.* 97, 1183, 1244; 98, 30, 62). An Italian commission (Rossetti—*Olii, minerali, grassi e saponi* 19, 141) has been studying means of evaluating the drying time of raw linseed oil. None of the standard methods gave results consistent enough for adoption.

Bauer (*Arbeitsschutz* 1939, 359) emphasized the danger in accidental and spontaneous ignition of vapor-air mixtures in linseed oil boiling plants. Thorough ventilation, safety planning and simple control devices to reduce this hazard were described. Meyer (*Farben-Chem.* 11, 5) described how linseed oil could be cooked with safety at 300°. Blowing with carbon dioxide, maintaining carbon dioxide atmosphere over oil and rigid temperature control were emphasized.

New information on gelation of tung oil was reported by Tatimori (*J. Soc. Chem. Ind. Japan* 43B, 102, 136, 139, 161, 194) and Cannegieter (*Paint, Varnish Production Mgr.* 19, 366). According to Tatimori, benzoic, cinnamic and malic acids, glycerine, fat acids, fatty alcohols, brominated oils and many natural resins were active retarders, while tartaric and tannic acids, asphalt pitches and pyrogallol accelerated gelation. Cannegieter compiled data on gelation time at various temperatures. The minimum time was at 350°, but decomposition of the oil started at this temperature. Kurz (*Fette u. Seifen* 46, 343) applied chromatographic technic in the study of tung oil gels. He was able to separate the gels into monomeric and dimeric fractions. The dimeric fraction was 47-65% of the total. Hill (*U.S. 2,172,974*) bodied tung oil for use with fibrous materials such as gaskets, at 280° and then before gelation occurred, cooled rapidly to below 175° in the absence of resin. A polymer suitable for molding was made by polymerizing a mixture of styrene with about

0.1-2.0% of tung oil (Dow Chem. Co.—*U.S. 2,190,906*). Similar compounds could also be prepared with oiticica oil (*ibid.*—*2,190,915*). Erastova *et al.* (*Trudy Inst. Lakovi Krasok* 2, 94) described methods of manufacturing varnish from tung oil.

A continuous laboratory oiticica oil bodying method was devised by Marchese and co-workers (*Ind. Eng. Chem. Anal. Ed.* 12, 77). Data to show the relation of time, temperature, viscosity, iodine value and gelation time of bodied samples were also developed. Rumyantseva (*Byull Obmen Opyt. Lakokrasochnoi Prom.* 1939, #4, 5) described the oil and its properties in commercial products when it was the sole oil and in mixture with others that were available in Russia. Rheineck (*U.S. 2,210,305*) partially acetylated the oil to decrease drying time and to obtain a product that gave a smooth, tough and glossy film. Jordan and Rossmann (*U.S. 2,220,906*) patented the use of a semicarbazone of oiticica oil for admixing with other drying oils.

Reviews on dehydrated castor oil were prepared by Greubel (*Am. Ink Maker* 18, #2, 20) and Solienko (*Org. Chem. Ind. U.S.S.R.* 6, 310). An economic study was prepared by Killeffer (*Ind. Eng. Chem.* 32, 1466). Forbes and Neville (*ibid.* 555) investigated and recorded data on dehydration of castor oil with 38 different catalysts. Most of the patents and the communications dealing with dehydration were on processes using sulfuric acid or its derivatives, *i.e.*, persulfuric acid, persulfates, sulfates as catalysts (Koninklijke Industriele Maat. Noury & v. d. Lande N. V.—*U.S. 2,195,225*; *Brit.* 508,516; *Dutch* 47,417; Priester—*U.S. 2,226,830-1*; Pelikan—*U.S. 2,198,884*; Shuraev *et al.*—*Org. Chem. Ind. U.S.S.R.* 7, 34; *Masloboino Zhir. Delo* 15, #5, 33; 16, #2, 16; *Novosti Tekhniki* 1939, #35, 31; Varlamov and Tikhomirova—*Masloboino Zhir. Delo* 16, #1, 22; Ivanova *et al.*—*Byull. Obmen Opyt. Lakokrasochnoi Prom.* 1939, #6-7, 24; #8, 18; Lab. Zavoda—*ibid.* 1938, #11, 32; Kulikov—*ibid.*, 1939, #3, 49). Brod (*U.S. 2,212,385*) dehydrated by acetylating and heating to split off acetic acid. Other methods of dehydrating involved the use of special catalysts such as certain Russian clays (Serb-Serbin and Sakharov—*Russ.* 52,919) and the use of ricinoleates and linoleates of lead, manganese or zinc (Shuraev—*Org. Chem. Ind. U.S.S.R.* 6, 595; Lebit *et al.*—*Byull. Lakokrasochnoi Prom.* 1938, #12, 25; Ivanova—*ibid.* 1939, #4, 11).

Beal (*Paint, Oil Chem. Rev.* 102, #11, 9) prepared notes and observations on the commercial use of dehydrated castor oil. It could not be substituted entirely for tung oil in varnishes. Osnos *et al.* (*Masloboino Zhir. Delo* 15, #6, 23) demonstrated that films of this product with or without the addition of linseed oil were inferior to the films formed by polymerized linseed oil. Priest and von Mikusch (*Ind. Eng. Chem.* 32, 1314) recorded that dehydrated castor oil contained 17.3-25.4% of the 9, 11 isomer of linoleic acid in the glycerides. Mikusch (*Am. Paint J.* 24, 18) pointed out methods of evaluating composition and the extent of dehydration by the use of iodine, acetyl and diene values. On distillation of dehydrated castor oil, Osnos *et al.* (*Masloboino Zhir. Delo* 15, #4, 27) obtained a 10.7% nonglyceride condensate which was composed of enanthaldehyde and undecylinic acid. Mikusch (*Ind. Eng. Chem.* 32, 1061) found that the dehydrated oil bodied 3 to 4 times faster than linseed oil. He also plotted chemical and physical data on the course of the bodying. The Cincinnati-Dayton, *etc.* Paint & Varnish Production Club (*Paint, Oil Chem. Rev.* 101, #23, 72) developed similar information on mixtures of the oil with other oils.

Auer (U.S. 2,180,342) polymerized castor oil by heating it with such compounds as ammonium iodide, barium thiocyanate, *p*-cresol, 2, 5-dichlorobenzenesulfonic acid and like compounds. Gamburg (*Byull. Lakokrasochnoi* 1938, #5, 32), Karasik and Sokolova (*ibid.* #4, 32) prepared polymerized castor oils by long heating at 250-80°. Lacquer made from the oil was more resistant to cracking than lacquer prepared from linseed oil (Erofeeva—*ibid.* #11, 47).

Surveys of production and consumption and suggestions for research and greater use of soybean oil were prepared by Kraybill (*Paint, Varnish Production Mgr.* 20, 144) and Holley (*Paint, Oil Chem. Rev.* 102, #15, 9). The drying properties of this oil were described by Carrick and Jigger (*Am. Paint J.* 24, 7). Methods of making alkyl lacquers from sunflower oil were described by Drimberg *et al.* (*Masloboino Zhir. Delo* 15, #5, 26).

Other substitutes or partial substitutes for drying oils were a by-product of the synthetic rubber industry (Petropavlovskaya and Erin—*Byull. Lakokrasochnoi Prom.* 1939, #8, 25), sulfur dioxide treated petroleum fractions (Lazar—U.S. 2,186,248), Pechory asphalt (Uranov and Orlova—*Byull. Lakokrasochnoi Prom.* 1938, #4, 21), condensation products of fat acids and phenols, acyclic olefinic alcohols, aldehydes, their esters or like material (Clocker—U.S. 2,188,885-90) and alkyl lacquers from tall oil (Romanova and Kotlyar—*Org. Chem. Ind. U.S.S.R.* 6, 257).

Due to curtailment of trade during the year, new substitutes for paint oils and promotional work for substitutes and for domestic production of such oils appeared. Some communications revealing these characteristics were as follows:

Vegetable drying oils. Gardner—*Natl. Paint, Varnish & Lacquer Assoc. Cir.* 602.

Tung oil conservation and substitution. Pickett—*Official Digest Fed. Paint & Varnish Production Clubs* #189; Gehardt—*Natl. Paint, Varnish & Lacquer Assoc. Cir.* 588, 103; Gardner—*ibid.* Nov. 1939; Mellings—*Paint Manuf.* 9, 347.

Preparation of drying oils from semidrying oils. Stingley—*Ind. Eng. Chem.* 32, 1217; Light—*Paint Manuf.* 10, 204; Strauss—*Farben-Chem.* 10, 389; Dexter—*Natl. Paint, Varnish & Lacquer Assoc. Cir.* 588, 124; Varlamov *et al.*—*Masloboino Zhir. Delo* 16, #2, 13; Ivanova—*Trudy Inst. Lakov i Krasok* 2, 236, 261; Suvorovskaya and Simova—*Byull. Lakokrasochnoi Prom.* 1938, #4, 42; Kulikov—*ibid.* #6-7, 64; Kiselev and Erastova—*ibid.* 1939, #3, 15; Suvorovskaya—*Org. Chem. Ind. U.S.S.R.* 6, 227; Bolotin and Levit—*Khim. Referat Zhur.* 2, #5, 112.

Use of synthetic resins as substitutes for drying oils. Huff—*Am. Paint J.* 23, in issues from Sept. 18 to Dec. 11; Sarx—*Fette u. Seifen* 47, 18.

New developments in drying oils (most of the writers emphasized dehydrated castor oil). Behr—*Paint, Varnish Production Mgr.* 20, 160; *Paint Ind. Mag.* 55, 303; Rudd—*Paint Manuf.* 10, 99; Walton—*Oil & Soap* 17, 84; Blom—*Farben-Ztg.* 44, 901; Blom—*Peintures, pigments, vernis* 16, 118.

PRODUCTS

Brief consumer information on fats and oils was prepared by Mrs. Whiteman and Miss King (*U.S. Dept. Agr. Leaflet* 204, 8 pp). The leaflet is a home-makers guide giving information on selection, grades, food value, digestibility, uses and care of the fats in the home. The care of fats both during processing and in the home was reviewed by Mitchell (*Refrig. Eng.*

40, 153). A short monograph on margarine and compound shortening was prepared by Langton (*Food* 9, 171, 174, 203).

In publications on the selection of fats for the manufacture of doughnuts (van Trees—*Chi. Retail Baker* 4, #10, 22) and potato chips (Broeg—*Food Ind.* 12, #4, 51), the desired characteristics were described. Cooperation was encouraged between the bakers and manufacturers of shortening and of equipment so that frying standards could be developed.

A newly patented cooling device for fats comprised a special method of using a drum cooler with scrapers (Brix-Hansen—U.S. 2,199,038). Haas and Renner (*Brit. 511,701*) partly oxidized shortening in the presence of enzymes and in an aqueous medium to secure a product with dough bleaching properties. A shortening prepared by Lever Bros. (U.S. 2,223,724) was steamed and subjected to vacuum to remove oxygen, nitrogen was added during cooling and the product was kept from contact with air after packing by filling unoccupied space in container with nitrogen. A shortening prepared by Schou (U.S. 2,220,976) contained 80% fat, some sugar, emulsifier, and water.

The work in the dairy industries on butter and cheese processes is considered as a field distinct from the processes covered herein, and only the information on statistics, deterioration and the characteristics of butter fat are reviewed.

Margarine, although a substitute for butter, definitely belongs among the products reviewed. A margarine manufacturing method described by Popov (*Masloboino Zhir. Delo* 15, #2, 28) began with the use of a hard fat which was brought to normal consistency by adding oil. Miller (U.S. 2,206,419) supercooled the liquid margarine emulsion under diminished pressure and then subjected it to increased pressure while working. Epstein (U.S. 2,217,309) incorporated emulsifier into margarine mix in solution in water or milk. New machinery for the margarine industry was described by Churngold Corporation (U.S. 2,197,457), Schaub (U.S. 2,166,197) and Erlandsen (*Fette u. Seifen* 47, 15).

A salad dressing that contained honey and vegetable oil, the honey being in sufficient proportion to the oil to eliminate the oily taste, but insufficient to mask the presence of oil, was patented by Straub (U.S. 2,221,957). Watts and Morse (*Food Res.* 5, 197) successfully used benzine-extracted, undenatured soybean flour as an emulsifying agent for the preparation of salad dressing which had a higher viscosity than when made with eggs. Gumminess of salad dressing can be reduced by using a thickener and aerating with air to 20% by volume (Musher—U.S. 2,217,699).

During the year there were several patents on miscellaneous fatty foods. An emulsion containing fat, salt, sugar, spices, gum tragacanth and vinegar was prepared for use with canned fish (Musher—U.S. 2,218,475). An emulsifier and plastic fat mixture was recommended for thickening catsup, mustard, syrup, salad dressing, etc. (Musher—U.S. 2,203,643). Some of the oily portion of nut butters was removed and a gelatinized water thickener added, to yield a product capable of being sliced (Musher—U.S. 2,217,701). An olive oil flavor was induced in other oils by infusing the oil at elevated temperatures with small amounts of low moisture containing macerated olive paste and removing the paste solids therefrom (Musher—2,221,404). Yeast was stabilized and improved in regard to cutting qualities and color by incorporating a lauric acid partial ester of a polyhydric alcohol (Schultz and

Frey—*U.S.* 2,223,465). Fat bloom at the surface of chocolate and chocolate-coated products was retarded by elaidinizing a portion of the cocoa butter in the products (Cook and Light—*U.S.* 2,216,660). A product for preventing crystallization of stearin in olive oil comprised cocoa butter, oxidized to molecular weight of 1050 to 1500 (Clayton *et al.*—*U.S.* 2,200,858).

Much of the information on emulsifiers dealt with mono- and di-glycerides or polyglycerides with some unesterified hydroxyl groups. The patents on the subject included methods of preparation, refining, and use (Best Foods—*U.S.* 2,197,339-40; Procter and Gamble Co.—*U.S.* 2,206,167-8; Kapp—*U.S.* 2,207,256-7; Epstein—*U.S.* 2,223,558; Brown *et al.*—*Can.* 389,953-4, 389,957; Lever Bros.—*Ger.* 679,971). The reviews on the subject included a survey of syntheses and food and technical uses by Norris (*Oil & Soap* 17, 257), a review of the uses in foods by Bennett (*Food Manuf.* 15, 187) and a description of their use in shortening by Miss Gaffney (*Bakers Digest* 15, 101). Kawai and Nobori (*J. Soc. Chem. Ind. Japan* 43B, 59, 110, 170) investigated the formation of mono- and diglycerides during heating of mixtures containing 0.8 to 1.4 mole of glycerol to 1 mole of fat acid. At 230-240° esterification was almost complete within 3 hours; at 170-180° 15 to 20 hours heating was necessary. Temperatures of 240-5° favored the formation of diglycerides.

Two publications on monoglycerides were of scientific interest only. One was on the preparation of pure β -monoglycerides (Daubert—*J. Am. Chem. Soc.* 62, 1713), the other on the melting point, heat capacity, and heat of combustion of α - and β -monopalmitin (Clarke and Stegeman—*ibid.* 1815).

Free fat acids were added to soybean phosphatides to yield an emulsifier having a soft consistency (Wiesehahn—*U.S.* 2,194,842). Other methods of converting the phosphatides into a handier form were dissolving in ethyl lactate (Jordon—*U.S.* 2,193,873), and preparation of a water suspension by addition of urea (Feibelman—*U.S.* 2,203,295).

Emulsifiers were thickened by additions of inorganic salts of alkylolamines. (Emulsol Corp.—*U.S.* 2,189,803). Both sodium caseinate (Ghellerova—*Farm Zhur.* 12, #1, 22) and dextrin (Afanas'ev—*Farmatsiya* 1940, #2/3, 28) were proposed as oil emulsifiers to replace gum arabic. The use of lanolin and sterols as emulsifiers was proposed by Hubscher (*Seifensieder-Ztg.* 67, 206, 216, 226) and by Janistyn (*Fette u Seifen* 47, 405).

King and Mukherjee (*J. Soc. Chem. Ind.* 59, 185) investigated the stability of various emulsions. Most emulsions were coarser and more stable than soap stabilized emulsions. Calcium chloride inverted emulsions stabilized with egg yolks and destroyed saponin emulsions. Hydrochloric acid had the same effect except that with egg yolk there was no reversal. Heating emulsions imposed coarseness; those stabilized by agar broke at the non-gelling temperatures of the agar. Data on the hydration of substituted amides of stearic acid were tabulated by Toms (*Nature* 146, 560). The water binding power varied from 0.7 to 88.5%. Introduction of radicals into the nucleus of stearamide had little effect through carboxyl groups in *o*- or *p*-position reduced the water-binding capacity. Replacement of the remaining hydrogen of the amino group destroyed water-binding capacity. An apparatus and a procedure for a new method of determining emulsifying efficiencies, based on turbidity measurement, were described by Cohan and Hackerman (*Ind. Eng. Chem. Anal. Ed.* 12, 210).

Information on cosmetic creams and salves included discussion on the selection of fat material (Rayner—*Soap, Perfumery, Cosmetics* 12, 898; Hubscher—*Seifensieder Ztg.* 67, 539), the use of hydrogenated oil as a base (Fiero—*J. Am. Pharm. Assoc.* 29, 18), the action of various fats on the skin (Edwards—*Oil & Soap*, 17, 82) and a formula for a substitute to replace cocoa butter (Santi—*Boll. chim. farm.* 78, 97). Mugisima (*Japan* 128,431) recommended stabilizing wool grease by hydrogenation.

A review of fats and fat derivatives used in textile processes together with a brief description on processing wool, silk, and cotton was prepared by Oberly (*Oil & Soap* 17, 152). Alkylolamine salts of fat acids were recommended as textile softeners (Kritchevsky—*U.S.* 2,213,673). Favorable reports appeared on the use of spurge oil (Balter and Shaferman—*Sherstyanoe Delo* 17, #8/9, 58) and dehydrated castor oil having one of the double bonds saturated (Colbeth—*U.S.* 2,225,552) for lubricating textiles. Tritetrahydrofurfurylamine salts, esters of tetrahydrofuroic acid and salts of dioxane were added to textile oils as antistatic compounds (Eastman Kodak Co.—*U.S.* 2,197,998-9, 2,198,000-1).

Two reviews appeared during the year on the fats used in the leather industry. (*Newbury Oil & Soap* 17, 43; Thuau and Lisser—*Le Cuir Tech.* 24, 329). One invention claimed the use of fat alcohols together with sulfonated products for impregnating leather (Deutsche Hydrierwerke A.-G.—*Ger.* 683,977 Cl. 28a).

Several methods of obtaining fat acids and other acids from fat were described. Kass and Keyser (*J. Am. Chem. Soc.* 62, 230) prepared stearic acid by hydrogenating a mixture of unsaturated C_{18} fat acids. Brown and Green (*ibid.* 738) relied on fractional crystallization procedures for preparing pure methyl ricinoleate and ricinoleic acid. Norris, Kass and Burr (*Oil & Soap* 17, 113) demonstrated that rapid debromination and production of colorless esters in the preparation of alkyl linoleates was most successful when reacting in anhydrous alcoholic hydrochloric acid solution according to the Rollet method. Buxton and Kapp (*J. Am. Chem. Soc.* 62, 986) purified alkyl fat acid esters by distilling the alcohol, neutralizing the unreacted fat acids and precipitating the soaps in dichloro-ethylene solution. Fat acids were decomposed by oxidation into their next lower homologs by bromination in the α position, conversion in α -hydroxy acid and oxidation with lead acetate and air (Mendel and Coops—*Rec. trav. chim.* 58, 1133).

Haupt (*U.S.* 2,217,515) converted ricinoleic acid to decanoic acid by heating its soap in water at 180-230°. Sebacic acid was formed at temperatures above 235° (Haupt—*U.S.* 2,217,516). Ellingboe (*U.S.* 2,203,680) reported that the oxidation on oleic and other fat acids by nitric acid to yield shorter and dibasic acids was improved in the presence of ammonium vanadate. Scanlan and Swern (*J. Am. Chem. Soc.* 62, 2305, 2309) pointed out that hydroxylated fat acids could be oxidized to lower aldehydes by the Crigee's reaction without isolating the hydroxylated products. The hydroxy fat acids were prepared by treating unsaturated fats or the ethyl esters of fat acids with hydrogen peroxide in glacial acetic acid solution.

Oils when hydrogenated in the presence of zinc dust yielded unsaturated alcohols (Simozaki and Sumi—*J. Agr. Chem. Japan* 15, 531, 537). When about 2 moles of methyl or ethyl alcohol per mole of oil (soybean, perilla, etc.) were added the reaction was accelerated

and gave 80 to 90% yields. Blown fat alcohol was recommended as an emulsifier (Robinson—*U.S.* 2,200,-298). Two publications (Egupov—*Russ.* 55,903; Mihalovici and Bors—*Curierul Form 8*, #6, 1) described methods of obtaining fat alcohols from sperm oil by saponification, precipitation of acids with inorganic salts or alkalis and extraction. Alcohols could be converted into the corresponding aldehydes by treatment at 50 atmospheres and 50-450°, in the presence of chromium sesqui-oxide.

A fat alcohol derivative-cetyl pyridinium chloride, was said to be a good germicide and in addition was odorless, non-staining, inexpensive, non-toxic and soap-like (Shendon *et al.*—*Sci. Suppl.* 91 #2368,11).

Mononitriles of fat acids were prepared from the fat acids, their anhydrides or esters and ammonium salts or amides by reaction with ammonia vapors at 425-450° in the presence of a dehydrating agent (Wortz—*U.S.* 2,250,076). Fat acids could be converted to their corresponding ketones by heating to 350-60° in the presence of aluminum oxide or hydroxide (Kino and Kato—*Bull. Inst. Phys. Chem. Research Tokyo* 19, 179). Ethinyl carbinols could be prepared from the ketones by reaction with alkali acetylide and hydrolysis to the corresponding carbinol.

Numerous amines containing fat acid radicals with other aliphatic and aromatic radicals were prepared and their melting points were recorded by Harber (*Iowa State College Doc. Thesis No.* 590). Since many of these have found applications as emulsifiers, waxes, disinfectants, detergents, etc., the data should be useful to the industries.

Several new cutting oil developments were recorded. Lincoln and Steiner's (*U.S.* 2,204,538; 2,186,646) preparations contained mineral oil and a minor proportion of sulfurized esters of mono- or dihydric alcohols and fat acids or rosin acids. Another mineral oil product (Pure Oil Co.—*U.S.* 2,211,250) contained a minor proportion of fatty material that had been sulfurized and then phosphorized. Pollak and Hastings (*U.S.* 2,198,-562) prepared cutting oils by sulfurizing an oil at 300-400° F. with 30% sulfur. The presence of aromatic amines or thiourea compounds retarded the thickening of both fatty and mineral oils during sulfurization (Bennett—*U.S.* 2,206,151-2). A review on cutting oils by Arend (*Chem. & Ind.* 59, 771) dealt principally with the character of sulfurized mineral, vegetable, and fish oils. Dombrow (*U.S.* 2,214,634) used naphthenic acid and mahogany soaps as emulsifiers for cutting oils.

An alkyl phthalimide in which the alkyl group was a fat acid was recommended as an ingredient for waxing and polishing compositions (Armour & Co.—*U.S.* 2,225,392). Hydrogenation of fish oils at 300-320° followed by distillation yielded a wax substitute (Sabun—*Russ.* 56,017). Stickdorn (*U.S.* 2,187,334) condensed hardened castor oil, boric acid and acetic anhydride to yield a wax.

Reactions yielding resin-like products containing fat acid radicals were covered by several patents. Mauerberger (*U.S.* 2,186,464) produced a resin by reacting fat acids with an alkylolamine and the amide produced was autoclaved with formaldehyde. A resin suitable for insulation was produced by reacting castor, tung or like oils with magnesium oxide (Grant—*U.S.* 2,202,-849). Ellis (*U.S.* 2,194,894; 2,197,855) prepared resins by heating glycerine, phthalic anhydride, fat acids and boric acid. Greth and Lemmer (*U.S.* 2,217,363) heated drying oils under vacuum during which time resin products were formed and the liberated fat acids were

distilled. By means of the Friedel-Crafts reaction investigators of the Armour & Co. Laboratories (*U.S.* 2,197,709-11) prepared resinous acyl styrenes, acylated indenenes and polymerized acylated coumarones containing fat acid radicals. They also prepared phenol-ketones for making phenol-ketone-formaldehyde resins (*U.S.* 2,209,903) by reacting phenols with fat acid chlorides. Rosenblum (*U.S.* 2,218,553) incorporated fat acids into glycerol resins in a 1:3 ratio.

Many miscellaneous uses for fat products and derivatives appeared. Water and castor oil emulsified with alkylolamine soaps was recommended for water colors (Zel'din *et al.*—*Byull. Laka-Krasochnoi Prom.* 1938, #4, 36). Fat acids incorporated into the dye molecule by the Friedel-Crafts reaction rendered the dye more soluble in oils (Armour & Co.—*U.S.* 2,209,902). Similar aims were realized also by Stallman (*U.S.* 2,183,-629) and General Aniline Works (*U.S.* 2,187,819) by incorporating a fat acid radical in the dye molecule. Leather-like products were prepared from mixtures of paper pulp and metallic salts of fat acids (Vulliet-Durand—*Fr.* 844,806) and from mixtures of gelatin, coconut oil, glycerine, potassium soap, borax, leather powder, rubber, barite, silk, hemp and other miscellaneous materials (Hukushima—*Japan* 128,712). Zirconium salts of fat acids were recommended for producing opalescent or flat finish in fibers, films, paints, lacquers, and the like (Kinzie and Wainer—*U.S.* 2,221,975). Diethylene glycol ethyl ether esters of coconut fat acids were claimed as new compounds for use as softening agents for nitrocellulose coatings (Ellis—*U.S.* 2,221,674).

Fats were transformed into aromatic oils capable of being used in the perfume industry by the action of heat in the presence of soda lime and formic acid (Bouffort—*Fr.* 844,106).

Portland cement was rendered waterproof and quick setting by adding a small amount of a mixture composed of stearin 5, lime 33, water 25, and casein 75 parts (Smith—*U.S.* 2,187,668). Glycerine foots produced bright cadmium plates from cadmium cyanide electroplating baths (Mathers and Guest—*Trans Electrochem. Soc.* 78, 2pp). A specific mixture of mineral oil, tall oil soaps and water was recommended as an ore flotation reagent (Ried—*U.S.* 2,202,601). Pollak (*Oil & Soap* 17, 87) listed the outlets for tall oil, among which were its uses in soap, flotation, the petroleum industry, paint, asphalt emulsions and for softening rubber.

Lincoln *et al.* (*Oil and Soap* 17, 73) in a discussion of the uses of fats and their derivatives in the petroleum industry evaluated the improvements in wetting ability or oiliness when they were added to lubricants. Derivatives containing chlorine, sulfur or phosphorus improved load capacity of lubricants.

Rossetti (*Olii, minerali, grassi e saponi* 19, 81, 97, 129) tabulated data on laboratory aging tests and motor tests on castor oils of various geographical origins. One of the Italian oils was derived from immature beans and showed somewhat larger increases in viscosity, acid number and gum formation than the oils from mature beans. Two Chinese investigators (Koo—*J. Chem. Eng. China* 5, 53) Ueno *et al.*—*J. Soc. Chem. Ind. Japan* 43B, 74) recommended air-blowing of fish, rapeseed and cottonseed oils at 150-200° to prepare substitutes for mineral lubricating oils. Another substitute proposed was a mixture of castor oil and coconut oil. Several patents issued during the year were on mineral oil lubricants containing small amounts of fats, phosphatides or fat derivatives (*U.S.* 2,186,346; 2,186,514;

2,188,863-4; 2,189,661; 2,197,153; 2,197,263; 2,197,433; 2,206,025; 2,212,020-1; 2,212,189; 2,213,943; 2,216,711; 2,223,127-30; 2,223,473; *Brit.* 509,097; 509,976; *Dutch* 47,234; *Ger.* 684,660; 684,821; 684,967; *Cl.* 23c; *Russ.* 51,901; 56,128.)

Corrosiveness and sludge formation in lubricants was decreased by reacting the oil with lecithin and triphenyl phosphite at 350° F. (Musher—*U.S.* 2,223,941). The pour depressors for lubricants which were derived from fats and were patented during the year included a reaction product of chlorinated paraffin wax with stearic acid (Cole—*U.S.* 2,183,009), phosphoric acid salts of fat acids (Jordan—*U.S.* 2,185,592) stearylated coumarone or indene compounds (Ralston and Hoffman—*U.S.* 2,197,712-3; *National Petrol News* 31, #6, 150R) and reaction products of fatty alcohols and cyclic carboxylic acids (Rosen—*U.S.* 2,199,187).

Experiments on producing gasoline-like fuel by cracking cottonseed oil, cottonseeds and mixtures of cottonseeds and oil showed that the best yields were obtained by cracking whole seeds (Lo—*Science, China* 24, 127). Many catalysts were tried without obtaining in-

creased yield. However, the catalysts hastened the reaction. Data on cracking coconut, peanut, sesame and mowrah oils were also tabulated (Dalal and Mehta—*J. Indian Chem. Soc. Ind. & News Ed.* 2, 213). Zinc chloride catalyst was reported most effective for accelerating the process.

A patented process of converting fats into petroleum oil comprised heating the fats in the presence of soda lime and formaldehyde (Bouffort—*Fr.* 844,105).

The production of synthetic fat acids from hydrocarbons was discussed by Meyer (*Riechstoff Ind. Kosmetick* 15, 1, 191), Wittka (*Soap* 16, #8, 28, #9, 34), Burwell and Camelford (*Natl. Petrol. News* 31, 424R). In a new patent (Henkel & Cie.—*Fr.* 842,261) the oxidation of hydrocarbons to fat acids by mixtures of chlorine with other oxidizing gases was claimed. New methods of removing synthetic fat acids from reaction mixtures were by washing with alkali (Lazar—*U.S.* 2,196,421), by use of selective solvents (Leithe—*U.S.* 2,193,321) and by saponification followed by distillation of the non-reacted constituents.

The Isolation of Sucrose from Tung Kernels

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IN the course of studies on the physiology of the tung tree, analyses have shown neither starch nor free reducing sugar present in mature tung kernels (*Aleurites fordii* Hemsl.). However, non-reducing sugar was found in moderate amounts. A search of the literature (1, 2) disclosed no report on the isolation of a non-reducing sugar from this oil bearing fruit. Consequently, it was of biological importance to identify this sugar. It was isolated in a crystalline state from an alcoholic extract of tung kernels and identified as sucrose. Its melting point, rotation and derivatives agree with those recorded in the literature for sucrose.

EXPERIMENTAL

3730 gms. of tung kernels were flaked on an inverted jack plane (3). They were then placed in a muslin bag and defatted in a large Soxhlet unit with 20 litres of petroleum ether for 36 hours. The petroleum ether was drained off and the extraction apparatus charged with 20 litres of 80% ethanol. Extraction was continued for 12 hours followed by recharging with fresh solvent and extracting for another 12 hours. The alcoholic extracts were combined and concentrated to about 6 litres at 40-45° C. and 20 mm. pressure. The solution was clarified of proteins by precipitation with saturated neutral lead acetate. The precipitate was filtered on a Buchner funnel through an asbestos mat. The solution was concentrated to a litre and the excess lead acetate removed by precipitation with hydrogen sulfide. The lead sulfide was filtered off on an asbestos mat on a Buchner funnel. The solution was concentrated to a thick syrup which was then taken up in glacial acetic acid. After seeding the solution with a crystal of sucrose and letting it stand in the refrigerator, the sugar crystallized in the form of rhomboids. These were collected on a Buchner funnel, washed thoroughly with absolute ethanol and dried

in a vacuum desiccator for several days over potassium hydroxide and calcium chloride. The crystals were dissolved in water and the trace of acidity neutralized with calcium carbonate. The solution was filtered and the liquid concentrated to a thick syrup. This syrup was dissolved in ethanol and upon standing in the refrigerator, the sugar separated as crystals. It was recrystallized until a constant rotation was obtained. The yield was 30.5 gms. of sugar. The time required for the formation of the osazone (4) was 28 minutes which agrees very closely with that of the osazone of sucrose. The sugar acetate was prepared according to the method of Hudson and Johnson (5), and Linstead, et al (6).

The following constants were obtained:

Decomposition point of sugar.....	185°C.
Rotation of sugar..... [α] _D ²⁵ = + 66.6 in water where C = 10 percent	
Melting point of sugar acetate.....	86°C.
Rotation of sugar acetate..... [α] _D ²⁵ = + 59.7 in U.S.P. chloroform where C = 1 percent	

From these constants it is evident that the isolated sugar is sucrose.

Summary

A non-reducing disaccharide has been isolated from the kernels of tung (*Aleurites fordii* Hemsl.) and identified as sucrose.

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