

REVIEW OF LITERATURE ON FATS, OILS AND SOAPS FOR 1938

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OILS and fats are used for foods, medicinals, paints, varnish, soaps or other technical purposes depending upon their properties which vary considerably. Some localities are rich in certain types of fatty oil resources, but they must depend upon imports for others. Climatic, economic or other conditions may render it impossible to produce all the necessary varieties in sufficient quantities to meet the local demands. Other localities may be poor in sources of all types of fatty oils. The present trend in leading countries is to encourage domestic production for their individual needs. For this reason the literature is permeated with monographs which describe the development of new sources, methods of increasing supplies, the evolution of new substitutes, and means of modifying oils to obtain properties desired for special applications or to render domestic supplies interchangeable.

The German efforts toward becoming self-sufficient in fats were described in a book by K. Brandt (*Publ. by Food Research Inst.*). This is a history of governmental regimentation of agriculture and dependent industries and its economic, social and political aspects. O. Engels (*Allgem. Oel- u. Fett-Ztg.* 35, 329, 379) points out that the fat situation in Germany can be improved by increasing butter and lard production, cultivating oil plants, increasing the production of fish oils, recovering oil from seeds and other wastes and developing fat production from microorganisms. Among some of the new oils investigated, H. P. Kaufmann and coworkers (*Fette u. Seifen* 45, 149, 152, 175) studied linden seed, tsubaki and horse

chestnut oils. F. Joseph (*Fette u. Seifen* 45, 292) examined chufa oil. In each case the source was analyzed from the standpoint of

season and area for hunting. Another requirement is that the fullest possible use be made of the whale.

A monograph prepared by W. Schnakenbeck (*Fette u. Seifen* 45, 450) on shark fishing deals principally with the yield and properties of the liver oil. At present this oil is utilized in the United States in prepared animal and poultry feeds as a vitamin supplement.

Methods of modifying fish oils for their application in paint, varnish and other drying oil industries were described by K. Buser (*Farben-Ztg.* 43, 803), F. Ohl (*Oberflächentechnik*, 15, 31), L. Reizenstein (*Am. Paint J.* 22, April 25; *Drugs, Oils & Paints* 53, 212), M. Takano (*J. Soc. Chem. Ind. Japan* 40, 429B), A. Drinberg and A. Matveenkov (*Org.*

Chem. Ind. U.S.S.R. 4, 296), V. Varlamov and Z. Bodyzinhina (*Masloboino Zhir. Delo* 14, No. 3, 28), W. Meyer (*Farbe u. Lack* 1938, 245) and I. G. Farbenindustrie (*Ger. 658,844 Cl. 22h*). Briefly, these methods include reacting the oils with phenols or polybasic acids such as succinic, maleic, phthalic, etc., replacing fat acid radicals having no drying power with acids having greater drying power, replacing the glycerol radical with alcohols having more than three hydroxyl groups, introducing conjugated double bonds by halogenating and dehalogenating and removing nondrying fractions by any of several methods. The German patent 658,844, mentioned above, deals with concentration of the drying constituents by short-path distillation in a high vacuum.

Other general papers on modifying semi-drying oils or preparing substitutes for protective coatings

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ease of obtaining the oil, extent of supply, properties and uses.

The January, 1938, issue of, *Fette und Seifen*, was devoted to a series of papers on the whaling and whale oil industry. This issue is a comprehensive monograph on whale oil because among the papers are included historical accounts, statistics and methods of processing and converting the oil into edible material. Other papers describe its use in paint, varnish and linoleum. A publication on improving the drying qualities of whale oil was written by W. Meyer (*Farbe u. Lack* 1938, 271, 283).

To complete the literature citations on whale oil, the recently adopted international regulations (*Treaty series No. 933, U. S. Printing Office*) should be mentioned. The slaughter of Grey or Right whales, calves and females with calves is outlawed. Other whales must be above minimum size. Other regulations restrict the

were written by H. Kaufmann and coworkers (*Fette u. Seifen* 45, 177, 670), T. Kotthoff (*ibid.* 634), Hönel (*ibid.* 636), E. Asser (*ibid.* 582), A. Foulon (*Allgem. Oel- u. Fett-Ztg.* 35, 289), I. Osnos *et al* (*Nitrocellulose* 9, 141), A. Ivanova (*J. Applied Chem. U.S.S.R.* 11, 564) and G. Rankov (*Fette u. Seifen* 44, 465). Rankov pointed out that sunflower seed oil could be made to yield a drying oil by elaidinization followed by removal of elaidins so formed. Kaufmann drew attention to methods of preparing dried films from oils with the use of sulfur chloride. Osnos suggested that 30 to 40 per cent of sunflower oil could be added to linseed oil. Ivanova recommends oxidizing cottenseed oil in presence of lead and calcium oxides. Asser, Kotthoff and Hönel suggested the use of phenolic and other resins. Patents assigned to Firma Theodor Kotthoff (*Ger. 656,132 Cl. 22h*) and N. V. de Bataafsche Petroleum Maatschappj (*Brit. 469,201*) cover, respectively, a method of obtaining drying fractions by crystallization from acetone and the use of a special mixture of solvents for separating polymerized portions.

Aids toward introducing castor oil into the drying oil field were supplied by V. Zhebrovskii and G. Sokolov (*Org. Chem. Ind. U.S.S.R.* 4, 563), P. Serb-Serbin and A. Sakharnov (*ibid.* 5, 203), F. Münzel (Swiss Pat. 193,931), and R. Bonney and W. Egge U. S. Pat. 2,133,889). The Russian papers recommended, respectively, mixing the castor oil with a semi-drying oil and polymerizing the mixture in the presence of cobalt catalyst, and a special polymerization in kaolin. Münzel patented the use of the oxides of several metals such as tungsten and molybdenum as catalysts. Bonney and Egge oxidized a mixture of tung and castor oil and removed the uncoagulated products by extraction with alcohol. Reviews on converting castor oil into a drying oil were prepared for the American readers by A. Reimold (*Am. Paint J.* 22, May 2, 21) and for Russian by I. T. Osnos and I. Golovistikov (*Masloboino Zhir. Delo* 14, No. 2, 17).

In the United States the greatest deficiency is in the drying oil field. This problem was discussed by A. Mathews (*Chem. & Met. Eng.* 45, 97), who mentioned that various organizations are encouraging the government to promote the domestic production of tung, flax, perilla, chia and other drying oils. Val-

uable information to producers and consumers is given in the papers on tung oil by P. Lawson (*Paint, Oil, Chem. Rev.* 99, No. 23, 142) and J. Holten (*ibid.* 29, 141). Papers on safflower oil were written by L. Carrick and H. Nielson (*Am. Paint J.* 22, Aug. 29, 12; Sept. 5, 24). A circular on chia oil was published by H. Gardner (*Natl. Paint, Varnish Assoc. Sci. Sect.* 535, 194). Reviews of the German developments in varnish materials were published by B. Scheifele (*Am. Paint J.* 23, Oct. 31, 54) and H. Gardner (*Am. Paint J.* 22, *Convention daily*, 7).

The U. S. Regional Soy Bean Industrial Products Laboratory contributed to the national economy through papers by A. J. Lewis and K. S. Markley (*Paint, Oil & Chem. Rev. Oct. 27 and Dec. 23*). The authors developed paint and varnish formulas using soy bean oil as one of the constituents and demonstrated their value by tests. M. Taggart (*Drug, Oils & Paint* 53, 177) reported that the heating of a mixture of soy bean and tung oils to 454° F. yielded an excellent paint oil. A report by E. Grove (*U. S. Dept. Agr. Tech. Bull.* 619) on the economic status and trend of the soy bean industry indicates that the major proportion of the oil is used for food: however, with modification this oil could replace more of the imported drying oils.

Information on tung oil production and use in the Orient was given in the form of bibliographies by K. Ho and H. Liu (*Gov. Testing Bur. of Hankow*, 1937) and R. Yei (*Chem. Rev. Japan* 4, 92, 145). According to D. Rowe (*Oil & Soap* 15, 45) the British industries consider tung oil coatings too brittle. However, production of the oil is fostered in many parts of the British Empire. A description of oiticica oil by A. Machado (*Rev. soc. brasil quim.* 6, 464; 7, 73) gave the composition of the oil and its behavior under various kinds of heat treatments. H. Kaufmann and O. Schmidt (*Vorratspflege u. Lebensmittelforsch.* 1, 150) demonstrated that linseeds of high oil content can be produced in Germany.

Several papers testified to the diligent work in the search for new sources and for methods of preventing waste. These were written on pumpkin seed oil (Belani-*Allgem. Oel- u. Fett-Ztg.* 35, 194), grape seed oil (Fachini *et al* —

Olii minerali, grassi, e saponi, colori e vernici 18, 78; de Buccar — *Mat grasses* 30, 196, 219), rice oil (Auriol — *Bull. mat. grasses inst. col. Marseille* 21, 112), wild mastic berry oil (Reinboth — *Farbe u. Lack.* 1938, 364), oil from coffee grounds (Bauer and Neu — *Fette u. Seifen* 45, 229), extraction of fatty oil from the coriander seed waste of essential oil extraction (Tanasienko-Masloboino *Zhir. Delo* 14, No. 2, 8), extraction of waste silk worm pupae (Bertensen — *Masloboino Zhir. Delo* 13, No. 6, 27), and *Cinnomoinum japonicum* seed oil as substitute for cacao butter (Kariyone and Iwao — *J. Pharm. Soc. Japan* 28, 238). Others will be tabulated in the section of this review on characteristics of fats and oils. A patent assigned to Hansa Mühle A. G. (*Ger. 658,986 Cl. 23a*) protects an electrical method of recovering fat acids from waste of soap boiling.

Another refuse matter which has been converted into a substitute for fats is pulp-mill waste from which tall oil is extracted. A monograph on this product giving methods of preparation, commercial treatment and available supplies was prepared by A. Pollak (*Oil & Soap* 15, 33). Means of using this product as a vehicle for corrosion-preventing paints were demonstrated in an anonymous paper (*Farben-Ztg.* 42, 1091). Preparation of a paint capable of resisting three to four years' exposure is described.

Production of fats by microorganisms is still in the experimental stages. H. Kaufmann and O. Schmidt (*Vorratspflege u. Lebensmittelforsch.* 1, 166) and the latter alone (*ibid.* 150) analyzed the fat from *Oidium lactis*. In proximate figures the analyses were: saturated acids 47, oleic 41 and linoleic 12 per cent. H. Fink *et al* (*Listy Cukrovar* 56, 319) prepared fats by the action of *Endomyces vernalis* on sugar; the yield was 15.5 kilograms per 100 kilograms of sugar. The method, however, was uneconomical because of the necessary amount of equipment, work and care. F. Fiedler (*Fette u. Seifen* 45, 183) presented data counter to the claim of K. Lüdecke (*Ger. Pat. 662,794 Cl. 53h*) that fat can be synthesized by the enzyme action of solutions of ground seeds or seed hulls on carbohydrates. Fiedler pointed out that the increase in the yield of petroleum ether soluble substances was due to the process rendering sol-

uble in petroleum ether certain components of the seed hulls which are otherwise insoluble in that solvent.

Preparation of substitutes for drying oils from mineral oils was patented by H. Schneider and J. Sommer (*U.S. 2,131,195*) who oxidized gasoline at 50 to 230°C. and concentrated a drying fraction by distillation and polymerization. A. Drinberg (*Russ. 44,253*) patented the esterification of naphthenic acids with polyatomic alcohols followed by chlorinating and splitting with hydrochloric acid at 250°C. in vacuum. He also (*Masloboino Zhir. Delo 13, No. 4, 40*) described a method of preparing drying oil from aluminum salts of synthetic hydroxy acids. Brief reviews on production of synthetic fat acids for soap manufacture were prepared by G. Wietzel (*Klepsig's Textil Z. 41, 528; Angew. Chem. 51, 531*), J. Baltes (*Fette u. Seifen 45, 196*) and A. Imhausen (*Chem.-Ztg. 62, 213*). A comprehensive review and bibliography on the subject was compiled by W. Meyers (*Seifensieder-Ztg. 65, 215, 238, 256, 277, 297, 317, 338*). Two analyses of the oxidation products of paraffin by E. Jantzen *et al* (*Fette u. Seifen 45, 388, 613*) revealed that the fatty acids produced by the Fischer-Tropsch method contain mostly seven to eighteen carbon atoms.

Works of a general nature include a good book on utilization of fats by H. Dean (*Publisher: A. Harvey, London*), a history of the fat industry in Italy by S. Fachini (*Fette u. Seifen 45, 289*), a history of the processing of fats at Gross-Hamburg by A. Meyer and H. Schmalfluss (*Fette u. Seifen 45, 445*), a review of 15 years' work on investigations on vegetable oils at the University of Delft by Boeseken (*Congr. intern. tech. Chim. ind. agar., Compt. rend. Ve. Congr. 2, 348*) and an annual review on wool fat technology by L. W. Greene (*Textile Colorist 60, 153*).

During the year the average monthly prices of oils and fats taken as whole varied only slightly; however, the annual average was less than that for the last three years. A summary of the monthly trends as given in "Chemical and Metallurgical Engineering" for the last three years yields approximate annual indices of prices as follows: 1938 — 80, 1937

— 105, and 1936 — 98, 100 being the index for the year 1935.

The following statistics were compiled from the U. S. Government bulletin, "Fats and Oils Trade of U. S. in 1938" by Charles Lund.

OIL AND FAT STATISTICS (all data in million lbs.)		
	1938	1937
Production	1,938	1,937
Lard (less farm production)	1,162	897
Shortening	1,539	1,595
Creamery butter (estimated)	1,788	1,624
Margarine	385	397
Tallow	609	517
Cottonseed oil	1,683	1,626
Soybean oil	322	194
Linseed oil (from foreign and domestic seeds)	441	665
Peanut oil	77	51
Fish oil (non-medicinal)	182	197
Whale oil	59	69
Stocks at end of year		
Lard	109	56
Shortening	56	46
Creamery butter	128	43
Tallow	202	205
Cottonseed oil	739	652
Linseed oil	142	191
Fish oils (non-medicinal)	143	106
Whale oil	82	91
Imports		
Vegetable oils	1,083	1,652
Oil equivalent of oil seeds	725	1,025
Animal and fish oils	93	152
Total imports	1,901	2,829
Exports		
Vegetable oils	39	42
Oil equivalent of oil seeds	26	17
Animal oil and greases	221	155
Total exports	286	214

PRIMARY TECHNICAL TREATMENT

In the field of rendering, extracting, refining, hydrogenating and polymerizing of fats new ingenious developments continually appear. Many of these will be only briefly mentioned here. As they are being tested and proved, the literature, and consequently the reviews, will reflect their due importance to the industry. This, together with the many small improvements in existing processes, causes considerable overlapping in a periodical review. However, the review committee will attempt to include notes on all new information on fats. Patent references are indicated by an abbreviation of the country's name with the patent number.

Developments in rendering apparatus tend toward the use of cylindrical digestion vessels containing rotatable sieves. A. Sommermeyer's (*Brit. 482,891*) apparatus contains special devices so that it may be fed while the contents are being treated with steam under pressure. In the digester patented by E. F. Heyerdahl (*Norw. 57,582; Brit. 477,636*) the sieve rotates under aqueous liquid from which the fat is skimmed. J. Schmidt (*Brit. 486,662*) subjects the charge to combined digestion in steam and centrifugal action. W. Steinmann's (*U. S. 2,118,421; Fette u. Seifen. 45, 338*) drum rendering process is devised for con-

tinuous operation and includes pretreaters, separators, and other necessary accessories.

Several other patents on rendering dealt particularly with the treatment of whale flesh to obtain a good grade of livestock feed in addition to the oil. These patents were issued to P. Fauth (*U. S. 2,105,982; Brit. 485,720*), K. Wilhelm (*Norw. 59,172*) and D. Hansen (*Brit. 457,348*).

A small extractor designed by A. Labrie and H. Fougere (*Fisheries Res. Board Can. Repts. Atlantic Stas. No. 21, 6*) is intended for small scale extraction of cod-liver oil. It is a percolator in which steam is the extracting agent. An apparatus developed by G. Jonsson (*Brit. 475,893*) comprises a continuous autoclave and means for pressing livers. H. A. Wentworth (*U. S. 2,134,163*) adds novelty to processing livers by mixing the ground livers with dehydrated beet, cereal, or grain pulp and pressing. An improved livestock feed is a by-product of the process. The use of caustic soda, hydrochloric acid, or sodium carbonate in the pretreatment of livers to release the oil is the subject of several patents (Abbott Labs. — *U. S. 2,136,481*, A. Thorsteinsson — *Brit. 486,277*; K. Kawai — *Brit. 465,547*, L. T. Hopkins — *U. S. 2,107,245*, Aktiebolaget Separator — *Fr. 821,791*).

L. H. Reyerson (*U. S. 2,107,505*) supplants the usual rendering method for animal fat by subjecting the charge to a current of electricity and adding hydrogen whereby it is claimed that the fat is both rendered and hydrogenated. A combined pressing and rendering process by J. Kernot (*Brit. 468,061*) is constructed so that the pressing equipment is submerged in water. During operation the fat floats and may be skimmed. For better economy of fat in the rendering industry, F. Hinko (*Ole. Fette, Waschse Seife, Kosmetik 1938, No. 6, 3*) recommends that the residues be further extracted by pressure or solvent methods.

The pretreatment of seeds influences the efficiency of oil pressing operations. V. Lava (*U. S. 2,101,371; Fr. 826,831*) recommends mixing ground cocoonut meats with water before pressing. Results of experiments on both cold and hot pressing of roasted flaxseeds according to A. Goldovskii and G. Chistyakova (*Masloboino Zhir.*

Delo 14, No. 2, 7) indicate that roasting causes thermally reversible and irreversible changes. G. Sitnikov (*ibid.*, No. 3, 13) recommends gradual heating to 85-123° C. as a pretreatment for sunflower seed meal. Cooking a succession of batches of cottonseed meats in a stack cooker with hot steam is an improvement for continuous operation by J. Dickinson (*U. S. 2,126,539*). R. Pickard's (*Oil & Soap* 15, 261) method of cooking of cottonseeds includes simultaneous adjustment of moisture content which thus obviates the necessity of a dryer in an expeller setup.

Definite superiority of ribbed over smooth plates in closed presses was demonstrated by T. Lapina (*Masloboino Zhir. Delo* 14, No. 3, 10). However, with wearing of the ribs the efficiency became equal to and even lower than that of smooth plates. A 100 percent greater wear of filter felt with ribbed plates was reported. A new oil press was patented by P. Weston (*Brit. 485,584; Fr. 827,653*).

A well organized test by R. Pickard (*Oil & Soap* 15, 259) revealed a 1.3 percent loss in material during an expeller operation on cottonseed. Definite accounting for the loss was not possible, although, it was suggested that sampling for analysis may have been faulty. Discrepancy of about one-percent in oil yield was revealed to be due to the roasting process on gossypol by V. Ryadovoi (*Masloboino Zhir. Delo* 13, No. 6, 25). The gossypol becomes insoluble during roasting by combining with albuminous products. Hence analytical laboratory extraction yields are always greater than the total oil accounted for in extraction yields plus residual oil in press cake.

Several developments were made in continuous solvent extraction apparatus. The methods included mechanical means for forcing charges countercurrently in both horizontal and vertical equipment, use of superposed zones in an extraction column and a few in which the charge was placed on sieves and sprayed with the solvent (G. Bottaro — *Brit. 482,434*; M. Bonotto *U. S. 2,112,805*; Extractol Process — *Brit. 484,117*; P. Fauth *et al* — *Ger. 659,575 Cl. 23a*; Hansa-Muhle A.-G.—*Brit. 484,794, Ger. 634,152 Cl. 12c.*; A. Olier — *Bull. mat. grasses inst. colonial marseille* 21, 138).

An intermittent type of extractor, which in principle comprises passing individual batches of solvent through vegetable material, was patented by H. Scholler (*U. S. 2,123,212*). Il'in's procedure for solvent extraction (*Masloboino Zhir. Delo* 14, No. 3, 5) involves the use of both solvent spray and vapors. The elimination of "dead spots" in the charge is an outstanding feature of the method.

A heat pretreatment of castor seeds coagulates the mucilaginous matter and allows easier extraction of the seeds according to Helen Donnier (*Brit. 487,366*).

The use of solvents introduces a health hazard. F. Ohl (*Allgem. Oel-u. Fett-Ztg.* 35, 483) classified the solvents now in use according to their toxicity. The physiological effects of the various groups were reviewed. The use of special chlorinated organic compounds as solvents for extraction of soybean oil was patented by C. Dinley (*U. S. 2,097,147*).

An invention by E. Boroughs (*U. S. 2,135,462*) relates to the recovery of maize oil. Grain meal is subjected to a treatment which converts the starch into water soluble products without substantially affecting the maize germ. The germs are separated for solvent extraction.

Extraction methods have considerable influence on the properties of drying oils. Tests showed that the oils extracted by pressure had higher densities and refractive indices, and that the length of the heating necessary for gelation was shorter than that for the ether extracted oil (M-T. Francois — *Compt. rend.* 206, 1321).

Increased chemical and engineering development enter into refining stages of oil processes. Corrosion resisting equipment is necessary. Corrosion test on commercial alloys and metals intended for the oil and soap industry were presented by G. Cox (*Ind. Eng. Chem.* 30, 1349) and F. Vilbrandt and L. Ward jr. (*Trans. Electrochem. Soc.* 73, 13 pp). The most resistant alloy was an 18-8, Chrom-nickel alloy with 3 percent molybdenum. Various types of high speed centrifuges and uses for them in the industry were outlined by F. Dectmars (*Fette u. Seifen* 45, 514). Electrical heating was emphasized by H. Kirchrath (*Seifensieder-Ztg.* 65, 682). Calculations for measurement of herring oil in bulk were prepared by N. Car-

ter (*Fisheries Res. Board Can. Rept. Pacific Sta.* No. 36, 16). Complication was evident in this step; as, for example, the weights of a U. S. gallon of oil at 60° F. of one sample were: 7.701 lbs. when liquid, 7.732 after stearin had separated on holding at that temperature for 24 hours, and 7.751 after holding at 32° F. for 24 hours and then warming to 60°.

Treatment with calcined gypsum was recommended for removal of moisture from oils. (W. Irwin — *Brit. 484,689*.)

Economic methods for refining fats were graphically presented (H. Kirchrath — *Fette u. Seifen* 45, 172). Estimation of amount of caustic and earth necessary, refining losses, cost of each step, and treatment necessary was simplified by use of the data. Refining losses were decreased, better soap stock was recovered, and an optimum refining was obtained by M. Singer (*Seifensieder-Ztg.* 65, 357, 375) with removal of "break" from raw oils before refining. W. Jones (*U. S. 2,113,942*) obtained improved results on fish liver oils by refining them in chlorinated hydrocarbon solvent solutions. The solvent does not dissolve the soap.

Patented innovations on the reagent used in caustic refining include use of caustic in combination with organic peroxides and subjecting oils to caustic treatments, the second being with a weaker lye (Autoxygen Inc. — *U. S. 2,121,545*; P. Beyer — *Fr. 824,700*; Metallges. A. G. — *Ger. 652,351 Cl. 23a*). According to A. Ryabov (*Masloboino Zhir. Delo* 13, No. 5, 13), black cottonseed oil was best refined at 40-5° C. with 10° Be. caustic and 1-1.5 percent of solid salt. Several new mechanical refinements were made in those continuous methods for refining oils that use centrifuges for separating the oils from the soap stock (*U. S. 2,100,274 to 2,100,277*; 2,115,668; 2,137,214; *Brit. 469,204 474,169*; 485,975; *Ger. 660,273 Cl. 23a*; *Fr. 827,903*).

Refining patents covering the use of hydrated amines such as trimethylamine, ethylenediamine, allylamine, and others were issued to Shell Development Company (*U. S. 2,126,334*) and N. V. deBataafsche Petroleum Maatschappij (*Fr. 582,176*). The latter firm (*Fr. 816,289*) also covered the use of allylaminolamines for the same process.

P. Boone (*Soap* 14, No. 9, 25) described continuous methods for acid refining fats. One acid refining patent described removal of acrid taste from soy bean oil with dilute sulfurous acid (M. Bonotto — *U. S.* 2,101,805). E. Kellens (*Fr.* 815,762; *Brit.* 474,504; *Ger.* 657,888 *Cl.* 23a) obtained improved results with the acid process by adding also a small amount of a finely divided metal oxide or salt. W. Kling (*Ger.* 653,302 *Cl.* 23a) patented the use of salts which are capable of maintaining the pH value of the aqueous phase between 1 and 7.

Apparatus and processes for deacidifying oils by distillation of the free fat acids were reviewed by M. Singer (*Seifensieder-Ztg.* 65, 258, 278).

Palm oil for soap making is usually air bleached. Due to difference in composition, Congo palm oil becomes over-bleached; i.e.; yields rancid or unstable soaps. This is due to the high linoleic acid content of the oil (F. Wittka *Allgem. Oel- u. Fett-Ztg.* 35, 187; *Seifensieder-Ztg.* 65, 235, 335). Simple heating to 232-243° F. is a means of bleaching cottonseed oil (L. Moore and A. Norman, *U. S. Pat.* 2,122,260). Combinations of heat treatments and subjection to vacuum were also patented as means of bleaching by R. Dunmire (*U. S.* 2,116,344) and B. Clayton and B. Thurman (*U. S.* 2,110,789). A continuous bleaching is accomplished by the use of hydrogen peroxide as the bleaching agent (F. Franz — *U. S.* 2,110,649).

Well known methods for bleaching fats were described by C. Kemp (*Soap* 14, No. 6, 24). M. Singer (*Seifensieder Ztg.* 65, 701, 722) described several economic combinations of bleaching agents. The cost data for various methods of bleaching in Germany were given. Decolorization of fats by Japanese acid clay was fostered by K. Yamamoto and M. Koda (*Waseda Applied Chem. Soc. Bull.* 15, No. 2, 6). Newly patented bleaching agents included the finely powdered colloidal substances from fresh or salt water mud and a mixture of charcoal and silica gel (J. Carpzow — *U. S.* 2,093,348; H. Hofmann — *Fr.* 822,338). Combination bleaching and refining of fat was accomplished by J. Harris and W. Welch (*U. S.* 2,105,478) by treatment with both

sodium carbonate and activated carbon. The soap formed was removed with the carbon in a filter press.

Three inventors devised methods of treating clays. E. M. Slocum (*U. S.* 2,117,223) recovered residual oil from it by heating in salt solutions. The released fat was skimmed off. Reactivating clay was accomplished by heating to 1600° F. for 4-5 seconds or by boiling in organic solvents. (H. Kaufman — *U. S.* 2,118,310; G. R. Fuchs — *Brit.* 482,549.)

A method of recovering used palm oil in the tin plate industry was invented (Hoesch A.-G. — *Ger.* 663,164 *Cl.* 23a). This oil contained a large quantity of tin soap. The oil is removed by extraction with trichloroethylene. The fat acid is split from the tin with inorganic acid and re-esterified with glycerine. A process for converting teaseed oil into an edible product by G. Barsky (*U. S.* 2,126,527) is similar to the above. The oil is split, the fat acids are distilled and reesterified with glycerine.

A continuous deodorization method described by D. K. Dean and E. H. Chapin (*Oil and Soap* 15, 200) comprises passing oil continually through a deodorizing tower which is supplied with steam injectors and vacuum developing accessories. The operation is less subject to variation than the batch system. Automatic control is easily adapted. Several new mechanical features were invented for steam deodorizing apparatus (R. C. Newton and W. Bollens — *U. S.* 2,124,707; J. Stewart — *U. S.* 2,136,029; *Brit.* 477,717; L. Moore — *U. S.* 2,122,260). Reviews of deodorization equipment are presented by M. Singer (*Seifensieder Ztg.* 65, 487, 507) and F. Wittka (*Allgem. Oel- u. Fett-Ztg.* 35, 11).

Preliminary cooling to 5° C. followed by crystallization at 1.5-2.5° C. reduces crystallization time in the winterizing process for cottonseed oil from 18 to 10 hours when compared to crystallization at 2.5-5° C. (N. I. Kozin and B. Azarkh — *Voprosy Pitaniya* 7, No. 2, 23). A patent issued to Edeleanu G. m. b. h. (*U. S.* 2,113,960) covers the use of carbon disulfide as a solvent with cooling to -15° C. in the destearinization processes.

Methods for production of phosphatides comprise treatment with selective solvent to precipitate the

phosphatides, removal of these by filtering or centrifuging and concentrating by evaporation of water from the emulsion (Hansa Mühle A. G. — *Ger.* 661,545; Noble and Thorl G. m.b.h. — *Ger.* 653,878 *Cl.* 53i I. Grabovskii — *Maslo-boino Zhur. Delo* 13, No. 5, 13).

A simple method for production of carotene described by T. Buckley (*Malayan Agr. J.* 26, 258) is simply acetone extraction of the used fullers earth from palm oil refining. Two methods for recovering waxes from marine animal oils are based on the same principle as the analytical determination for unsaponifiable (Zschimmer & Schwarz Chemische Fabrik Dolau *Ger.* 656, 25 *Cl.* 23a; R. Nichols — *U. S.* 2,103,193).

Splitting data on various oils, with several catalysts at 7 to 12 atmospheres pressure and 2 to 8 hours time were tabulated by K. Humhal (*Chem. Listy* 32, 150). H. Sturm and J. Frei (*Fette u. Seifen* 45, 219) developed an equation which indicates the degree of splitting. The degree of splitting at equilibrium (X) was expressed as a function of the amount of water (W) used in relation to fat and also of the saponification value (VZ) of the fat. The equation was:

$$X = \frac{3100W}{31W + VZ}$$

A new method for splitting fats or liberation of fat acids comprises heating the fat with distillation residues of colophony (Albert Prod. Ltd. — *Brit.* 486,341; Kurt Albert G. m.b.h. — *Fr.* 820,492). Several recent patents were concerned with continuous or semi-continuous methods of splitting. The principle of these methods was passing water and oil through a heating zone either in the same direction or counter-currently. These were also combined with distillation facilities. (*Colgate-Palmolive Peet Co.* — *Fr.* 822,503; *U.S.* 2,139,589; E. Hoffman — *Fr.* 817,886; *Brit.* 477,197; American Lurgi Corp. — *U. S.* 2,108,990; Proctor & Gamble Co. — *Brit.* 466,596; Henkel & Cie — *Ger.* 637,938 *Cl.* 23d.). Simultaneous splitting and hydrogenation of an oil were carried out according to H. Kaufmann (*Brit.* 468,170; *Fr.* 811,797) by hydrogenation in an amount of water equal to the amount of oil. Combined extraction and splitting was possible by drying the oleaginous

pulp material, extracting with a hot alcohol-benzene mixture containing sulfuric acid and filtering (W. Rees — *U. S.* 2,124,168).

Fat acid stills were described in patents issued to New Process Fat Refining Corp. (*Ger.* 665,824 Cl. 23d) and V. Mills (*Can.* 369,451). They are built on the principle of spraying heated fat acids into a column against a counter-current of superheated steam which is re-used. Another continuous distillation process comprised heating the fat acids in a thin layer on a moving band enclosed in a vacuum chamber (F. Meyers — *Ger.* 656,308 Cl. 12a).

Many inventions dealt with improving short-path distillation apparatus and its uses. With some materials the oils or fats can be distilled from their sources, thus eliminating extraction. Other patents claimed improvements in separation of vitamins and sterols, and production of an improved and odorless soybean oil. These patents which were issued to Eastman Kodak Co. and to Imperial Chemical Industries Ltd. (*) are as follows: *U. S.* 2,117,776, 2,177,802, 2,117,803, 2,124,879, 2,126,466, 2,216,467, 2,288,223,* *Brit.* 479,816, 480,265,* 482,881 to '4, 485,549, 487,697, 488,878, 489,623; *Fr.* 811,766. C. Bills *et al* (*J. Biol. Chem.* 126, 241) used short-path distillation in separating vitamins D in their work to substantiate the evidence that cod liver contains several vitamins D. Work by M. Tsujimoto and H. Koyanagi (*J. Soc. Chem. Ind. Japan* 41, 41) demonstrated that fat acid-esters of high molecular weight alcohols can be separated from certain marine oils by distillation.

Reviews on hydrogenation of fats were prepared by B. Wolff (*Prze-glad Chem.* 2, 385-94), L. Mander-son (*Fette u. Seifen* 45, 251) and anonymously (*Seifensieder-Ztg.* 64, 901, 921, 941). Mander-son's review was on the continuous methods. New developments were emphasized.

M. Morlock (*U. S.* 2,134,571) added to hydrogenating apparatus a means of spraying oil into a hydrogen atmosphere above the oil level. A hydrogen preheater was added as an accessory to hydrogenation apparatus (S. M. Konstantino — *Russ.* 45,029). Lever Bros. Co. (*U. S.* 2,123,332) patented the pretreatment of hydrogen which comprises the usual

method of purification plus passing it over hot nickel, nickel-iron, nickel-Chromium, or nickel-aluminum catalyst.

A few inventions were on control of hydrogenation to obtain special effects. A. Barbour (*U. S.* 2,125,215, O. Brucke (*U. S.* 2,127,716) and M. Schurman (*U. S.* 2,111,573) used low temperatures and hydrogen under pressure. A low yield of saturated fats and non-destruction of vitamins are the advantages of the methods. H. Moore (*U. S.* 2,136,655) preferred hydrogenation at higher temperature with use of a relatively inactive catalyst for production of a margarine fat from soybean. The finished fat preferably contains less than 10 percent linoleic glycerides, 20 to 50 percent isooleic acid and saturated glycerides not to exceed 20 percent.

Colorimetric studies on hydrogenation by C. F. Holmboe (*Ber.* 71B, 532) yielded information on the energy changes of the reaction at various temperatures. The mechanism of hydrogenation was followed on peanut oil (R. Viollier and E. Iselin — *Mitt. Lebenson Hyg.* 29, 1) sunflower seed and cotton seed oils (G. Ravich — *Tech. Phys. U.S.S.R.* 4, 1020). The data showed the changes in characteristics and properties of the oils with progress of hydrogenation.

The most outstanding work of the year on the course of hydrogenation of fats was by T. P. Hilditch and his co-workers (*J. Chem. Soc.* 1937, 1767; *J. Soc. Chem. Ind.* 57, 363T). When cottonseed oil and lard were hydrogenated the palmito di-unsaturated fats passed to palmito stearins before much tristearin was produced from unsaturated tri C₁₈ fats. The tendency during hydrogenation was towards the attack of the more unsaturated until both components reached the same degree of unsaturation after which hydrogen of both proceeded simultaneously and indiscriminately. However, hydrogenation of less unsaturated components proceeded to some extent while the more unsaturated components were still being reduced to that stage. Partial hydrogenation of a 50:50 mixture of di- and trioleins gave 39 percent tristearin. A mixture of 75 percent di- and 25 percent triolein gave only a trace of tristearin. Less homogeneous conditions of hydrogenation, such as by the drip process, yielded less

selectivity. The products contained a greater proportion of stearic acid in the fully saturated components due to complete hydrogenation of the original tri-unsaturated C₁₈ glycerides.

S. Chatterjee *et al* (*J. Ind. Chem. Soc.* 15, 433) pointed out that the development of isooleic acid during hydrogenation can be ascribed to the hydrogenation catalyst acting to promote a conjugated state in linoleic acid and then to partial hydrogenation of the latter. Development of a Diene value in oil boiled with finely divided metal was submitted as evidence for this theory.

The system of hydrogenation of oils in presence of ethyl alcohol was studied by V. Puzanov (*J. Applied Chem. U.S.S.R.* 11, 670). Linseed oil hydrogenated by this system to a solid fat still contained linoleic acid. Some catalysts promoted the formation of isooleic acid. The presence of copper in the catalyst retarded the decomposition of the ethyl alcohol to carbon monoxide and methane. With mixed catalysts the yielded products contained least isooleic acid and free fat acid and formation of completely saturated components was retarded. Methods for hydrogenation of marine animal oils by this system were described.

A completely new innovation in hydrogenation, still in the experimental stage is the method of E. Zappi and H. Degiorgi (*Anales Assoc. Quim. Argentina* 26, 33) and comprises passing hydrogen through a tube containing a tungsten filament which dissociates the hydrogen. The atomic hydrogen readily converts oleic and elaidic acid to stearic acid.

Elaidinization in combination with hydrogenation for hardening fish oil was patented by Armour & Co. (*U. S.* 2,119,141). H. Waterman and C. V. Vlodyrop (*Rec. trav. Chim.* 57, 629) pointed out that hydrogenation was always accompanied by isomerization. This was demonstrated by elaidinization of oleic acid at 290° in presence of Ni-kieselguhr catalyst. Bertram (*Öle, Fette, Wachse Seife Kosmetik* 1938, No. 7, 1) reported that only 66 to 67 percent oleic acid was isomerized whether the original acid was pure or mixed with paraffin or with stearin. It was definitely proved that the reaction is trimolecular. Iso-acids can be separated from hydrogenated fat mixtures by precipitation with mercury acetate

and decomposing the mercury salts with acid (E. Oleshevskaya *et al*, *Masloboinoe Zhir. Delo*. 13, No. 6, 27).

In addition to the well known hazards with hydrogenation equipment, it was recorded that active hydrogen may be formed and may combine with decomposed phosphorus compounds to give phosphine which explodes spontaneously (V. Smirnov—*Masloboino Zhir. Delo* 13, No. 6, 15). This explains explosions with oils rich in phosphatides. Removal of phosphatides by previous refining was recommended.

The experience in the Russian hydrogenation industry was gathered into the form of a symposium (*Vsesoyuz Nauch. — Issledovatel. Inst. Zhur. Hydrogenation of Oils 1937*). Methods of preparing almost all types of catalysts and results from their use were recorded. Catalyst poisons, methods of refining, equipment, chemical engineering problems and other hydrogenating problems were featured in the investigations and reviews.

Electrical precipitation of nickel as hydroxide followed by reduction in the usual manner is an innovation in catalyst manufacture (Lever Bros. — *U. S. 2,123,342*). S. Faulkner (*U. S. 2,140,400*) found advantages in preparing the carbonate and boiling this to remove part of the combined carbon dioxide before reducing. K. Coons (*U. S. 2,120,958*) reduced nickel carbonate, in the preparation of catalyst, by hydrogen at low pressure and at temperatures from 175° C. to about 500° C. W. Baenah and W. Klaphake's (*U. S. 2,112,643*) method comprised dropping the metal oxide through hot hydrogen and then through a cold cooling gas. The above inventors claimed various advantages for their respective catalysts, among them, ease of preparation, high activity, and good selectivity during hydrogenation. F. Durrans and B. Sully (*Fr. 822,222; Brit. 478,386*) recovered catalyst while still in the oil by blowing superheated steam through the oil to oxide the metal and then reducing by passing hydrogen through the suspension.

Data presented by H. P. Kaufmann and co-workers (*Fette u. Seifen* 45, 223, 304) demonstrated the improvement one can expect under various conditions with a copper-nickel catalyst. Investigation with Ni-Cu formate catalyst with kieselguhr carrier showed that

10 per cent copper based on nickel accelerated early stages of hydrogenation and that the maximum effect was with a 1:1, Cu:Ni catalyst. Without carrier copper up to 40 percent reduced catalyst activity, while larger amounts had an activating effect. The theoretical aspects of the work were discussed. A method was described for preparing Ni-Cu catalyst in pyridin solution from the formates. The pyridin was removed from the reduced catalyst by evaporation. With this procedure maximum catalyst activity was shifted from a 1:1 ratio of Cu:Ni to a 7:3 ratio. The addition of cobalt to the catalyst had no effect. Tabulated and graphical data on the use of Ni-Cu, Ni-formate and several Ni-Cu catalysts were also prepared by W. Norman (*Fette u. Seifen* 45, 664). He described an apparatus made from ordinary laboratory glassware for small scale experimental work on catalysts. A review and discussion of the theories regarding improvement of nickel catalyst by copper suggested that the copper may act as carrier, it may prevent sintering or it may enter into a crystal formation with nickel, thus producing greater activity. The odor of fats hardened with Ni-Cu catalyst was weaker and somewhat different than the odor of fat hardened with pure nickel catalyst, but the odor increased rapidly on standing in air. A comparison of various Cu-Ni catalysts was also recorded by E. Yamaguchi *et al*, (*J. Soc. Chem. Ind. Japan* 40, 366B). Contributions on preparation of economical Cu-Ni catalyst and its recovery were made by Russian investigators (M. Gusev *et al* — *Masloboino Zhir. Delo*. 14, No. 2, 12; A. Laptin — *ibid*, 13, No. 6, 16; G. Klein *et al* — *ibid*, No. 4, 31). An active catalyst was prepared from Cu-Ni waste of electrolytic copper production. Difficulty in recovering this type of catalyst was due to the relatively low solubility of copper in dilute acid.

Using Raney catalyst in hydrogenation of peanut oil, R. Escourrow (*Bull. Soc. Chem.* 5, 1184) reports that the hydrogenation stopped at the stage where the linoleic was converted into oleic acid. It was also said that constituents which produce odor and rancidity can also be removed with the use of the catalyst. One French patent was issued on manufacture of Raney type catalyst (*Fr. 821,-*

015). M. Raney (*U. S. 2,139,602*) devised a process for recovery of catalyst. The spent catalyst was ignited to destroy oil and oxidize the nickel. This was mixed in a crucible with glass flux, borax and aluminum powder, and the mixture was ignited. The nickel alloy settled to the bottom while silica and borax glass were removed from the top as a slag. The alloy is treated with caustic soda to yield active powdered nickel.

Catalyst for continuous hydrogenation can be prepared by passing nickel carbonyl over metal grates, and heating to 100° C. The metal plates on the grates (J. Francon — *U. S. 2,132,613*). Nickel wire was reported to be the best catalyst for the continuous process (V. Athavale and S. Jatkari — *J. Indian Inst. Sci.* 20A, 95). Monel metal, ferry wire (Ni:Cu::54:46) were poor catalysts.

With use of formate catalyst a good grade of fat was produced from a 1:1 mixture of cottonseed oil and sunflower oil (E. Etinburg—*Masloboino Zhir. Delo*. 14, No. 3, 14). Other catalysts yielded dark colored, off-flavored products. The presence of up to 0.77 percent phosphates and 1.42 percent phytin caused no deactivation of the catalyst (M. Smolino-*ibid* No. 2, 11). The course of hydrogenation of marine animal oil with nickel formate catalyst was tabulated by T. Pedersen (*Hvalradets Skrifter Norkse Videnskaps-Akad. Oslo* No. 16, 31). A high degree of selectivity was evident.

Considerable disagreement is apparent on the physical and chemical phenomena of oil thickening and dryng. T. Bradley (*Ind. Eng. Chem.* 30, 689, 1087) maintained that the general colloidal aspects are secondary in importance. Departure from polymerization theory was attributed to those cases where intramolecular additions, partial hydrolysis, or other extraneous reactions have occurred. These are more prominent with linseed oil than with other oils. The author supported the chemical theory which he feels was put on a firm basis by the quantitative evidence that functional groups disappear at a rate predicated by theory. L. Auer's (*Ind. Eng. Chem.* 30, 1087) reply to the above contains references to literature which uphold his gas coagulation theory. C. Kappelmeier (*Chem.-Ztg.* 62, 821, 843; *Paint, Oil Chem. Rev.* 100,

No. 1, 5; No. 2, 9; No. 3, 9, 19) in reviews on the subject concluded that the preparation of all types of stand oils is based not on more or less vague colliodo-chemical processes but on purely structural changes of the fat acid glycerides.

Hot drying of oil films was recommended by V. Kisselev (*Org. Chem. Ind. U.S.S.R.* 4, 502). Such films had a greater hardness and resistance to water. Graphical presentation of effect of humidity during drying of linseed, poppyseed, sunflower seed, and walnut oil was given by I. Auer, (*Paint Varnish Production Mgr.* 17, 12, 16, Nov.) For linseed oil paints there was a critical oil content which gave the best weather resistance with red lead pigments; while with zinc white, lead white, and red iron oxide the critical oil content was of little importance (H. Matthijsen-Verfkronek 11, 136). The effect of the type of vehicle could not be correlated with weather-resistance results. D. Nicholson and C. Holley's (*Ind. Eng. Chem.* 30, 563) drying curves of linseed oil in presence of light indicated that the opacity due to pigments retarded drying. The drying time was shortest for unpigmented films and increased by addition of white lead, zinc oxide, and titanium oxide in that order. G. Petrov *et al.*, (*Org. Chem. U.S.S.R.* 5, 25) demonstrated that the linseed oil used for linnoxyn products oxidizes more energetically with hydroxycellulose filler than with hydrocellulose. Mathematical equations for the speed of oxygen absorption by linseed oil films were developed by S. Iwai (*Proc. Phys-Math. Soc. Japan* 20, 223). Laboratory investigations by V. Zinov *ev* and A. Orlov (*Org. Chem. Ind. U.S.S.R.* 5, 15) showed that polymerization of linseed oil can be accelerated by reducing the pressure.

Laboratory experiments on heat treating tung oil by D. Davidson (*Paint, Oil & Chem. Rev.* 100 No. 17, 11) led to the following conclusions: On exclusion of air a decrease in tendency to wrinkle is not obtained without diminishing drying tendency. Presence of air increases gelatinization tendency and also darkens product. M. Tachimori (*J. Soc. Chem. Ind. Japan* 41, 39, 100, 142) pointed out that gelation time of tung oil is affected by the size of the vessel. Other information included graphical presentations of changes in viscosity and refractive index with treat-

ment. The polymerization reaction was said to be bimolecular. Tabular and graphical data on the changes in viscosity, molecular weight, acid number, saponification value, specific gravity and refractive index of both oiticica and tung oils was prepared for the American literature by S. O. Sorenson *et al.*, (*Ind. Eng. Chem.* 30, 211). J. Stancil (*U. S. 2,139,864*) improved oiticica oil standoil with removal of stearin by crystallization.

A patent review on production of standoils was presented by A. Foulon (*Fette u. Seifen* 45, 355). New developments in treatment of drying oils were: an apparatus for continuous heating under pressure to be followed by vacuum distillation equipment (B. Thurman — *U. S. 2,110,780*), a continuous process using activated nickel as a catalyst (R. Priester-Brit. 470,498), equipment to heat treat under 1,000 lb. per square inch pressure of carbon dioxide (Continental Can Co. — *U.S. 2,120,044*), use of oxidizing agents to destroy natural antioxidants (T. Hodgins — *U.S. 2,133,894*) and methods of mixing gelling oils with other oils with polymerization technic to give an ungelled standoil (F. Reece and M. Taggart — *U.S. 2,113,358*).

Oils thickened with sulfur and selenium were found to be superior to oils thickened by the usual method (H. Waterman *et al.* — *J. Soc. Chem. Ind.* 57, 87). Low acidity and clearness were the advantages possessed by the sulfur and selenium thickened oils. Means of polymerizing oils in presence of sulfur dioxide were developed (Imp. Chem. Industries Ltd. — *Brit. 480,677*).

PRODUCTS

The shortening fats used in bakeries influence the various properties of baked goods to different extents. For this reason baking formulas must be adjusted to the fat used. Belle Lowe and her co-workers (*Iowa Agr. Exp. Sta. Research Bull.* 242) have prepared a series of tables showing the effect of physical and chemical characteristics of lards and other fats on their culinary value. This first of a series of publications deals with shortening value in pastry and cookies. In addition to the effect produced by various fats there is information on influence of manipulative technic, baking time, and composition of mix. J. Grossfeld and H. Damm (*Z. Untersuch. Lebensm.* 75, 137) investigated the

behavior of sugar and butter additions in the preparation of several test cakes. In most cake formulas the amount of butter fat can exceed 10 per cent based on the amount of flour. This corresponds to 4 per cent total fat in a sugar-containing cake. Reviews on the requirements of fats used in baked products and on shortening economy respectively, were prepared by F. Wittka (*Seifensieder-Ztg.* 65, 650, 681) and W. Hofmann (*Angew. Chem.* 51, 721).

A shortening compound of liquid fat and solid fat to which was also added a solution of phosphoric acid salts was patented (Soc. C. Schlieper, *Fr. 825,542*). A. Müller (*Hung.* 177,214) recommended adding calcium salts of glycerol phosphoric acid to dough. It is assumed that this is usually part of the shortening constituents. C. Morris (*U.S. 2,125,849*) found that small amounts of lecithin and triethanolamine improve shortening.

Various methods of preparing and using mono- and di-glycerides in cake or shortening were the subjects of many patents (*U. S. 2,132,393 to 2,132,398; 2,132,406; 2,132,416; 2,132,417; 2,132,436; 2,132,437; 2,132,687; 2,132,700; 2,132,701*). H. Schrader and H. Stahl (*Ger 663,065 Cl. 23; U. S. 2,121,305*) supplemented the mono- and di-glycerides with reaction products of fat acids and split proteins to further improve the emulsifying qualities. In the usual production of fats containing excess glycerin, H. H. Young and H. C. Black (*J. Am. Chem. Soc.* 60, 2603) demonstrated that chiefly α -monoglycerides were formed. Methods of synthesis for various mono- and or di-glycerides with the aid of trityl-compounds were reviewed by P. Verkade (*Fette u. Seifen* 45, 457).

Shortenings comprising fat emulsified in sugar solutions with condensation products of higher fat acids and polysaccharides as emulsifiers were invented by H. Schou (*Brit. 489,111; 472,086; Fr. 825,701*). A similar emulsifying agent was used in the manufacture of non-blooming chocolates (W. Eipper, *U.S. 2,137,667*). The inventor specified that the fat acids used in its preparation were those of natural chocolate.

Other emulsifiers which were patented include fat acid derivatives of hydrophilic radicals (F. Cahn and B. Harris, — *U.S. 2,111,042*), a mixture of fat acids, sol-

uble borates and disodium phosphate (H. Bennett and F. Braude, — *U.S. 2,095,955*) and partially saponified wool fat. (I. G. Farbenindustrie — *Brit. 483,315*). A general review of emulsions was prepared by H. Bennister and A. King (*J. Soc. Chem. Ind. 57, 717*).

A full description of the recently developed oxidized oil emulsifying agents for margarin was prepared (A. Prokhorov and E. Klyachkina — *Masloboino Zhir. Delo 14, No. 2, 26*). Refined sunflower or mustard oils are air blown at 120-30° C. for 6 hours with 5 liters of air per kilo of oil. At this point the viscosity reaches 68.6-71.2 and content of oxy acids 35.8-43.5 per cent. This is deodorized with superheated steam. Good dispersion, consistency, stability and retention of water are obtained with 0.8 to 1.5 per cent of the product. A new patent on the process was issued to H. Schou (*Brit. 478,697*).

Innovations for preparation of the aqueous ingredient for margarin have been presented. F. Seelein (*Ger. 651,699 Cl. 53h*) cultured milk, added salt and removed the precipitate that was formed. Malt seasoning was added to the milk used in the manufacture (B. Behrend — *Ger. 654,742 Cl. 53h*). To improve the keeping qualities of the finished product H. Lundsgaard (*Brit. 468,810*) saturated the ripened milk with carbon dioxide and emulsified in closed container filled with gaseous carbon dioxide. H. Tillisch (*Dan. 54,611*) colored margarin by using part of the fat stock to extract vitamin-containing coloring matter from plant substances.

A historical review of the mechanical technic involved in margarin manufacture was prepared by A. Robinson (*Oil & Soap 15, 203*). This reflects a trend toward the use of continuous equipment. A new process described comprises mixing ingredients, supercooling, and discharging continually into a horizontal tube. While passing through the latter tube the product "sets". The procedure of supercooling fat and emulsifying at the point was patented by R. C. Newton and L. C. Brown (*Can. 376,083*). Another patent (C. Walters — *Can. 372,464*) protected a method of cooling and forcing the mixture through an orifice under pressure.

The information on butter was too bulky for complete presentation. The major portion was already known facts and methods by

which trade publications stimulate the industry's technicians towards greater knowledge and better technic. E. Bird (*Iowa Agr. Expt. Sta. Res. Bull. 227, 173*) prepared data on the relations between cream acidity, churning loss and churning time. The losses varied little in the pH range 7.0 to 5.5. Losses dropped sharply and practically in linear fashion from pH 4.8 to 4.5. The churning loss data correlated very well with electrokinetic potentials of the fat globules. A theory of churning was suggested. The utilization of labile protective materials to stabilize foam interfaces decreases their concentration at the fat-serum interface. When the labile to nonlabile protective material ratio is small the fat globules merge and lose their identity. This merger weakens the forces at the force centers of the fat globules to such an extent that the nonlabile materials are released from the fat globule surfaces and are incorporated in the buttermilk while the fat unites to form butter.

The removal of moisture from butter to enhance its keeping qualities is a foreign practice. The methods and chemistry involved in this technic were reviewed by W. Ritter (*Mitt. Lebensm. Hyg. 28, 206*). The treatment allows the lecithin to remain in the product. It was assumed that butter contains lecithin-protein combinations, which split during rendering and lecithin passes into the fat.

Chemical engineering advances have made it technically possible to synthesize many products from fats. In the past these new derivatives have opened many new industrial channels for fats and will continue to do so to a greater extent. The compounds of special interest are dicarboxylic acids, alcohols, aldehydes, nitriles and esters. Some of the products are used as such, but their main outlets are as intermediates for emulsifiers, detergents, plastics, resins and other preparations.

Dicarboxylic acids are prepared from fats by oxidation with hypochlorites (Armour & Co.— *U.S. 2,133,008*). These acids e.g., suberic, azelaic and sebacic, are used in the manufacture of plastics and resins. Another patent (*U.S. 2,107,062*) assigned to the same concern was on improving fish oils for industrial purposes. The oils were partially hydrogenated and then hydroxylated to yield a substi-

tute for industrial castor oil. Castor oil-like products were also prepared from soybean oil by treatment with hydrogen peroxide in glacial acetic acid solution (R. Oda — *J. Soc. Chem. Ind. Japan 41, 195*). Another source of hydroxylated fats was the hydrogenation of oiticica oil as described by J. Berliner and C. Sly (*U.S. 2,121,580*). A method for separating hydroxy fat acid from castor oil was described by M. Jakes and J. Hökl (*Chem. Listy 32, 15*). The care necessary for preventing the formation of di-, tri- or even polyricinoleic acid was emphasized.

Fat acids were converted to alcohols by hydrogenation at 250 to 400° C. and 13.5 atmospheres pressure (W. Lazier — *U.S. 2,109,844*). The use of nickel, cobalt or copper with magnesium oxide as a catalyst for the process was patented (I. G. Farbenindustrie A.-G. — *U.S. 2,121,367-8; Brit. 484,995*). Fatty alcohols were also prepared by hydrogenating copper soaps under high pressures (S.-S. Ueno *et al* — *J. Soc. Chem. Ind. Japan 41, 62*). The use of copper-cadmium catalyst made possible the reduction of the carboxylic radical to a hydroxyl group without saturation of the fat acid (Böhme Fettchemie G.m.b.H. — *Fr. 819,255*). The same concern (*U.S. 2,127,367*) covered the use of catalyst poisons, i.e., sulfur, phosphorus compounds, carbon monoxide, etc., to control the hydrogenation in the same direction. Data on producing the unsaturated higher alcohols by the use of zinc-chromium oxide catalyst were presented by S. Komori (*J. Soc. Chem. Ind. Japan 41, 219*). A yield of 90 per cent alcohols from an oil was obtained by hydrogenating at 330° C. for 1.5 hours at 100 atmospheres pressure with 20 per cent catalyst. The manufacture of higher fatty alcohols was reviewed by C. Mullin (*Soap 14, No. 12, 27*).

Data on the preparation of ketones by heating fat acids with manganese catalysts were obtained by K. Kino (*J. Soc. Chem. Ind. Japan 41, 91, 311, 437*). Foaming was prevented by using 50 per cent of the chemical equivalent of manganese oxide or carbonate instead of the usual 100 per cent. The product was brown to black with manganese oxide, but pale with manganese carbonate. Heating magnesium powder with fat acids also yielded ketones. These were easily separated from the magnesium soaps by extraction with or-

ganic solvents. With manganese, zinc and magnesium catalysts the amount of frothing was dependent upon the amount of soaps formed. The thermal decomposition rates of soaps of the above metals were ascertained. The data should aid in control of the process. Properties and characteristics of ketones prepared from hydrogenated sardine, coconut, hardened rapeseed and soybean oils were also presented. Ketones may also be prepared by heating fat acids in a vapor phase in presence of a chromite catalyst according to a patent assigned to E. I. du Pont de Nemours & Co. (U.S. 2,108,156). The same concern owns a patent (U.S. 2,108,133) on converting the ketones to alcohols by hydrogenation.

Fat acids may be converted into aldehydes by high temperature hydrogenation with zinc, copper and cadmium chromite catalysts (W. Lazier — U.S. 2,105,540), by passing fat acids with formic acid at high temperatures over a mixture of pumice and manganese carbonate that has been reduced with methanol vapors (O. Schmidt *et al* — Ger. 660,735 Cl. 120) and by preparing the alcohol and passing it over silver containing catalysts at temperatures over 400° C. (D. Babcock and J. Wertz — U.S. 2,123,520).

Solutions or dispersions of semi-gelled fats in organic solvents were prepared by E. I. du Pont de Nemours & Co. (U.S. 2,120,083; 2,120,089) for use in cellulose compositions. Another preparation by the same (U.S. 2,091,988) was dilauric-acetic glyceride, which they use as a softener for nitrocellulose. Two other cellulose compositions plasticizers were esters of fat acids with alcohols (H. P. Smith — U.S. 2,108,452) and aromatic derivatives of fat acids (Siemens-Schuckertwerke A.-G. — Fr. 821,865).

R. Bhattacharya and B. S. Gidvani (*London Shellac Res. Bur. Tech. Paper 14*) demonstrated that shellac (or lac) combines with mono- and or di-glycerides to yield a varnish that compares favorably with other varnishes made from rosin or ester gum. This same method was suggested by W. Schütze (*Fette u. Seifen 45, 357*) for incorporating rosins in oils used for varnish.

Several rubber-like compounds were made from oils. W. Butler's (U.S. 2,120,124) preparation was a blown mixture of drying oils,

resin and ammonium hydroxide. L. Auer (U.S. 2,106,708) obtained a solid product by heating linseed oil with lithium sulfate. Castor oil when heated with boron compounds yields a tough resilient product (I. Colbeth — U.S. 2,125,544). The products made by H. Kaufmann and his coworkers (*Ber. 70B, 2519; Fette u. Seifen 45, 177*) by the action of sulfur chloride on oils were also elastic substances. Theories on the mechanism of this reaction were also suggested.

The resins patented were: condensation products of oil and any of several organic acids, e.g., phthalic, phenols, etc. (R. Priester — U.S. 2,117,255; N. V. Industriele Maatschappij voorheen — Fr. 819,829; W. Koenig — U.S. 2,108,893), reaction product of urea, glycerol, phthalic anhydride and linseed oil (C. Ellis — U.S. 2,106,523), reaction product of phthalic anhydride, triethanolamine and a drying oil (C. Ellis — U.S. 2,106,522), and condensation products of drying oils with aldehydes, alcohols or ketones (W. Koenig — U.S. 2,135,976). Operating data on the reaction of phthalic anhydride on glycerol for the production of resins were prepared by S. Hirano and K. Ohashi (*J. Soc. Chem. Ind. Japan 41, 90*). V. H. Turkington *et al* (*Ind. Eng. Chem. 30, 984*) fostered the use of phenolic resins in linseed oil films. Resistance to alkali and boiling water were in general increased by the addition of the resin.

Insecticides which were derived from fats were: a nicotine salt of coconut oil fat ester of glycerol monosulfate (B. R. Harris — U.S. 2,134,917), preparations of thiocyanacetates of fatty alcohols (A. Epstein & B. Harris — U.S. 2,123,186) and a complex compound of three molecules of copper arsenate united with one molecule of copper salt of a fat acid (F. Dearborn — U.S. 2,104,584).

Many patents on preparation and uses of nitriles derived from fats were issued to Armour & Co. (U.S. 2,107,904; 2,116,472; 2,125,851; 2,125,853; 2,133,007; 2,135,327; *Brit. 479,813; 484,352; 484,353; 488,808; Fr. 812,369*). Preparation of the nitriles was by the action of liquid ammonia on the fat acids. These may be polymerized or cracked to obtain nitriles of various molecular weights. Separation of nitriles from a cracked mixture

which contains hydrocarbons was accomplished with the use of selective organic solvents. The products are used as ingredients of lubricants to increase "oilness" and some are added to motor fuels to impart anti-knock qualities to the fuel. Chlorinated ketones and other ketones of fat acid derivation were also prepared for use in lubricating oils by the same concern (U.S. 2,100,287; 2,107,905). A review of recent developments in the preparation and use of fat nitriles, amides and ketones for extreme pressure lubricants was prepared by the research staff of Armour & Co. (*Natl. Petrol. News 28, No. 50, 59*). R. Greenhalgh (*Brit. 488,036*) prepared nitriles by reacting carbonyl chloride with a primary amide of a fat acid. The use of amino alcohols, derived from fat acids, to deter sludge formation in lubricating oils was patented by M. Dietrich (U.S. 2,104,796).

Polymerized products of non-drying or semidrying oils were recommended as supplements for mineral oil lubricants (N. V. de Bataafsche Petroleum Maatschappij, *Brit. 478,927*). Polymerization in this case was in the presence of boron fluoride catalyst and the products were separated with the use of solvents. J. Wesson (U.S. 2,115,354-5) prepared lubricating oil blends comprised of polymerized soybean oil, mineral oil and a small proportion of isopropyl alcohol.

Cracking of oils and fats to produce mineral-like oils by E. Lege (*Brit. 485,123*), was accomplished by distillation at 250 to 600° C. in the presence of alkali salts. In an investigation on pyrolysis of coconut oil, phosphoric acid, calcium oxide, iron and steam were used as catalysts (S. Balce *et al* — U. *Philippines Nat. and Applied Sci. Bull. 5, 65, 151*). With calcium oxide, iron turnings and steam as catalysts the yield averaged 73.8 per cent of the volume taken. The product was glycerides 11, fat acids 7 and hydrocarbons 80 per cent. With acid catalysts the product was principally fat acids.

Chaslyn balls, tablets, discs, etc., for hydrometric units which when placed in liquid, will sink or swim according as the density of the units is greater or less than that of the liquid under test are prepared by mixing hydrogenated castor oil and chlorinated naphthalene (Chaslyn Co. — U. S. 2,133,300).

A monograph giving preparation, properties and uses of metallic soaps was written by L. Ivanovsky (*Seifensieder Ztg.* 65, 671, 713, 733, 752, 771, 792, 812). The uses discussed pertain to paint driers, organic synthesis, paints, lacquer, varnish, dyeing, glass and porcelain painting, dry cleaning, lubrication, wax, candles, polishing agents, resins, cosmetics, medicine, beverages and other miscellaneous uses. A discussion of the properties of aluminum stearate lubricating greases was by F. Licata (*Ind. Eng. Chem.* 30, 550). Pat-

ents on greases containing metallic soaps were issued to G. Kaufmann (*U. S.* 2,108,016; 2,108,672), L. Brunstrum and E. Adams (*U. S.* 2,108,643-4) and G. Suit (*U. S.* 2,121,748).

General information on the properties of several metallic soaps as related to their use in the protective coating industry was prepared by F. Licata (*Drugs, Oils & Paints* 53, 173). Varnish containing about five per cent calcium stearate protects textile cable coverings and renders them non-wettable by min-

eral oil. A method of preparing metallic soaps by reacting metallic halides with fat acids was patented by W. Plechner (*U. S.* 2,132,997).

The committee that assisted the chairman in preparing this paper by reviewing and submitting additions, suggestions and corrections is composed of:

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(To be continued)

ABSTRACTS

Oils and Fats

Edited by
M. M. PISKUR and RUTH LINDAHL

INDUSTRIAL QUESTIONS ON APPARATUS AND MACHINES FOR THE FAT INDUSTRY. K. Schober. *Fette u. Seifen* 46, 71-7 (1939). Comparative tests on many metals for use in equipment of the oil, fat and soap industry are presented.

SEPARATORS (CENTRIFUGES) FOR THE FAT INDUSTRY. W. Schneider. *Fette u. Seifen* 46, 77-82 (1939).

CENTRIFUGES AND ROLL DRYING IN THE RENDERING INDUSTRY. W. Martin. *Fette u. Seifen* 46, 82-6 (1939).

THE THEORY AND DEVELOPMENT OF HIGH-VACUUM DISTILLATION. C. R. Burch and W. J. D. Van Dijck. *J. Soc. Chem. Ind.* 58, 39-42 (1939). Mol. Distn. is characterized by the use of permanent gas pressures so low (10^{-6} atm.) as to play no essential part in detg. the speed of distn., or even whether distn. takes place or not. The historical devel. of this method of distn. and the theoretical considerations governing the process, are outlined, and factors limiting the large-scale appln. are discussed. Two types of "self-pumping still" which remove the limit set by the finite rate of gas flow in the still itself, are described. The limit set by splashing due to traces of decompn. remains.

SYNTHETIC GLYCERIN — CAN IT BE PRODUCED COMPETITIVELY? H. A. Levey. *Chem. Ind.* 44, 143-5 (1939) Review. Bibl. contains a list of about 50 patents.

HEAT BLEACHING OF FATTY OILS. P. D. Boone. *Soap*, 15, No. 2, 23-5, 32 (1939). Both batch & continuous processes have been employed by investigators. Steam or other inert gases are frequently employed, supplemented sometimes by a vacuum, vacuum alone has been used. The effective temperature varies with the type of oil, and also doubtless on operating conditions. Heat bleaching of oils for the soap kettle might find wider uses in the interest of economy.

QUANTITATIVE DETERMINATION OF STEARIC ACID IN FATS. A. Heiduschka and W. Böhme. *Z. Untersuch. Lebensm.* 77, 33-8 (1939). With the development of new thermostat and filtration and extn. app., which

are described, the modified Hehner and Mitchell method (*Analyst* 21, 316) for detn. of stearic acid was improved to 1% possible error. Method: To 0.5 g. sample in a 200 cc. tared Erlenmeyer flask add 100 cc. stearic acid soln. (4.5 g. stearic acid to 1.1 99% alc. at 20°); place in thermostat, stir and maintain at 0° for 6 hrs. The ppt. is filtered and extd. in a special app. A table of corrections (−3 to +2) is included. Arachidic and behenic acids are pptd. with stearic acid. The breast, back and kidney fat, resp., of beef contain 7.5, 11.0 and 27.0% stearic acid; for pork the figures are 12.0, 13.5 and 30.0% resp.

SIMPLE METHOD FOR DETERMINING THE UNSAPONIFIABLES AND COMPOSITIONS IN FOOD FATS. J. Grossfeld. *Z. Untersuch. Lebensm.* 76, 513-30 (1938). Two unsap. detns. are made using a ratio of 1:10 (A) and 1:80 (B), resp., of fat to petrol ether. Method A: Weigh 5 g. fat in 100 cc. bottle; add 20cc. 95% alc. and 3 cc. 47% NaOH, saponify, and cool. Add 50 cc. petrol ether, shake once, add 20 cc. water, shake 30 times and let stand until the next day. The evapn. residue of a 25 cc. aliquot of solvent is detd. Method B: To the point of standing until the next day the method is similar to method A except use of 2.5 g. sample, 1 cc. 47% NaOH, 200 cc. petrol. ether and 12 cc. water. Aliquot 150 cc. of solvent soln., add 20 cc. .01 N. NaOH, let stand until next day. The evapn. residue of 100 cc. aliquot is detd. The % of sterines (y), hydrocarbons (x) and total unsap. (x + y) are calcd. from the unsap. results derived by method A (p) and method B (q) and the use of constants m and n in the equations: $x = p \frac{m(q-p)}{n-m}$

and $y = 100 \frac{q-p}{n-m}$. Constants m and n were detd.

by adding sterines to oils and testing. For butter fat, whale oil, linseed oil, peanut oil, olive oil, cocoa butter and lard the av. figures 26 and 74 (resp., m and n) can be used; for coco fat m = 44 and n = 82. The method depends on the different amts. of sterines extd. by the two detns. Coco fat soap retains less