

REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1936

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THE world production, trade, interchange, price and scientific developments in the fat and oil field during the year 1936, were predominantly distinguished by the effects of increased unnatural influences such as economic and political difficulties and government control; and in the United States there was added the effect of poor weather conditions. Outstanding among these influences were: (1) the excise taxes passed in this country, (2) the nationalization with complete technical and administrative control placed on the tung oil industry by the Chinese government, (3) the efforts of countries lacking domestic supplies toward making themselves independent of foreign sources, and (4) efforts of those countries having large supplies to develop new uses, substituting the excess fats for materials formerly imported. The increase in literature regarding the new substitutes reflected the irony following the trend of the industry, because in most cases neither the substitute for fats nor the substitution of fatty oils for such use as motor fuel can economically compete with the usual materials unless assisted by legislative encouragement and protection. On the other hand, this course has led to many new scientific developments and has fostered a more intense study in this field along lines which otherwise would not have support.

Legislation in this country which affected fatty material is mainly in the form of excise taxes on imported oils and laws regarding margarine and oleomargarine. These are well summarized in two bulletins of the United States Department of Agriculture, Bureau of Agricultural Economics. Since coconut and palm kernel oils seemed to have gathered a goodly share of adverse legislation because of their use as

butter substitutes and for reason that Brazil and the United States have entered into a reciprocal trade treaty, the importation of babassu oil has increased. This oil, however,

In Russia, U. Bolduiren and son (Masloboina Zhirovoe Delo 12, 310-11) called attention to a dwarf almond plant, *Amygdalus nama*, L., growing profusely in the wilds of Siberia, because it can be developed into an oil supply. A. E. Ermakov *et al.* (Bull. Applied Botany Genetics Plant Breeding U. S. S. R. Ser. III, No. 10, 6-24) pointed out that it is possible by breeding to obtain varieties of lupines with high oil content and practically no alkaloids.

In Germany there has been encouragement toward better economical utilization of fats. The quantity of soap used in laundry work according to C. Stiepel (Fette u. Seifen 43, 159-60) may be reduced by use of soap fillers, alkaline salts and softened water. C. Becker (Chem.-Ztg. 60,

373-5) has reviewed the subject of "tall oil," a by-product of the wood pulp industry that may be used in soap making. Extraction of fat from sewage aids in fat economy. In this field F. Sierp (Allgem. Oel-u. Fett-Ztg. 33, 411-20; also Fette u. Seifen 43, 187-92) has surveyed the subject and presented some new investigations. He calculated that about 40,000 tons of fat could be recovered from the sewage of large cities of Germany. Activities of other investigators toward fat economy will be evident in subsequent parts of this review.

Organizations during the year showed increased activity toward promoting the study of fats and oils. In Germany the fat chemists and technicians have reorganized under the name of "Deutsche Gesellschaft fur Fettforschung" or briefly "D. G. F." (cf. Fette u. Seifen 43, 88-90, 121) in an effort to increase cooperation among members and to assist in the national problems. In the United States we have similar activity in the American Oil Chemist Society and among government

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according to an editorial (Food Industries 8, 617, 653) will not fully satisfy the old demand for its equivalent, *i.e.*, coconut or palm kernel oil, because only small supplies are available. Brief monographs on this oil and palm oils are presented by Margaret J. Hausman (Soap 12, No. 9, 28-31; No. 2, 26-30, 62). Urukury nut fat, also called ouricoury kernel oil and licoury fat is another Brazilian product of similar nature which has entered into foreign commerce during the year. Informative literature on this oil is very meager, giving only the source and characteristics; therefore, a brief monograph on this oil giving data on amount of natural supplies, methods of production, etc., would be desirable.

In time our supplies of drying oils will increase with the development of young tung oil plantations in the southern states. F. Rabak (U. S. Dept. Agr. Circ. 366) suggested the production of safflowers as a new dry land irrigation crop on the northern plains for increasing domestic supplies of this type oil.

workers. Activity in the soybean industry seems promising according to the proposed research program reported by O. E. May (OIL & SOAP 13, 229-31).

Statistical information on oils and fats for the years 1931 to 1935 has been compiled by H. J. Zimmerman (U. S. Dept. of Commerce, Bureau of Census, bulletin). The material in this bulletin along with other information was transferred to chart form by editors of Chemical Industry (39, 473-80). It was designed to show graphically a complete statistical study of the significant interchanges among fats and oils during the last five years. These charts illustrate the movement of each oil as compared with others; and the displacement, changes in trends of consumption and changing demands for oils and replacements within certain industrial groupings may be gauged. Statistics on oleomargarine which include production, materials used in manufacture, consumption, trade and price were compiled by Anne Dewees and O. C. Stine (U. S. Dept. of Agr., Bur. of Agr. Economics). The price indices of fats and oils, according to the market reports of "Chemical and Metallurgical Engineering," based on 1927 price index as 100, increased from 92.36 for Jan., 1936, to 109.35 for Jan., 1937. In order to present a brief review on production, imports, and exports of fats and oils, the following data were compiled from the "1936 Review of Vegetable and Competing Oils" by C. E. Lund of the U. S. Department of Commerce, Bureau of Foreign and Domestic Commerce:

(Data in million pounds)			
United States Imports:	1936	1935	
Vegetable oils	1,394	1,473	
Oil equivalent of oilseeds	723	812	
Animal and fish oil (excluding butter)	193	355	
Butter	10	22	
United States Exports:			
Vegetable oils	29	26	
Oil seeds	109	93	
Animal and fish oils	142	134	
United States Production (estimated):			
Lard	1,052	782	
Tallow	562	466	
Lard compounds and lard substitutes	1,554	1,547	
Butter (creamery)	1,610	1,634	
Oleomargarine	393	382	
Soy bean oil	225	105	
Cottonseed oil	1,245	1,183	
Linseed oil	455	415	
Peanut oil	70	45	

Commercial Treatment

The technical staff of vegetable oil processors will find the communications by R. Heublyum and J. Japhé (Allgem. Oel- u. Fett-Ztg. 32, 401-5, 497-502; 33, 13-17, 49-55, 96-103, 141-9, 199-203, 254-61) and A. M. Goldovskii (Fette u. Seifen 43, 21-6, 57-64) very informative. These au-

thors reviewed the subject of extraction of oils from the chemical and physical-chemical viewpoint. Physical structure of seeds, change in seed protein on cooking and effect of various factors such as heat, moisture and hydrogen-ion concentration on extraction are considered. Ordinarily, little attention is devoted to these subjects; most articles seem to deal with the mechanical technique of the extraction operation. The patents issued on extraction of oils during the five years previous to the year 1936 are reviewed by R. Strauss (Fett-chem. Umschau 42, 219-29).

The circulating rendering process described by Würster (Soap 7, (12), 79-82) several years ago was the subject of a new paper by K. Schneider (Allgem. Oel- u. Fett-Ztg. 33, 266-72). Illustrations indicated that some slight improvements in mechanical detail have been made. A rendering apparatus patented by L. A. Molin (U. S. 2,035,090) contains crushing rollers and mixing paddles. Apparatus for grinding animal material and means of introducing it into a pressure digester for rendering through a nonreturn valve are the novel features of H. P. Christensen's invention (Brit. 444,619). Other patents issued to Ges. für Verwertung Fauthscher Patent m.b.H. (Brit. 438,410 addn. to 420,040; Brit. 446,997 and Ger. 625,981 Cl. 53c addn. to 617,304), A. Sommermeyer (Brit. 444,337) and Escher Wyss Maschinenfabriken A. G. (Swiss 177,269 Cl. 23a) described drying apparatus in which rendering or partial rendering takes place and the extraction may be completed by pressing or with solvents. Novelty was claimed, respectively, on the basis of construction of drums, method of heating, and use of vacuum at low temperatures. A special rendering apparatus in which the raw material is run over warm surfaces and subjected to alternating vacuum and pressure to burst the fat cells, was invented by A. Nyrop (Ger. 630,158 and Brit. 418,107). Means of combining refining with rendering are described by J. P. Harris (U. S. 2,035,126) and C. B. Upton (Can. 355,866). The former adds decolorizing carbon previous to rendering. The latter uses a special apparatus in which the rendered fat gradually drains off to a separate part of the rendering chamber. Here it is continually mixed with solid refining agents and stirred. Both portions of the chamber are subjected to partial vacuum. The refined fats, the refining agent and the

cracklings are removed separately from the chamber.

Data on the effect of various processing factors affecting the quality of steam rendered lard were presented by C. E. Morris (OIL & SOAP 13, 60-2). Increase in storage time of raw material, and increases in pressures and time of rendering resulted in an increase of free fat acid content of lard. Cold storage of raw material up to 96 hours, rendering pressures up to 40 pounds and rendering time up to 10 hours did not affect the stability of the finished lard.

Several patents have dealt with production of medicinal fish liver oils. J. F. Ward (Brit. 438,349 and 449,246) treated minced livers with dilute alkali at 40° for one or more days. The scum which rises to the top is removed and the oil is separated from it by treatment with either alcohol or adjusting the pH to 8 with hydrochloric acid to break the emulsion. F. M. Hamilton (Brit. 436,489) preferred expressing the oil from the disintegrated livers, while B. A. Rewald (Brit. 441,545) contended that more potent vitamin activity in the oil is obtainable by extraction with solvents.

In the literature on pressure extraction are two inventions by L. A. Malin (U. S. 2,055,697) and W. C. Richardson (U. S. 2,057,312), dealing with the mechanical features of presses for oil seeds. Innovations in this type process indicated a trend toward use of centrifuges to take the place of the hydraulic press. G. Johnson (Brit. 448,584) claimed that fish refuse can be dried in vacuum and the oil extracted by either centrifuge or press. H. J. M. Nanz (Brit. 449,277) extracted like material by centrifuging in the heated and comminuted form. A similar process was claimed by W. L. Marston (U. S. 2,032,543) for obtaining animal oils from mixtures containing water. The Russian investigators, A. Goldovskii (Masloboino Zhirovoe Delo 11, 530-4) V. G. Leites (Russian Pat. 41,100), and S. S. Il'in (Russian Pat. 39,296) claimed better oil yields resulted from seeds by additions of water and electrolytes and steaming or heating before the pressing. A. Goldovskii (Masloboino Zhirovoe Delo 12, 227-32) found flaking the seeds followed by roasting ruptures the cell walls, thus improving oil yields.

Continuation of new patents on continuous counter flow apparatus for solvent extraction of oil seed was maintained with such an invention by K. F. Wilhelm (Ger. 623,-

275, Cl. 23a). A. Pfänder (*Fette u. Seifen* 43, 137-9) contributed a general discussion on the steam, power and solvent economy of the extraction processes. R. Fussteig (*Mat. grasses* 27, 10619-20) recommended extraction methods for production of olive oil and showed their advantages over the pressing methods. If the olives were not dried before extraction a better grade of oil was obtainable according to C. Kerkhoven (*Öle, Fette, Wachs, Kosmetik* 1936, [9], 7-8); however, it was admitted that 2% of the oil remains in the residue.

Experiments on the choice of solvents for extraction of cottonseed oil were reported by E. C. Koo *et al* (*Ind. Research, China* 5, 71-5, 137-41, 338-43). Benzene and benzene were found suitable. Acetone and carbon tetrachloride were less desirable. The best grade of oil was obtained by treating the seeds with alcohol, distilling off the alcohol, adding water, and finally extracting with benzene. Extraction of cottonseed oil on large scale yielded 92% of the available oil.

General surveys on refining processes were contributed by T. Andrews (*Oil Colour Trades J.* 89, 367-71) and I. Zubov (*Masloboino Zhirovoe Delo* 11, 477-9; 12, 237-8). Both addition of phosphoric acid and cellulose was favored by Harburger Ölwerke according to a recent patent (Ger. 631,224 Cl. 23a). L. D. Jones (*Can.* 358,178) and E. M. James (*Can.* 355,720) have added new inventions to the series which make use of centrifuges in the refining processes. Desirability of acid refining cottonseed oil before manufacture of soap was investigated by M. Irodov (*Masloboino Zhirovoe Delo* 11, 494). Factory samples were subjected to various acid treatments after hydrogenation and then saponified. Data indicated improved saponification resulted after the treatment and removal of coagulated residues. These residues were shown to have an anticatalytic effect on the saponification process.

Several suggestions were made concerning the caustic refining process. Destruction of vitamin A is reduced by maintaining low temperatures during contact with caustic. A means of carrying this out was invented by V. Jersey (U. S. 2,029,722). Methods of removing impurities after the refining are contributed by M. Sandomirskii and O. Mikhailovskaya (*Masloboino Zhirovoe Delo* 11, 357-9) and O. Brucke (U. S. 2,035,589). The former two contributors reported that less

oil losses occurred when washing after caustic refining with very dilute sulfuric acid solutions. The latter treated the oil with alcohol by a method in which stratification occurred on cooling. The lower layer containing the soap solution and impurities was then removed from the layer of neutral oil. The most radical innovation using an alkali process was the method of W. Fuchs (Ger. 630,790 Cl. 23a). The oil was emulsified with barium hydroxide solution, subjected to electric current and finally treated with sulfuric acid to remove barium. Oil was separated from water and impurities by centrifuging.

Novel systems of refining appeared both in patent literature and in a descriptive report. A. Sergeen (*Masloboino Zhirovoe Delo* 11, 551-3) reports that the mucilaginous and albuminous substances are removed from fish and marine animal oils by precipitation with oak bark extract. Patents assigned to Elact Ges. für elektr. Apparate G. m.b.H. (Brit. 433,576 and 436,372, and Austrian 146,506) claimed that deacidification, bleaching and deodorization was accomplished by emulsifying the oils with skim milk, subjecting the emulsion to electrolysis and separating the added liquids. Poor grades of oil can yield a satisfactory product according to E. W. Fawcett (Brit. 438,056, Fr. 789,919 and U. S. 2,047,196) by the usual acid, alkali or combined refining processes with subsequent high vacuum distillation. The materials distilling off at low temperatures are part of the impurities while the triglycerides distill at the higher temperatures; a small amount of residue remains in the still. A still for this purpose has a condensing surface very close to the oil surface.

New mechanical features of apparatus for deodorizing oils by injecting vapor or gas are described in the patents issued to W. Gensecke (U. S. 2,042,711) and H. Lambert (Ger. 630,159 Cl. 23a). According to the patent of Harburger Ölwerke Brinckman and Mergell (Ger. 617,520 Cl. 23a), the deodorization with steam was more effective when dichloroethylene was added to the oil before treatment. Fuller's earth was also added to augment the refining. In some deodorizing operations it is desirable to prevent volatilization of free fat acids during the steaming. According to the patent of Deutsche Hydrierwerke A. G. (Ger. 622,697 Cl. 23a), this was accomplished by first neutralizing the acids with caustic.

New chemical and physical means for bleaching oils were invented. Among the chemical processes, hydrogen peroxide with acetic anhydride were the active agents of the method patented by P. Langenkamp (Ger. 632,516 Cl. 23a). G. Adam (Ger. 634,043 Cl. 23a) used treatment with zinc dust at temperatures over 150°, and L. Mellerish-Jackson (Brit. 444,813) claimed a special method for bleaching with alkali hypochlorites. Patents on use of absorptive material were issued to J. B. Carpzwow (Fr. 788,239) and Societa industrie chimiche (Fr. 794,695). The former used treatment with dry pulverized slime from the sea or fresh water. The latter claimed improvements with the usual decolorizing earths or charcoals by treating the oils dissolved in organic solvents with them in the presence of small amounts of organic or inorganic acids or salts.

The properties of several commercial bleaching earths and carbons were investigated by E. Erdheim (*Öle, Fette, Wachs, Seife, Kosmetik* 1935, [1], 6-7; 1936, [7], 9-12; [9], 4-6; [12], 9-12; [15], 1-3). Activity of these against dyes in organic solvents and natural impurities in both fatty and mineral oils were evaluated. Additions of water to the several oils yielded improvements in bleaching capacity of various earths, which varied from 1.5 to 83% over control tests on oils without water. Reviews on methods for activating bleaching earths were contributed by O. Eckart (*Chem.-Ztg.* 60, 153-5) and R. Fussteig (*Mat. grasses* 27, 10652-4, 10688-90). A new process for activating clays which comprises forming a suspension of the material in water and subjecting the mixture to electrolysis, was originated by H. Endell (U. S. 2,057,232). New natural deposits of bleaching clays were reported in western Kentucky and Tennessee by G. I. Whitlatch (*OIL & SOAP* 13, 38-44).

Since phosphatides are considered impurities in an oil and because they are removed in the usual refining operation, it is important that refining is carried out with an aim of recovering these valuable by-products. Their chemistry and importance in industry were elucidated by E. B. Working (*OIL & SOAP* 13, 261-3). A review of extraction methods for their recovery from soy beans was contributed by A. A. Horvath (*Chem. & Met. Eng.* 43, 418). New production methods were predominantly directed at soy bean phosphatide production. W. W. Ginn (U. S. 2,029,261) claimed

centrifuging the crude oil from hot pressed beans separates the oil from the phosphatides. Patents issued to Noble u. Thorl G.m.b.H. (Fr. 788,632 and 788,633) described precipitation of phosphatides with materials such as water glass, sugar, starch, etc. These products are intended for special uses. Thus, phosphatides precipitated with water glass were proposed for use in soap, and those containing sugar, starch and other edible material can be used in food products. Mixtures of phosphatides and oil were separated from soy bean sludge according to the patent issued to A. Gehrke (U. S. 2,018,781) by adding glycerol. The oil and phosphatides formed a top layer; the glycerol contained the other components of the sludge. A. Schwiager (U. S. 2,057,695) concentrated crude phosphatides by dissolving out fat with solvents. Pure lecithin was extracted from solutions of crude phosphatide in acetone or carbon tetrachloride as cited by a patent of I. G. Farbenindustrie A. G. (Ger. 617,508 Cl. 53i) by precipitation with oxides of trivalent metals or of silicon.

Other products recoverable from oils which received consideration were wax and unsaponifiable. A waxy sediment was deposited on the bottom of tanks during storage of coconut oil according to S. S. Tanchico (Philippine J. Sci. 57, 423-6). This when purified may be used for the preparation of floor waxes and furniture and leather polishes. Special means of saponifying fats and extraction of unsaponifiable was described in a patent assigned to Aktieselskabet Ferrosan (Danish 50,271).

General discussion and description of the chief processes for splitting fats were contributed by R. Heublyum (Mat. grasses 28, 10699-700, 10728-9). Operating data on splitting sardine oil of various degrees of hardness with zinc powder and magnesia catalyst were graphically presented by S. S. Ueno and G. Inagaki (J. Soc. Chem. Ind. Japan 39, 107-10). Curves relating to the time of splitting, acetyl number, effect of pressure, per cent splitting, etc., were given. J. O. Peirce patented (U. S. 2,042,411) the use of sulfonated products of polymerized oils for catalytic splitting purposes. E. K. Wallace and J. R. Moore (Am. Perfumer 33, 47) reported that rapid hydrolysis takes place by autoclaving 100 parts of the fat with 400 parts of acetone, 15 parts of water, and 0.5 parts of sulfuric acid. The acetone was evaporated until the glycerol formed a separate layer

from which it could be recovered. Advantages claimed were: acid pretreatment was unnecessary; time required was shortened and fat acids could be separated in two fractions by proper mixtures of water and acetone. Other activities in this branch of the fat field were directed toward establishing procedures for splitting that can be either combined with distillation or followed by distillation without necessitating intermediate steps. This was accomplished as described in patents issued to Metalgesellschaft A. G. (Brit. 449,451 and Fr. 799,793) on wool fat by a predistillation at 400° to remove unsaponifiable and some fat acids and until the residue resembles pitch. The treatment splits the fats, and the alcohols and the unsaponifiable underwent changes to hydrocarbons. A final distillation in vacuum was performed. The process yielded hydrocarbons which were useful as lubricants and fat acids. A new method developed by E. Hoffman (Öle, Fette, Wachse, Kosmetik 1936, [13], 4-6) combines fat splitting and distilling into a continuous process. A refined fat was emulsified with water and passed through a splitting zone maintained at a temperature between 220 and 260° and a pressure from 20 to 60 atmospheres. In a continuous manner the split products were forced into a high vacuum expansion zone where they were converted into the gaseous phase. The unsplit oil and unsaponifiable remain in the liquid phase and can be drained off. Remainder of the process pertained to fractionation of the volatile products into water, glycerol and fat acids.

Improvements in methods of steam distilling fat acids were described by E. M. Schönberger (Fette u. Seifen 43, 109-112), R. H. Potts and J. E. McKee (U. S. 2,054,096) and J. W. Gray (U. S. 2,042,713). These were mainly apparatus and operation details. Advantages were gained in this process according to A. W. Ralston *et al* (U. S. 2,042,729; 2,033,536 and 2,033,537) by converting the fat acids into the nitriles previous to the distillation. The separated nitriles can be reconverted to the corresponding fat acids. Discoloration during the distilling process was inhibited according to M. L. Sheely (U. S. 2,062,857) by preheating the oil to 150-225° in presence of hydrogen.

Distillation methods for preparation of pure individual acids were also described. T. H. Rider (U. S. 2,045,727) claimed a special pro-

cedure for manufacture of pure ricinoleic acid from castor oil. Production of pure oleic acid by pretreatment to remove saturated acid, followed by distillation in vacuum was described by L. Keffler and J. H. McLean (J. Soc. Chem. Ind. 54, 362-7T).

Some current methods and equipment used for fat hardening were reviewed by I. Taussky (Öle, Fette, Wachse 1935, [2], 3-8). Other reviews contributed by R. Heublyum (Mat. grasses 27, 589-90, 618-9) and V. Puzanov and G. Ivanova (Masloboino Zhirovoe Delo 11, 365-8) treated that hydrogenation procedure which makes use of a stationary catalyst composed of aluminum-nickel alloy.

Selective saturation of double bonds without side reactions was the paramount issue of the greater percentage of communications on fat hardening. Data presented by E. Etinberg *et al* (Masloboino Zhirovoe Delo 11, 471-3) were interpreted and correlated. A selective hydrogenation of cottonseed oil occurred with a minimum of catalyst and a maximum of hydrogen; the converse was also true. Under all conditions of catalyst-hydrogen ratios, selectivity was greater at the higher temperatures. M. Zaayer (Chem. Weekblad 32, 393) developed similar data for correlation of selectivity with activity of catalyst. The most active catalysts were most selective. The poly-ethenoid fat acids may be selectively converted to the mono-ethenoid acids as verified by patent of Metallgesellschaft A. G. and O. Brucke (Brit. 452,887) by hydrogenation at temperatures between 80 and 130° and about 25 atmospheres pressure. T. P. Hilditch and H. Paul (J. Chem. Soc. 1936, 664-7) showed that the course of hydrogenation of oleyl oleate was non-selective although the alcohol group of the ester was slightly more readily hydrogenated than the acidic group. Tests on strongly unsaturated oils by F. Wittka (Allgem. Oel- u. Fett-Ztg. 33, 305-9, 515-8) added information on the course of the hydrogenation reaction. Linseed oil was hardened at several temperatures between 50 and 100°. Striking differences were noticed between the products hydrogenated to iodine value of about 98 at 70° as compared to that hardened at 90°. The product from the latter operation solidified at 30° while the former remained liquid even at 0°. Composition and characteristics of both were reported. These showed that unsaturated solid acid formation during the hydrogenation of linseed oil

began to increase rapidly at some critical hydrogenation temperature between 70 and 90°. Perilla oil did not show the same property. Unsaturated solid acid formation was very evident even on hydrogenation at 50°. Similar tests on Chinese wood oil indicated that α -eleostearic acid glycerides are isomerized to β -eleostearic acid glycerides during the course of hydrogenation. A. Bömer and F. Brehm (*Z. Untersuch. Lebensm.* 72, 1-34) investigated the reduction of the hydroxy fat acids contained in castor oil. This acid was reduced to stearic acid. Evidence was submitted to show that double bonds of fat acids were reduced more easily than the hydroxy groups.

Several papers recorded experiments on new hydrogenation catalysts. Successful results were reported by I. Petryaev (*Masloboino Zhirovoe Delo* 12, 92-3, 145-6) with nickel carbonate reduced in oil either with or without carriers, and also with reduced nickel formate, by Etinburg and M. Popov (*Masloboino Zhirovoe Delo* 11, 363) with catalyst prepared from mixtures of nickel carbonate and nickel formate, by K. Butkovski and A. Kolyu (*Masloboino Zhirovoe Delo* 12, 249-50) and Vasilev (*Masloboino Zhirovoe Delo* 11, 444-8) with reduced mixtures of nickel and copper, by E. Balani (*Allgem. Oel- u. Fett-Ztg.* 33, 420) with reduced nickel borate and by Moschkin and Kosokova (*Masloboino Zhirovoe Delo* 11, 81-2) with reduced nickel which was precipitated with bicarbonates. The predominating tone of these communications seems to be extol the advantages of their own respective catalysts. The latter investigators were criticized by W. Norman (*Fette u. Seifen* 43, 133-5) who refuted their claim that catalyst prepared by reduction of bicarbonate precipitated nickel was superior to that prepared from nickel precipitated with a carbonate. Methods of preparing catalyst were patented by A. A. Svitzuim (Russian Pat. 38,724) and W. W. Myddleton (U. S. 2,029,786). The former electro-deposited nickel on an iron or copper gauze with gradually increasing current density to produce a strong but porous precipitate, oxidized the plate anodically and then reduced the nickel with hydrogen. Myddleton mixed nickel oxide with ethyl orthosilicate, coagulated with ammonium hydroxide, dried and broke up the precipitate and finally reduced it with hydrogen. Reactivation of waste nickel catalyst was accomplished as disclosed in patents issued

to Asaki Denka Kogyo K. K. (Japan 110,805) by washing with chloroform, oxidizing at temperatures below 600° and finally reducing with hydrogen. Several catalysts were prepared and tested by J. C. W. Frazer and C. B. Jackson (*J. Am. Chem. Soc.* 58, 950-2). A catalyst composed of nickel and chromic oxide proved to be highly active for hydrogenation of oil. Traces of compounds of sulfur, selenium and tellurium promoted the activity of this catalyst; but, larger quantities were extremely deleterious.

The influence of carriers on the activity of nickel catalyst was investigated by E. Botkovskaya and P. Artamonov (*Masloboino Zhirovoe Delo* 11, 468-51). Nickel precipitated on clays rich in aluminum and ferric oxides gave better selective hydrogenation than nickel on kieselguhr. Various commercial kieselguhrs used for catalyst carriers or filtering retained oil to the extent of 17.1 to 19.15 grams per 10 grams of kieselguhr according to tests by F. Krczil and H. Wejroch (*Seifensieder-Ztg.* 63, 352-4).

A general discussion and review on hydrogen manufacture for use in oil hardening was presented by T. G. Rickert (*OIL & SOAP* 13, 33-7). Special emphasis was placed on the Bamag type electrolytic method.

Fatty oils used for lubrication may or may not require some processing. Refined olive oil was recommended for motor lubrication by J. Hubscher (*Seifensieder-Ztg.* 63, 325-6). E. Eichwald patented (Dutch 36,242) the use of polymerized rape oil. Means of applying castor oil for lubrication were patented by A. L. Blount (U. S. 2,031,045), W. E. Jaques (Swiss 177,588) and G. K. Knoffler (Ger. 632,478 Cl. 12a). The claims in these were, briefly: (1) mixtures of the oil and mineral oil containing small amounts of mono-butyl ether of diethylene glycol and aluminum soap of higher saturated fat acids; (2) mixtures of the oil, benzene, camphor, naphthalene, acetone and graphite, and (3) making castor oil soluble in mineral oil by heating in vacuum with presence of 4-6% bleaching earth. Lubricants which are stable at high temperatures were prepared as disclosed in patent issued to Sulfo Corporation of America (Fr. 793,602 and 793,603) by mixing polymerized and oxidized drying or semidrying oils with substances such as waxes, minerals, oils, resins, etc. G. Schneider (U. S. 2,041, 728) and G. W. Seymour

(U. S. 2,041,729) respectively patented use of polymerized castor oil, and oxidized mixtures of vegetable and whale oils for lubricating textile fibers previous to spinning or weaving. Partially hydrogenated oils are preferred for this purpose by A. H. Gill (U. S. 2,026,735) according to his recent patent.

The literature indicated that there was increased interest in new sources and development of new sources of drying oils. M. Brambilla and G. Balbi (*Chimica e. industria* 18, 353-5, 399-400, 450-2) tested the possibility of using grape, tomato and rape seed oils for varnish purposes. The first two yielded suitable polymerized products; while the latter was considered unsuitable. M. Sreenivasaya and N. Narayana (*J. Indian Inst. Sci.* 19A, 1-8) contributed a brief monograph on sandal seeds. These seeds contain 50 to 55% of a valuable drying oil. Oils of general interest for enamels and lacquers are discussed by H. Ulrich (*Farben. Ztg.* 40, 1037).

Oiticica oil, which during the last few years gained prominence as a substitute for China wood oil has been the subject of publications prepared by various paint and varnish production clubs (*Paint Oil & Chem. Rev.* 97, [23], 66-8, 72, 74, 76; *Oil Paint and Drug Repr.* 128, [22], 53-5) and communications by H. Kemmer (*Farbe u. Lack* 1935, 545-6), E. Stock (*Farben Chem.* 7, 45-6; *Paint Varnish Production Mgr.* 14, [6], 14), C. Holdt (*Drugs, Oils & Paints* 51, 191-8, 240-2), H. A. Gardner, Jr. (*Paint Varnish Production Mgr.* 14, [6], 16, 18, 30) and C. P. A. Kappelmeier (*Drugs, Oils, Paints* 51, 237-8; *Paint Varnish Production Mgr.* 14, [6], 7-8, 10). Information in these papers was on characteristics of the oils and its films, advantages and disadvantages as compared to other drying oils, methods of oxidizing, methods of using and other notes of general interest to paint and lacquer manufacturers. H. A. Gardner (*Am. Paint J.* 20, 18, 48, 50, Nov. 21) stated that no oil or resin product at present matches tung oil in formulation of water-proof spar varnish and that the most likely material for replacing it is the alkyd type resin.

Papers dealing with tung (wood) oil by E. Fonrobert (*Paint Manuf.* 5, 364-7; 6, 4-7) cover the cultivation, yield, quality chemical composition, and outline the preparation of tung oil stand oils, of mixed tung-linseed stand oils and manufacture of varnishes. H. A. Gardner (*Natl. Paint, Varnish, Lacquer*

Assn. Circ. 514, 239-44) reported the species of tung trees which thrive best in the West Indies. Gelation of tung oil and the liquefaction of the gels was reviewed by A. Ruff (Farben Chem. 6, 415-6). A comparison of treated and untreated wood oils in modified phenolic resin varnishes by V. N. Sheets (Paint Varnish Production Mgr. 13, [11], 17, 18, 19, 37) favored the untreated oil from the standpoint of durability, darkening, fume proofness and drying time. The cause of "crystallization" of tung oil vehicles was investigated by J. Hyman and T. Greenfield (Ind. Eng. Chem. 28, 238-41). This was attributed to presence of traces of nitrogen dioxide in the atmosphere. The critical nitrogen dioxide concentration necessary to produce crystallization in standard varnish under controlled conditions was 0.4 parts per million parts of air. The source of nitrogen dioxide in air is from flames, sparks and ultra-violet light. According to C. A. Thomas (U. S. 2,035,250 and 2,035,251) the crystallization was inhibited by adding to the oil 1 to 10% β -naphthol or coumarone-indene resin.

Changes of characteristics of linseed oils during oxidation were recorded by R. S. Taylor and J. G. Smull (Ind. Eng. Chem. 28, 193-5), A. F. H. Ward and D. G. France (J. Soc. Chem. Ind. 54, 435-8T) and V. M. Breitman (Plastmassni U. S. S. R. 1, 404-23). Similar data accumulated during polymerization of the oil were presented by K. Dorn and R. M. Erastova (Film Forming Substances U. S. S. R. 1, 35-9), P. S. Varma *et al* (Allgem. Oel- u. Fett-Ztg. 33, 249-54) and H. I. Waterman and C. van Vlodrop (Chim. et Ind. 34, 1036-44). Papers by F. E. Riep (Verfkroniek 9, 217-21) and H. A. Boekenogen (Verfkroniek 9, 254-5) elucidated the characteristics and manner of extraction of Russian linseed oil. H. Levecke (Farbe u. Lack 1936, 41-3) investigated the self-ignition of linseed oil containing pigments by air-blowing for 20 hours. Rapid temperature rise was observed with Prussian blue dispersions in linseed oil; hence, he warned that caution must be exercised in grinding Prussian blue with drying oils. C. H. Rose and D. S. Bolley (Ind. Eng. Chem. 28, 115-8) studied the softening of linseed oil films. This softening which occurs after the unpigmented films of oil were dried and hardened, was more pronounced with the less saturated oils. Driers and pigments delayed and reduced the amount of after softening.

Attention was drawn to modifying fish oils so that they may be used in the paint industry. G. Kaempfe (Farben Ztg. 40, 1009) recommended treatments for removing the saturated and less highly unsaturated components. Informative data on carrying out this treatment were recorded by O. M. Behr (Ind. Eng. Chem. 28, 299-301). He estimated that removal of the 5% saturated acid radicals necessitates a loss of 30% of the original oil. In tests on phenolic resin preparations more reaction took place with winterized sardine oil than with linseed oil. Sardine oil was therefore recommended for substitution in place of linseed oil and part of the China wood oil in making synthetic resin varnishes. Graphical representation of the variations in specific gravity, surface tension, cloud test and acid, iodine, octabromide and saponification values with viscosity of commercial batches of Menhaden fish oil during heat processing was prepared by L. T. Work, C. Swain, A. Wasmuth and J. Mattiello (Ind. Eng. Chem. 28, 1022-4). General properties of pilchard oil and pilchard oil films and comparison of these with linseed oil were investigated by O. F. Denstedt and H. N. Brocklesby (J. Biol. Board Can. 1, 487-96; 2, 13-40). Pilchard oil dries more rapidly than linseed oil. Defects such as softness, tackiness and permeability to moisture may be partly corrected by using proper drier combinations and incorporation of gums, but they can be entirely eliminated only by steam distillation of the polymerized oil to remove unpolymersed substances.

Methods for polymerization, oxidation and increasing the viscosity of oils appeared in moderate numbers. E. W. Fawcett *et al* (Brit. 442,000), N. V. Industrielle Maatschappij vorheen Noury & van der Lande (Dutch 36,952) and A. Hill with E. E. Walker (Brit. 428,864) patented methods for polymerizing oils which constituted heat treatment followed by vacuum distillation to remove the unpolymersed glycerides. E. W. Fawcett *et al* (Brit. 452,039) discovered advantages in heat polymerization at pressures from 500 to 3,000 atmospheres. A polymerization apparatus in which the oil may be quickly heated and maintained at a definite temperature during a predetermined time period and then quickly cooled was described by R. A. Carleton (Brit. 448,956). Improved oxidized linseed oil product was obtained according to J. Scheiber (Ger. 625,902 Cl. 12o) by blowing at 160°

until it had an acetyl value of about 80, adding about 50% linseed oil fat acids, heating two hours at 200° and then progressively raising the temperature to 300° before allowing it to cool. Glycerin may be applied and the mixture reheated to reduce the free fat acid content. J. S. Long and G. L. Ball (U. S. 2,059,259) preferred blowing the oil at temperatures between 50 and 160° F. until a product was obtained which was soluble in ethyl alcohol by which formation of a gel at normal temperatures was prevented. A seemingly converse method of producing blown oils was described by G. W. Seymour (Can. 360,252). The raw oil was sprayed into a stagnant atmosphere of gas containing oxygen at 120° temperature and 48-50 pounds pressure.

Other literature on polymerization and oxidation of oils for use in protective coatings report new catalysts for the processes. W. Krumbhaar (U. S. 2,024,103 and Brit. 444,440) used electrically dispersed heavy metals. Sulfur dioxide was effective according to H. J. Waterman and C. van Vlodrop (J. Soc. Chem. Ind. 55, 333-4T). F. Vissert Hooft (U. S. 2,032,554) patented the use of dibenzoyl peroxide or a diacyl peroxide. The catalyst for auto-oxidation of castor oil patented by M. DeGrootte and B. Keiser (U. S. 2,025,800 to 2,025,809, inclusive) were octadeca-9, 11-dienoic acid glyceride, hendecenoic acid glyceride, α -pinene and dipentene. R. L. Sibley (U. S. 2,022,301 and 2,022,302) controls the oxidation of drying oils with dimethylhydroquinoline or hydracridine.

Data on viscosity changes of several oils during treatment with sulfur monochloride were recorded by G. Rossi (Ann. Chim. Applicata 6, 251-8). The capacity of the oils to become more viscous with the treatment were in the following descending order: olive oil, peanut oil, linseed oil, sesame oil, cottonseed oil and pure oleic acid. Olive oils containing admixtures of the other oils named above showed greater viscosity increases after treatment than the pure olive oils.

New controversies regarding reactions occurring during polymerization of oils signify that no explanation so far has been adequate. An interesting polemic on the subject was carried on between H. Kurz (Angew. Chemie 49, 235-8; Fette u. Seifen 43, 184-5) and J. Scheiber (Farbe u. Lack 1936, 315-6, 329-30, 341, 351-2, and Fette u. Seifen 43, 103-5). Kurz originated a theory and accumulated data to sup-

port his contentions. He said that polymerization of oils did not deal with reactions between double bonds of unsaturated groups, but is a condensation taking place at the methyl group situated between conjugated double bonds and a carbon atom of the glyceride radical with the liberation of a free fat acid. His opponent's argument was based on a usual theory which explains polymerization by reactions at the conjugated double bonds of unsaturated acids. The formation of free acids and disappearance of glycerol during linseed stand oil production was ascribed to pyrolytic fusion of triglyceride molecules into vinyl compounds and not condensation as explained by Kurz. Among replies which ensued it was stated that if Scheiber were correct tetramethylene rings and vinyl compounds should be identifiable in polymerized oils. No positive test for vinyl compounds was obtained. The report of K. Kuro (Sci. Papers Inst. Phys. Chem. Research, Tokyo, 29, 31-6) also complicates the usual theories. He heated the methyl esters of linseed and sesame oils and oleic acid at 280-290° and tabulated the characteristics of samples taken at hourly periods during the heating. The iodine value of all heated products increased. He suggested that it is possible that intermolecular polymerization products, unsaponifiable substances resulting from these products and distillation products with high boiling points may be responsible for the increase in iodine value. A little substitution also takes place during the iodine value determination. The change of specific refraction of linseed oil during polymerization was graphically represented by H. I. Waterman and C. van Vlodrop (Chimie & industrie 34, 1031-44). The relatively high specific refraction found at the beginning of polymerization was in agreement with the theory that isomerization to conjugated double bonds occurs first. He also reports that other reactions occur during the polymerization. A. Steger and J. van Loon (Fettchem. Umschau 43, 17-21) continued their series of researches, in which they found that cyclic compounds and polymers form on heating oils, by reporting that isomers and cyclic compounds are most prevalent in ethyl eleostearate after heating above 300° and this is more so in the presence of sulfur. They also found that wood oil containing sulfur either does not gel or the gelatinization is severely hindered. E. A. Daniels and L. A. Donovan

(U. S. 2,056,832) patented the use of wood oil heated in presence of sulfur for use in nitrocellulose coating. The treatment is said to make the wood oil compatible with nitrocellulose.

A study of polymerization of various fat acids in the presence of tin tetrachloride was made by J. K. Chowdbury *et al* (J. Indian Chem. Soc. 12, 441-54). Oleic acid produced highly viscous polymers which could be used as a lubricating oil. In this reaction carbon dioxide was evolved indicating that the carboxyl group was involved. Methyl esters of oleic acid under the same conditions polymerized very slowly. The reaction with linoleic acid took place through the conjugated system rather than the carboxyl group since the acid value remained constant and the iodine value decreased. In polymerization of ricinoleic acid the iodine value remained constant except when 20% or more tin tetrachloride was added, after which acetyl value also decreased. Molecular weight determinations indicate that at least six molecules of this acid were involved in the polymerization and ester formation.

A study of the reaction of α - and β -eleostearic acids with maleic anhydride and their subsequent oxidation by R. S. Morrell and W. R. Davis (Trans. Faraday Soc. 32, 209; J. Soc. Chem. Ind. 55, 237-46T, 261-5T and 265-7T) yielded several conclusions. Peroxides were produced at the double bond only with the β -acid condensate. Tautomeric keto-hydroxy compounds were formed after oxidation of the α -acid-maleic anhydride compound. The ring double bonds were not attacked. Peroxides in nonpolar solvents formed molecular aggregates. In polar solvents, β -compounds showed association due to the combination of primary valences from the peroxide group. Decomposition of peroxide aggregations to chain-like polymers of oxides may account for changes occurring during the aging of drying oils and the disappearance of bloom which was ascribed to free peroxide groups. The maleic anhydride addition compounds of α -eleostearic acid absorbed two atoms of oxygen in acetic acid at 20° in presence of cobalt acetate. Comparison with the corresponding β -derivative which formed peroxides and polymers readily, indicated that only remote ethenoid linkages are concerned in the drying process. Reactions based on change in peroxide activity of β -eleostearin-maleic anhydride com-

pounds were also suggested. General concepts of structure of drying oil molecules and the structures which occur after polymerization or oxidation were reviewed by A. V. Blom (Fettchem. Umschau 43, 43-6 and Verfkroniek 9, 130-3).

Yellowing of oil films and its prevention was discussed by A. Eibner (Paint Varnish Production Mgr. 14 [3], 12, 14, 30-1). Current theories on the phenomenon were reviewed and practical suggestions for manufacture and use of the various oils were made.

Among the non-fatty substitutes for drying oils, resins, rosin and mineral oils all received recognition. The chief disadvantages of rosin or resins plasticized with cheaper fatty oils or solvents as cited by H. Pfanner (Farben-chem. 7, 209-10, 219) were production of films that were too thin and a tendency to react with pigments containing lead and zinc. R. C. Palmer and P. O. Powers (U. S. 2,022,973 and 2,022,974) modified the partly esterified wood rosin used in protective coatings by heating to 260-325° with fuller's earth until the acid value of the mixture was considerably reduced.

A Ya. Drinberg (Russian Pat. 39,293; Natl. Paint, Varnish & Lacquer Assoc. Circ. No. 501, 1-20 and Film Forming Substances U. S. S. R. No. 1, 56-8, 81-90) prepared synthetic drying oils from oxidized petroleum oil fractions, fats, naphthenic or resin acids by reacting them with halogenated alkylenes obtained from gas oil. Coatings made from these synthetic drying oils were not suitable for surfaces exposed to outside weather conditions. S. L. Varshavskii and I. K. Shenfinkel (Russian Pat. 39,899) treated gasoline with hydrochloric acid at 120° for 4 hours in the presence of aluminum chloride. A lower layer which separated was claimed to have the drying properties of a drying oil. A similar process was invented by E. Kennecke and R. Werner (Ger. 624,229 Cl. 12o) for producing fat acid products from coal-hydrocarbon residues. Varnish oils were obtained by A. P. Bierregaard (U. S. 2,035,455) from the distillates of hydrocarbon polymer residues derived from treatment of cracked gasoline with solid absorptive material. During the distillation these residues were blown with air, and the air and vapor mixture was cooled to obtain the product. N. V. Pharmaceutische Fabrieken V/h Brocades Stheeman and Pharmacia (Ger. 617,728 Cl. 12h) obtained drying oils as a by-product in the purification of mineral and tar

oils with sulfuric acid. The sulfonic acids from the purification are dry distilled, purified with caustic and finally vacuum distilled to give a drying oil.

Patents on resins, varnish bases, or like titles which dealt with preparation of reaction products of fats, oils or fat acids and polybasic acids such as maleic, fumaric, cinnamic or the like acids were issued in the respective countries abbreviated under the following numbers: U. S. 2,027,466; 2,033,131-2; 2,044,747; Fr. 788,584; Brit. 431,951; 432,103; 432,158; 441,912; 446,276, and Can. 354,089. A communication on such a process for preparing resins by heating castor oil with glycerol or other polyhydric alcohols and reacting with phthalic anhydride was contributed by J.-C. Wee (J. Chinese Chem. Soc. 3, 321-4). Resins were prepared by J. S. Long (U. S. 2,059,260) from oils, fats and fat acids by reacting them with aromatic compounds through means of the Friedel-Craft synthesis. The synthetic resin patented by M. M. Brubaker (U. S. 2,046,318) comprises mixtures of polyhydric esters of drying oil acids, together with formaldehyde-phenol condensation products.

Products Derived from Fats and Oils

This section of the review includes a survey of the information on finished commercial fat products, products derived from fats with the exception of detergents, and materials and operations required in their preparation.

Methods of preparing a new form of shortening were patented by G. H. Kraft (U. S. 2,035,899) and E. J. Fechner (U. S. 2,065,675-6). Fat was emulsified with liquid whey or milk by homogenization and this was then dried by a spray process thus producing shortening in a powder form. Comminuted shortening of this type is especially designed for use in the manufacture of bakery products. Other improvements in shortening agents pertain to additions of special emulsifiers to yield baked products of larger volume or allow greater ratios of sugar to flour in the ingredients of bakery products using shortening. This was accomplished by inventors of Procter and Gamble Company (Brit. 437,737; U. S. 2,061,121-2 and 2,065,520) by adding either lecithin or free fat acids to the shortening or cake ingredients. H. Schou (Brit. 431,065) added both emulsifier and 0.2 parts of water or milk to improve the shortening.

The relative value of various lards and other fats for deep-fat-frying of potato chips was studied by Florence B. King *et al* (J. Agr. Res. 53, 369-81). The significant conclusion was that from the standpoint of palatability tests made on the potato chips, the vegetable oils, *i. e.* peanut, corn, and cottonseed, were preferable to lard. Most desirable flavor was imparted to the potato chips by peanut oil. As cited in a patent of Kosmos Werke Emil Pick & Company (Ger. 621,892 Cl. 53h), the flavor of peanut oil was improved by mixing with partly condensed egg yolks, heating and filtering.

Several salad oils partially crystallize or become cloudy during cool weather conditions. This property of olive oil was inhibited by W. Clayton *et al* (Nature 138, 806) by adding small quantities of air-blown cacao butter. D. P. Grettie (U. S. 2,050,528) accomplished the same effect for winterized cottonseed oil with lecithin.

J. C. Bird (U. S. 2,021,044) and T. H. Rider (U. S. 2,019,933) have converted our time-honored medicinal castor oil to more pleasant products. Bird prepared an emulsion of the oil using aluminum hydroxide as the emulsifier. Rider prepared magnesium and calcium ricinoleates from the castor oil fat acids and emulsified these with mineral oil.

Apparatus for mixing and kneading margarine were improved by A. Gerstenberg (U. S. 2,050,654) and G. Westerink (Ger. 621,326 Cl. 53h). Manufacturing technic was altered by a few inventors. A. D. Joyce (U. S. 2,024,647) incorporated the milk component into the supercooled uncrystallized margarine base. M. C. Reynolds (U. S. 2,022,924) claimed a process of manufacture of margarine by which it is prepared in the form of a liquid emulsion, crystallized and then processed to form plastic margarine. If a margarine has a viscosity of 36 centipoises of 50°, H. Schou (Fr. 787,383) reported that it would closely resemble butter. This was attained when the aqueous component was very finely divided. H. W. Vahlteich *et al* (U. S. 2,047,530) patented the use of a special hydrogenated cottonseed oil for margarine manufacture. This oil melts at about 35°, has a setting point of about 25°, and contains 16-20% glycerine of iso-oleic acid and 5% or less linoleic acid glyceride. F. Files (U. S. 2,042,173) colored margarine by adding a coloring agent in the form of dried milk containing a dye. Recent patents issued

to Akt. fur medizinische Produkte (Ger. 628,250 Cl. 53h) and to Noble and Thorl G. m. b. H. (Ger. 621,327 Cl. 53h) are additions to earlier inventions claiming use of lecithin in margarine manufacture and vary from the old patents by using cholesterol-lecithin and glycerol-oil-lecithin mixtures in place of lecithin.

The preparation of margarine, salad dressing, and other emulsions has become sufficiently popular as a household art that several small types of emulsifiers (U. S. 2,030,251; U. S. 2,041,068 and Brit. 437,752) were invented for home use. New industrial types of emulsifying machines were patented by Lancaster Processes Ltd. (Brit. 441,537) and C. F. Chapman (U. S. 2,033,412 and 2,033,413). The application of supersonic radiation for production of emulsions has found use in medicine. R. J. Myers and H. Blumberg (Proc. Soc. Exp. Biol. and Med. 35, 79-84) found that this method is most suitable for preparing fat emulsions for intravenous injections.

Among the new emulsifying agents patented, R. Hueter (U. S. 2,054,257) claims use of alkyl piperidinium salts; R. H. White and J. A. Vaughan (U. S. 2,054,399 and 2,054,400) emulsified wood preservatives with phosphatides; S. Frommer (Ger. 626,880 Cl. 23c) used esters of propyl or butyl alcohol and aliphatic monocarboxylic acids containing not more than 8 carbon atoms, and H. A. Piggott and C. S. J. White (U. S. 2,049,512) reacted ethylene oxide with partly oxidized marine animal oils in presence of caustic to obtain emulsifying agents. The most numerous patents on emulsifying agents were those claiming use of, or a method of preparing fat acid esters of glycerol, polyglycerol, or glycol, which contained some unesterified hydroxyl groups. Novelty was claimed for either emulsifying and wetting property or for some improvement in finished products. Their use in cake ingredients allows a greater sugar to flour ratio and also yields larger cake volume. These patents are as follows:

U. S. 2,022,766	Can. 359,911
U. S. 2,023,388	Can. 359,912
U. S. 2,024,356	Can. 359,913
U. S. 2,024,357	Can. 359,914
U. S. 2,025,955	Can. 359,915
U. S. 2,025,985	Can. 359,916
U. S. 2,025,986	Can. 359,917
U. S. 2,026,631	Can. 359,918
U. S. 2,033,195	Ger. 623,482 Cl. 12a
U. S. 2,048,818	Brit. 440,642
U. S. 2,052,025	Brit. 440,888
U. S. 2,052,026	Brit. 452,138
U. S. 2,052,028	

Among the above, T. P. Hil-

ditch's patent (Brit. 440,888) and (J. Chem. Soc. 1935, 1774-8) described a method of reacting fat acids and glycerol to yield a product containing as high as 90% monoglycerides. This was accomplished by heating a solution of the correct proportions of reactive products in solvent in which both are soluble. The solvent was removed by steam distillation. Laboratory methods for preparation and characteristics of pure mono- and diglycerides of several fat acids are recorded by P. E. Verkade and J. Van der Lee (Rec. trav. chim. 54, 716-24; 55, 267-77).

Information of general nature on emulsification has appeared. M. H. Fischer (Oil & Soap 13, 30-3) discussed some of the theories involved. J. P. Parke (Quart. J. Pharm. Pharmacol. 8, 484-9) illustrated various examples of good emulsions. He pointed out that to insure stability, an emulsion should contain a suitable phase ratio. The relationship between zeta potential and stability in emulsions was reported by C. Robinson (Trans. Faraday Soc. 32, 1424-5). Droplets of a water-in-oil emulsion stabilized by sodium oleate became increasingly stable as their surface area decreased until an expanded film had become a close-packed unimolecular film. The reason for this may be that the zeta potential effective in preventing contact between droplets is that of the adjacent sides of the droplets. He also found that cataphoretic measurements for the potential that affects stability can only be trusted when a condensed film exists.

Emulsions of the oil-in-water type can be prevented from foaming during processing as discovered by H. E. Buc (U. S. 2,052,164) by additions of stearic acid equal to 0.2 to 2% of emulsifying agent present.

Means of breaking emulsions were patented by M. DeGroot and B. Keiser (U. S. 2,025,803), T. B. Wayne (U. S. 2,050,639 and 2,050,690) and R. Heinrich (Ger. 629,922 Cl. 12d). The first inventors used the oxidation products obtained by subjecting linseed oil type fat acid sulfonates to hydrolysis. T. B. Wayne breaks water-in-oil emulsions by adding a condensation product of a cyclic sulfonic acid with either an oil soluble, non-hydroxy alkyl amine, or aralkyl amine. R. Heinrich used pulsating electric current characterized by 1×10^{-5} second pulsations.

Many practical suggestions have been made in the technical utilization of oils. S.-S. Ueno and Tsuchi-

ikawa (J. Soc. Chem. Ind., Japan 38, 693B) recommended autoclaved stearin made from fish oils as a substitute for paraffin. H. G. Meyers (Allgem. Oel-u. Fett-Ztg. 32, 397-401) prepared butyl and methyl esters of fat acids and acetate esters of fat alcohols and recorded their characteristics. He suggested that they are more convenient than the glycerides for many technical applications. A dehairing agent for animal hides and skins as prepared by J. W. Archibald (Australian patent 19,020) comprised a mixture of sulfur and oil heated to 140-180° for two hours.

Investigations on sulfurized oils and sulfur tanning were conducted by A. Abbassi (Cuir tech. 24, 238, 251-3, 305). Changes in properties of oils with increasing amounts of sulfur were given. General information on sulfur tanning and oil used in the process was also presented.

Old and new uses for wool fat were briefly reviewed by W. Obst (Allgem. Oel-u. Fett-Ztg. 33, 468-9).

For cases where animal fats or oils must be denatured J. Endraszka (Przemysl Chem. 20, 1-14) recommended as the most suitable denaturant a mixture comprising 2 parts by weight of pine tar and 1.5 parts of heavy naphtha or a mixture of pine tar and soybean oil. For the same purpose J. E. Muth (U. S. 2,025,954) recommended a benzyl derivative of a saccharide.

A. W. Ralston and coworkers (U. S. 2,033,536-48 and 2,061,314) obtained several patents for preparing fat acid derivatives and for uses of these derivatives. Nitriles were prepared from fat acids by the action of aqueous ammonia in the presence of a dehydrating catalyst. These were prepared for the purpose of obtaining better fractionation in fat acid distillation; they may be reconverted into fat acids or they may be pyrolytically cracked to shorter chain nitriles. The addition of small amounts of nitriles to mineral oil lubricants for increasing oiliness was also patented. Products of the Friedel-Craft reaction with coal tar materials and fat acids were prepared and also recommended as adjuncts to mineral oil lubricants. Mixed furyl alkyl ketones were manufactured by means of Grignard synthesis. These were especially adapted for use in furniture and auto polishes and floor wax formulas. Higher fatty aldehydes were prepared by treating fat acids with formaldehyde vapor in the presence of an oxidizing catalyst.

These aldehydes are recommended as intermediates for preparing high molecular weight condensation products. Dihydroxystearic acid was obtained by the action of alkali hypochlorites on oleic acid or its alkali salts, in the presence of a hypochlorite decomposing agent such as nickel oxide. A more detailed description of the preceding method was presented by the inventor in a recent paper (Oil & Soap 13, 170-1). The manufacture of hydroxy acid is intended for augmenting our supplies of this type product from domestic sources. In addition to Ralston's patents on preparing nitriles one was issued to I. G. Farbenindustrie A.-G. (Fr. 785,622) on the same subject. The methods vary slightly.

Alcohols which are prepared from fats or derived from waxes have achieved a position in commerce because they yield sulfated and sulfonated detergents with special characteristics and are also in demand for manufacture of cosmetic creams and furniture and automobile polishes. The properties and uses of several fatty alcohols and mixtures of alcohols were presented in a communication by L. Ivanovzky (Ole, Fette, Wachse, Seife, Kosmetik 1936, (10), 10-11) under the title "Lanette" waxes, that being one of the trade names for the products. Methods of manufacturing or improvements in current methods of manufacturing fatty alcohols from the corresponding acids by hydrogenization at high temperatures and pressure were invented by W. Schrauth and T. Böttler (U. S. 2,023,383), W. Normann and H. Prückner (Ger. 617,542 Cl. 12o) and by assignors to Imperial Chemical Industries Ltd. (Fr. 758,718). Innovations according to the patents were respectively, use of about 100 atmospheres pressure with temperatures of 280-300°, application of copper catalyst and passing a rapid current of hydrogen through the strongly agitated charge to distill off the alcohols as they were formed.

Patents on methods for obtaining fatty alcohols from waxes such as beeswax, spermaceti and vegetable waxes were issued to Deutsche Hydrierwerke A.-G. (Ger. 616,754 and 617,975 Cl. 12o), M. Schellmann and H. Franzen (U. S. 2,056,984) and W. A. Sexton and D. Ward (U. S. 2,021,926). These described improved methods for saponifying the substances and then distilling the alcohols from the soaps. Alcohol esters were separated from the glycerides of spermaceti by V. Rubenshtein *et al* (Masloboino Zhirovoe

Delo 12,254-5) with use of a method that depends on the greater rate of saponification of the glycerides. Saponification was carried out in the cold with 1.5 parts caustic—based on triglyceride. The product after washing away soap contains 75-85% cetyl esters.

The literature on the transformation of vegetable oils into hydrocarbons for use as motor fuel or the direct use of the oil in Diesel motors indicates commercial possibilities along this line in some countries. Experimental results obtained on a plant at Segou, French Sudan, and favorable commercial possibilities of processes for this purpose were reported by C. Berthelot (*Industrie Chimique* 23, 416-8). Laboratory investigations on this subject were recorded by E. C. Koo, S.-M. Cheng and coworkers (*Ind. Research, China* 4, 64-9, 239-44, 466-79). They prepared gasoline and crude fuel oil from rapeseed and cottonseed oils by both vapor phase and catalytic cracking. Vapor phase cracking of rapeseed oil yielded 52.5% by volume of a crude oil which on fractionation was divided into 53% gasoline and 47% fuel oil. A maximum yield of 43.4% gasoline from cottonseed oil was obtained by T.-S. Lo and L.-S. Ts'ai (*J. Chinese Chem. Soc.* 4, 157-71). This was more than could be obtained from any other oil by autoclaving. A dissertation on the mechanism of reactions occurring in the production of hydrocarbons from fat acids by hydrogenation at high temperatures and pressures was contributed by Y. Yendo (*Bull. Inst. Phys. Chem. Res., Japan* 14, 965-1080). During the process carbon monoxide and carbon dioxide were produced and converted into methane and water. Oleic acid was first converted into stearic acid and at higher temperatures into higher paraffins, which at 450° break down into lower paraffins, the breakdown being endothermic and accompanied by an abrupt fall in temperature.

The carbonization of oil-bearing seeds by the "Bonnie" retort process is another method of obtaining petroleum substitutes. Commercial scale tests on a number of oil seeds by J. Boizard de Guise (*Bull. soc. encour. ind. natl.* 134, 571-81) showed that oils produced by this process could be refined into stable motor fuels, gas oils and heavy oils, which in some respects could even be superior to corresponding petroleum products.

A comparison of peanut oil with mineral oil as fuel for Diesel engines by G. Manzella (*Energia*

Term. 3, 153-60) indicated that the consumption of peanut oil is higher than that of mineral oil at normal loads, but it is lower at reduced loads in spite of the fact that the vegetable oil has the lower calorific value. Use of peanut oil according to his conclusions therefore, seems particularly advantageous in motors operating over a wide range of loads. The efficiency in all cases is greater than with mineral oil. According to L.-T. Kao (*J. Chem. Eng., China*, 2, 112-6) and E. C. Ku and S.-M. Chen* (*Ind. Research, China*, 4, 239-44) peanut or soybean oil blown for 8 hours at 200° yields a product which has good lubricating properties.

Biochemical

Recent literature on fat metabolism was reviewed by E. F. Terroine (*Ann. Rev. Biochem.* 5, 227-46). The topics treated were fatty components of the organism, physiological role of lipids, origin of the lipids and their products, fat transport and fat catabolism.

A technic for determining the rate of absorption of fats was developed by Margaret H. Irwin, H. Steenbock, and others (*J. of Nutrition* 12, 85-101, 103-11, 357-64, and 365-71). The method involved the feeding of a definite quantity of fat to rats and subsequent analysis of the intestinal residues. They found that: (1) partially hydrogenated vegetable oils were absorbed as rapidly as lard or corn oil, and (2) butter oil, halibut liver oil and cod liver oil were absorbed uniformly at a more rapid rate than lard, corn oil, or partially hydrogenated fat. In four-hour tests the following oils were absorbed in descending order: Linseed oil, olive oil, whale oil, soybean oil, peanut oil, rancid lard, cottonseed oil, cocobutter, coconut oil and oleo stocks. Avitaminotic A, B, or D, anemic and semi-starved rats absorbed fat less rapidly than normal animals. The addition of vitamins A, B, or D to a fat had no effect upon its rate of absorption by normal rats. Small amounts of water, bile salts, sodium benzoate, ethyl alcohol, peptone, sucrose, potassium chloride, calcium chloride, monosodium phosphate, glycerol, and sodium glycerophosphate had little or no effect on fat absorption but larger amounts invariably decreased the rate of fat absorption. G. Perotti and co-workers' (*Bull. soc. ital. sper.* 10, 871-3 and 873-4) investigations were carried out in practically the same manner. Their results indicated that there was no parallelism between the degree of unsaturation

and absorption of fats. The absorption of oleic acid, mono-olein and diolein six hours after administration was determined. Mono- and diolein were absorbed with a velocity of the same order as triglycerides while free oleic acid was absorbed at about 25% of that rate. G. Valette and R. Salvanet (*Bull. soc. chem. biol.* 18, 911-17) measured the absorption of castor oil in man by giving a purgative dose with a low fat diet and analyzing the feces. About 22% of the oil was absorbed in the intestinal tract. J. E. Thomas and J. O. Crider (*Am. J. Physiol.* 114, 603-8) added information on the mechanism of fat digestion. They found that following a meal of fat the acidity of the duodenal contents was less than after meat alone, and administration of oil in the course of meat digestion caused a prompt decrease in the acidity of the duodenal contents. They suggest that this mechanism may be important in providing suitable medium for fat digestion.

H. J. Deuel, Jr., L. Hallman, J. S. Butts, and S. Murray (*Proc. Soc. Expt. Biol. & Med.* 34, 669-70; and *J. Biol. Chem.* 116, 621-39) reported quantitative studies on the oxidation of ethyl esters of fat acids fed to rats. The excretion of acetone bodies from ethyl esters of the caproate, butyrate and acetoacetate was approximately quantitative, whereas, the amount of acetone bodies after administration of ethyl esters of fat acids with 8 or more carbon atoms was greater. Low values with ethyl palmitate and stearate were attributed to lack of absorption. No appreciable ketonuria followed the administration of fatty acids containing odd numbers of carbon atoms. The authors postulated that palmitic, stearic, and oleic acids broke up into at least three fragments per molecule which were capable of transformation into acetone bodies.

J. H. Quastel and H. M. Wheatley (*Biochem. J.* 29, 2773-86) and F. P. Mazzo (*Bull. soc. ital. biol. sper.* 11, 143-5) have added new communications to those reported in last year's survey on the *in vitro* studies of fat metabolism. Quastel found that acetoacetic acid was broken down under both aerobic and anaerobic conditions by rat and guinea-pig kidneys. Mazza's experiments on living sections of rabbit and guinea-pig organs showed that dibasic acids are oxidized to some extent by the liver and to a greater extent by the kidney. Monobasic acids underwent ω -oxidation when the carboxyl group was blocked, and

unsaturated dibasic acids underwent β -oxidation. The activity of kidney and liver tissue from animals fed different fats was studied by A. K. Pikkat and O. Ya. Kurtzina (Voprosui Pitaniya 4, [4], 58-66). They discovered that feeding unsaturated fats such as linseed and sunflower seed oils produced more active oxygen consumption in the tissues than did saturated fats such as mutton fat.

Some relationships between the pancreas and fat metabolism were elucidated by F. G. Young (J. Physiol. 87, 11-13P) and A. I. Lewin (Z. ges. exptl. med. 96, 548-60). Young reported that the conversion of fat acids to sugar occurred in the liver either in the presence or absence of the pancreas. Lewin reported that pancreatectomy in dogs produced a considerable increase in blood lipoids, a decrease in peripherally stored fat, and infiltration of fat in some organs. This was attributed to lack of insulin because metabolism became normal on administration of insulin.

The specific dynamic action of butter fat, eaten as heavy cream, was studied by J. R. Murlin *et al* (J. Nutrition 12, 613-43, 645-70) on nine human subjects by means of a new respiration calorimeter. With six subjects, sugar was superimposed on the high fat at 3 to 5 hours and 11 to 15 hours after the fat meal. The dynamic response to sugar was of two types, (1) a complete summation to the fat metabolism, and (2) an increase greater than that due to the same amount of sugar alone; this difference was reckoned as fat metabolism. In other tests, sugar caused a marked reduction in total ketosis within 3 to 4 hours. The effectiveness of sugars in decreasing order were: sucrose, fructose, and glucose. A late dose of sugar following an early dose was much more effective than the early one. This was interpreted as due to replenishment of glycogen in the liver, possibly because of the insulin production stimulated by the early dose.

New means of studying certain phases of fat metabolism were originated. R. G. Sinclair (J. Biol. Chem. 115, 211-220) fed elaidin to cats and found considerable amounts of elaidic acid in the phospholipids of the blood plasma within a few hours. After several days' feeding of elaidin, as high as 37% of the fat acids in the plasma phospholipid consisted of elaidic acid. He concluded that plasma phospholipids definitely served as a mechanism for the transport of fat acids to

the tissues where they are burned. Deuterium was used as an indicator in the study of intermediary metabolism by Schoenheimer and Rittenberg (J. Biol. Chem. 113, 505-10). Deuterium was present in the unsaturated fat acids from mice fed saturated acids containing deuterium. This was interpreted to mean that fat acids can readily be desaturated in the organism.

The problem of fatty livers concerned several investigators. R. P. Cook (Biochem. J. 30, 1630-6) and R. P. Cook with W. L. Edson (Biochem. J. 30, 1637-9) reported their findings on the action of cholesterol on rats. On a synthetic diet containing fat and cholesterol, the growth rate decreased and fatty livers developed. On a normal diet cholesterol was without action. The fatty livers had a lower respiration than controls. It was postulated that the action of cholesterol in synthetic diets appeared to cause a lower respiration of liver tissues and a mobilization of fat in the liver. H. C. Eckstein and C. R. Treadwell (J. Biol. Chem. 112, 373-8) reported that the amount of sterol in the livers of growing rats was increased when the percentage of corn oil or soybean oil in the diet was increased. They considered it impossible to state whether the amounts of sterols in the liver were due to ingested sterols, fats, or both. The effect of various dietary fats in producing fatty livers in animals on fatty liver producing diets was recorded by H. J. Channon and H. Wilkinson (Biochem. J. 30, 1033-9). The fat content of the livers of rats fed a diet containing 40% of the various fats were: butter 30.67, beef fat 27.05, palm oil 26.35, coconut oil 20.54, olive oil 15.57, and cod liver oil 7.18%. During the course of the studies by H. Steenbock, Margaret H. Irwin and coworkers mentioned above, no fatty livers were produced in rats on diets containing 30% of lard, butter fat, oleo stock, partially hydrogenated vegetable fat, coconut oil, or olive oil. G. Peretti (Boll. soc. ital. biol. sper. 10, 875-6, 876-7) administered oils to rats; six hours later the livers were removed and total fat acids contents determined. The percentage increase compared to that found in livers of fasting rats was: cacao butter 94.0, olive oil 108.1, sesame oil 9.3, poppy seed oil 44.6, linseed oil 18.8, oleic acid 63.2, mono-olein 24.1, and diolein 39.5.

Means of preventing fatty livers were investigated by H. J. Channon, A. W. Beeston and coworkers (Biochem. J. 29, 2651-8, 2659-67;

30, 115-20, 121-6, 280-4, 1040-6). Administration of choline or triethyl- β -hydroxyethylammonium hydroxide was effective with certain dietary precautions. Graded protein percentages in a low-choline diet containing 20% fat and 2% cholesterol produced fatty livers of widely varying composition. Diets with high cystine content favored extreme fat deposition in livers. Increasing the amount of choline prevented deposition of glycerides but only partly prevented increase of cholesterol esters. Choline had no preventive effect with raw or dried liver diets, since the effect may have been exercised already by the lecithin contained in such diets.

A few observations on the action of fat metabolism hormone of the anterior pituitary were made by C. H. Best and J. Campbell (J. Physiol. 86, 190-203) and H. J. Anselmino, G. Effkemann, and F. Hoffmann (Z. ges. exptl. Med. 96, 209). Both communications report increases of fat in the liver following administration of the hormone. Best and Campbell found this to occur even in fasting rats. A decrease in body fat and an increase in excretion of ketone bodies also occurred.

It is well known that the body fat of certain animals is affected by the fat in the diet. Rats fed on diets known to produce from firm to very soft hog carcasses show striking parallel body-fat deposition according to H. E. Robinson, R. E. Gray and R. C. Newton (Food Res. 1, 413-8). Supplementing a diet containing soybean or peanut oil with high-melting, low iodine value fats tended to offset the effects of the oil. The authors concluded that rats were satisfactory animals for studying the soft fat problem. R. D. Sinclair (Sci. Agr. 17, 31-41) revealed other factors which affected the firmness of hog carcasses. Winter-fed hogs had higher iodine values in the fat than summer-fed hogs. This condition was also related to the thrift of the pig, rate of growth and individuality. Since individuality was of some importance, he suggested breeding as a partial solution to the problem. Experiments on steer calves by F. J. Beard, J. A. Schulz and C. C. Culbertson (Am. Soc. Animal Production, Rec. Proc. 28th Ann. Mtg. 1935, 286-90) indicated that consumption of menhaden and coconut oils at the rate of 15-18.8 pounds per 100 pounds weight gain was not injurious to calves and had no deleterious effect on the carcasses or the palatability of the beef. The feeding of men-

haden oil increased the iodine value of the kidney and caul fats, but had no effect on the back fat. Diets containing coconut oil had no effect on the kidney and caul fats but tended to decrease the iodine value of the back fat. J. M. Spadola and N. R. Ellis (J. Biol. Chem. 113, 205-17) recorded the effects of ingestion of cottonseed oil before and after hydrogenation on the composition of the body fat of the rat. The amount of linoleic acid deposited was approximately proportional to the amount ingested. Increased deposition of linoleic acid was accompanied by a decreased deposition of palmitoleic and oleic acids. The body fats contained a small amount of arachidonic acid and saturated acid of more than 18 carbon atoms. Ingested iso-oleic acid was deposited in the depot fat.

T. P. Hilditch and H. M. Thompson (Biochem. J. 30, 677-91) accumulated considerable data on the effect of rations containing cod liver, linseed, and rape oils on composition of cow milk fat, in their attempt to ascertain which of the cod liver oil components was responsible for diminishing the fat content of milk. Half the normal amount of lower saturated acids, an increase in oleic acid and the presence of 5-7% of highly unsaturated C20-22 acids were characteristic of milk from cows fed cod liver oil. Linseed oil merely increased the proportion of oleic acid. Rape oil had an influence similar to that of linseed oil, but small amounts of erucic glycerides were present in the milk fats. The most significant aspect of the work was the evidence which showed that some of the highly unsaturated C20-22 glycerides of cod liver oil passed into milk fats. The authors suggested that selective absorption of these highly-unsaturated compounds by the enzymes responsible for the elaboration of typical cow milk fats retarded their normal function and caused the observed effects. R. W. Riemenschneider and N. R. Ellis (J. Biol. Chem. 114, 441-7) observed a decrease in butyric acid, and an increase in capric, lauric, myristic, and stearic acids at the expense chiefly of oleic acid in milk fat from cows fed rations containing cottonseed oil. No evidence of the presence of linoleic acid was obtained. The speed of changes in iodine value of milk fat after changing the ration fats from high to lower unsaturation or *vice versa* was investigated by L. A. Maynard, C. M. McCay, and L. L. Madsen (J. Dairy Sci. 19, 49-53). These changes occurred between 18 and 24

hours after altering the diet. Corresponding but less marked changes were found in the blood. These authors concluded that the course of fat metabolism in lactation must be very direct or that the various processes must take place very rapidly.

Data presented by R. H. Snider (J. Biol. Chem. 116, 503-10) showed that the ratio of saturated to unsaturated acids in the phospholipid of muscles was quite constant in different muscles in a variety of animals both exercised and unexercised. The influence of exercise was not reflected in the degree of unsaturation of fatty acids of muscle phospholipid.

The proportions of the various fatty acids in a number of algal fats were recorded by J. A. Lovorn (Biochem. J. 30, 387-90). The algal fats fall into groups agreeing with their botanical relationship and no difference between salt and fresh water forms as such could be detected. The results suggested that while fresh water plankton crustacea may deposit ingested fat largely unchanged in type, the corresponding marine organisms are forced to modify it considerably.

S. Ueno *et al.* (J. Soc. Chem. Ind., Japan, 39, 112-3B) reported considerable variation in the nutritive value of several samples of margarine. Only one sample approximately equalled butter when fed to albino rats. T. S. Sutton and R. B. Stoltz (Ohio Agr. Expt. Sta., Bull. No. 548, 59-60) recommended adding carotene as a coloring agent and to increase the vitamin A potency of butter. Means of extracting carotene from soaps and its use in food products were the subject of patents issued to S. M. A. Corporation (U. S. 2,031,991; 2,032,006 and 2,032,165). H. I. Waterman and J. A. Van Dijk (Brit. 452,442) prepared a vitamin A concentrate from cod liver oil by hydrogenating the oil at 60-70° temperature to a shortening consistency and distilling about 8% under vacuum at 180°. This distillate may be added to foods to increase their vitamin A potency.

The toxic effect of cod liver oil in the ration of the rabbit and the calf was studied by W. A. Turner, E. B. Meigs and H. T. Converse (J. Biol. Chem. 114 civ.) Animals died at 90 to 150 days when fed a grain ration containing 5% cod liver oil. Stiffness of limbs and emaciation preceded death. When cod liver oil was supplied at not more than 0.7 gram per kilo of body weight daily, calves survived and grew normally;

while two grams or more per kilo body weight daily caused death. A study of the skeletal muscle dystrophy which occurs in guinea pigs and rabbits fed synthetic diets containing cod liver oil or its concentrates with other oils was reported by L. L. Madsen (J. Nutrition 11, 471-89). The basal synthetic diet without added fat other than the non-saponifiable fraction of cod liver oil as a source of vitamins produced dystrophy to nearly the same extent as the same diet which included 6% lard. The use of cottonseed oil in place of lard resulted in a high degree of protection against the development of muscle lesions.

A. M. Pappenheimer (J. Biol. Chem. 114, 673-87) discovered a new nutritional factor in vegetable oils. This factor protects chicks on synthetic diets against deleterious changes in the central nervous system. It is present in corn, cottonseed, peanut, soy bean, and hydrogenated cottonseed oils. It is thermostable and is resistant to aeration and to ultra-violet irradiation. With proper solvents, it can be extracted along with the non-saponifiable fraction of oils.

The reported vitamin nature of certain fat acids, also called vitamin F, when used as a shampoo in the form of soap for curing scaly tails of rats on a diet deficient in unsaturated fat acids, was proved effective by Kathryn Glennon (Soap 12 [11], 30-32). Published reports on the curative effect of unsaturated fat acids on certain skin lesions prompted S. J. Taub and S. J. Zakon (J. Am. Med. Assocn. 105, 1675) to test their efficacy in the treatment of eczema. Daily ingestion of 15-30 cc. of highly unsaturated oil, i.e., linseed oil, did not benefit patients suffering from eczema.

A patent issued to A. J. Lorenz (U. S. 2,060,228) described a method of incorporating vitamin D concentrate in soap.

A bactericidal effect of the so-called "peroxides", "active oxygen" or "ozonides" of irradiated oils was demonstrated by F. A. Stevens (J. Infect. Diseases 58, 185-9 and J. Bact. 32, 47-55). These peroxides are either soluble in or miscible with salt solution. By adding reducing agents such as cysteine or thioglycolic acid to their salt solutions the bactericidal effect is destroyed. The vapors of the irradiated oils also have bactericidal properties.

A treatment for obesity by P. Hanssen (Acta. Med. Scand. 88, 97) is included in this survey because of the relatively large amounts

of fat in the diet used for the treatment. Hanssen cited investigations of others which proved that obesity resulted from an increased transformation of carbohydrates into fat. His patients were given a diet that provided generous amounts of

greens, some fruit, 100-125 grams of meat or fish, 100 grams of bread, 65 grams of cream, 65 grams of butter, 35 grams of cheese, 2 eggs and 25 grams of olive oil. He compared the results with those obtained in other hospitals and found that his patients lost the same amount of

weight with an intake of 1,850 calories as was the case in other hospitals in which the intake of patients under treatment for obesity was only 950 calories.

[Editor's Note: Due to the length of this paper, it has been divided into two sections. Second section will appear in the April issue.]

THE ANALYSIS OF SULFONATED (SULFATED) OILS COMMITTEE REPORT*

Committee Report, No. 3 Determination of Inorganic Salts in Sulfonated Oils

By RALPH HART, Chairman

INCIDENTAL to manufacture or through admixture, commercial sulfonated oils may contain various amounts of inorganic salts, such as alkali chlorides, sulfates, and less frequently acetates, carbonates, etc. The determination of inorganic sulfate in sulfonated oils is part of the regular procedure for finding organically combined sulfuric anhydride by the barium sulfate method, but the other inorganic salts are practically always included with the "undetermined," largely because no satisfactory methods of analysis for inorganic salts have been described. For a more complete and thorough analysis of a sulfonated oil, it is desirable that the total inorganic salts be determined separately rather than grouped with the "undetermined."

Available Methods

Herbig¹ determines inorganic sulfate by dissolving the sample in ether, washing with a saturated solution of sodium chloride, and precipitating the sulfate in the wash water with barium chloride. To overcome troublesome emulsions, which highly sulfonated oils tend to form, he replaces one-third of the ether with benzene. If emulsions still persist the oil is dissolved in absolute alcohol, filtered, the residue dissolved in hot water, and the inorganic sulfate determined in the filtrate. Nishizawa² attributes such emulsions to the comparatively easy solubility of the normal or di-sodium salt of sulfonated oils in concentrated sodium chloride solution. On the other hand, the mono-sodium salt is practically insoluble in a saturated solution of sodium chloride. Accordingly he modifies the Herbig method by first converting the compound into the mono-sodium salt

with hydrochloric acid — using methyl orange as the indicator — before washing with the salt solutions.

Burton and Robertshaw³ determine total inorganic salts by digesting the dehydrated sample with alcohol or a mixture of alcohol and ether, filtering, dissolving the residue in hot water, and determining the solids in the filtrate by evaporation. The inorganic salts, they state, are not completely precipitated by alcohol with many sulfated oils. Some tests made in this laboratory indicate that the Burton and Robertshaw method may yield good results with sodium sulfate but it is not satisfactory with sodium chloride, using 95% alcohol and ether as the solvents. The results on a sample, in which the inorganic salts contained about 90% sodium chloride and the rest sodium sulfate, were as follows:

Solvent—	Inorganic Salts Added Per cent	Found Per cent
2 parts ethyl ether and 1 part 95% alcohol	7.84	6.32
2 parts ethyl ether and 1 part absolute alcohol	7.84	7.52

Difficulties may also be experienced with the alcohol-ether solvent in the case of dehydrated oils containing at the same time large amounts of fatty glycerides or mineral oils and neutral soap, since the former are sparsely soluble in alcohol and the latter in ether.

Wizöff or Herbig Method

In the official method of the Wissenschaftliche Zentralstelle für Öl- und Fettforschung (Wizöff),⁴ a mixture of 40% of ether and 60% of amyl alcohol is used as solvent for the oil, otherwise the procedure is the same as the Herbig benzene-

ether method. The procedure for this method is as follows:

Determination of Inorganically Combined Sulfuric Acid—5 to 7 g. of oil is shaken in a separatory funnel with 10 c.c. saturated sulfate-free common salt solution, 10 c.c. ether, and 15 c.c. amyl alcohol; the clear salt solution is separated from the ether and then washed three times with 10-20 c.c. of concentrated salt solution. The combined salt solutions are made up to 25 c.c., 1 c.c. of concentrated HCl (D-15 = 1.19) is added, and the sulfuric acid estimated by precipitating at the boil with barium chloride solution in the usual way.

The A.L.C.A. Method

Another method for total inorganic salts is that of Hart.^{5, 6} This method has been used in the writer's laboratory for a number of years as a means of control during manufacture with entirely satisfactory results. According to this method, total non-volatile inorganic salts are determined indirectly from the ash, fixed alkalinity, and organically combined sulfuric anhydride in the sample. This procedure is also the official method of the American Leather Chemists Association (A.L.C.A.).⁷ It yields reliable and accurate results, except in the presence of ammonium salts and sodium acetate, since the former is volatilized during the ignition and the latter changed to the carbonate. Moreover, the formulas are calculated for sodium salts and in the presence of potassium it becomes necessary to determine the metallic elements. The following are the details of this method:

Ash—Weigh accurately from 5

*A report presented at the Fall Meeting of The American Oil Chemists' Society, at Chicago, October 8-9, 1936.