REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1935

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TABLE OF CONTENTS

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The plan followed in preparing this survey is, in general, similar to that of the first annual review by this committee (OIL AND SOAP **12**, 106-21). In addition to the material collected during the year 1935, some contributions of the previous year which were not available to the reviewers at the last writing were included. The extreme condensation of the material gave rise to some unavoidable discontinuity. The failures in grouping the subjects according to the outline are due in part to the overlapping nature of many of the communications.

During the period being reviewed there has been a slight increase in the prices of oils and fats; the December "Chem. & Met's" weighted indices of the years 1933, '34 and '35 were 51.89, 83.32 and 93.05, respectively—basis: 100 for the average price during 1927.

According to an editorial in "Chemical Industries" (Chem. Ind. **37**, 23-6) various unnatural influences have affected the commercial situation of the fat and oil industry. These influences were currency exchange, flight of silver from oil producing countries, crop control, reduction in consumption, and taxes. The editorial also presents information relative to uses, sources, price, interchangeability, production, exports and imports of various vegetable oils and fats. A second review (Chem. Ind. **37**, 331-2) presents like information on fish oils. Similar information giving distribution of total oil and fat production is presented by T. G. Richert (OIL AND SOAP **12**, 148-52). The statistics and information, although for years previous to 1935, are interesting to show the trend. In order that the most recent statistics may be presented in this review, the following summary has been compiled from official sources:

(Data in million pounds)*

	Year ending October 1 1934	1935
Production:		
Animal fats (excluding butter)..	2,288	1,434
Butter (creamery)	1,659	1,707
Greases	346	290
Lard compounds and substitutes.	1,053	1,429
Fish oils	163	228
Vegetable oils	2,231	2,125
Factory Consumption:		
Animal fats (excluding butter)..	703	869
Greases	241	197
Fish oils	151	230
Vegetable oils	2,751	2,797
Apparent Consumption:		
Butter	1,713	1,664

	Jan. 1, 1935	Oct. 1, 1935
Stocks:		
Animal fats (excluding butter)..	418	361
Butter (in storage)............	47	149
Greases	74	67
Lard compounds and substitutes.	28	33
Fish oils	242	188
Vegetable oils		
Crude	558	537
Refined	595	356

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*Survey of Current Business **16** (1) and ibid. **15** (1) 37-8.

The production of soap during 1935 was less than for the preceding year; this may have been in consequence of several factors, such as overproduction during 1934, recent increases in prices, and uncertainty of the future trend in the cost of raw materials. H. J. Hausman (Soap **11**, No. 11, 3-33, 64) discusses the increase in the practice of recovery of low-grade fats by soap makers who were forced to do so because of competition and price levels of raw materials.

The above statistics show an increase in the consumption of marine oils, which probably resulted from improvements in processing and increase in the literature promoting these products. H. N. Brocklesby and B. E. Bailey (Biol. Board Canada Bull. 46), W. Alexander (OIL AND SOAP **12**, 89-90) and L. J. Reisenstein (Paint Varnish Production Mgr. **12**, 18, 20, 22-3, June) review and discuss the subject. The first two papers are concerned with the use of fish oils for edible purposes, and the last paper deals with their merits as a raw material in the manufacture of protective coatings.

Governmental agencies have been promoting the planting of soybeans as a substitute for those crops whose foreign markets have been lost. This, together with the promotional program adopted by the Soybean Association (Cotton Oil Press **19**, No. 5, 15) for the coming year, will result in large production of soybeans. In addition to the effect this will produce on the market futures of seed oils, there is the threat of increasing the amount of poor quality meat and animal fats coming to the market; for, according to a University of Illinois Agriculture Department publication (Bull. **366**), much of the recent oily butter, soft meat, low melting point lard and tallow now being marketed is the result of feeding soybeans to farm animals.

The search for new sources of oils has continued. The object of these searches is not only to find newer and cheaper sources but is also fostered by the strong nationalistic feeling in most countries which favors independence in regard to raw materials. Notable among the new sources is the neglected grape seed, which is a by-product of the raisin and wine industry. Discussions on the value and uses of grape seed oil and presented by G. S. Jamieson and R. S. McKinney (Oil and Soap **12**, 241) and F. Fritz (Chem. Ztg. **59**, 704). Tea seed is another by-product which can supply oil. This oil, according to J. Pritzker and R. Jungkunz (Z. Untersuch. Lebensm. **69**, 542-7), is edible and resembles olive oil in its characteristics. M. Guzovskii (Masloboino Zhirovoe Delo. **11**, 167-8) recommends safflower and sunflower as a farm crop to supply Russia with a needed oil source. A paper by Krohn (Fettchem. Umsch. **42**, 127-31) discusses and suggests possible solution of the problem of supplying German domestic requirements from home sources. A. Steger and J. van Loon (J. Soc. Chem. Ind. **54**, 1095-7) have presented information on Jaboty fat and suggest this as a new edible fat source. Large scale production of fat from glucose by molds as described by G. E. Ward, L. B. Lockwood, O. E. May and H. T. Herrick (Ind. & Eng. Chem. **27**, 318-20) may supply some of our future demands. In order to increase our source of drying oils G. S. Jamieson and R. S. McKinney (Oil and Soap **12**, 141-8) and H. A. Gardner (Paint, Varnish & Lacquer Assoc. Circ. No. **490**, 248-57) are encouraging the cultivation of the soft lumbang tree in the southern portion of Florida. Substitutes for drying oils are proposed by Russian writers. I. L. Potolovskii and coworkers (Azerbaidzhanskoe Neftyanoe Khoz. **1934**, No. 10, 91-7) showed that the mineral oil fraction boiling between 27-84° can be treated with aluminum chloride at 10-20° for 3-4 hours to form a high molecular weight drying oil suitable for preparation of commercial protective coatings. A. Y. Drinberg (J. Applied Chem. U.S.S.R. **7**, 1046-54, 1206-21) prepared drying oils from chlorinated derivatives of unsaturated hydrocarbons and sodium salts of acids obtained by the oxidation of oil gas.

A. Bag (Masloboino Zhirovoe Delo. **11**, 73-4) states that rape seed oil can be used successfully in the production of olein and oleic acid. This is a very good outlet for the oil, as it is not easily hydrogenated and hence the demand is low. The oil of caper spurge is also potentially an excellent commercial source of oleic acid according to B. Tyutyunnikov and coworkers (Masloboino Zhirovoe Delo **11**, 131-3); this oil cannot be used for edible purposes because of its strong purgative power. A. Eselevskii (Masoloboino Zhirovoe Delo **11**, 133-5) recommends growing the caper spurge seed as a farm crop because of the good yield of oil and the quality of soap it produces.

The use of vegetable oils and fats as motor fuel was investigated by M. Gautier (Rev. combustibles, liquides **13**, 129-36), who published experimental results on the Diesel engine efficiency with various vegetable oils and fats. Chinese and Japanese investigators are suggesting the coversion of oil or fat to gasoline and have published considerable information on the subject which will be presented in this review. In this country the supply of mineral oil fuels makes economically unimportant the conversion of vegetable or animal oils into motor fuels.

Commercial Treatment of Oils and Fats

The literature on commercial treatment of fats and oils, although very abundant, deals principally with improvements in known methods. Recent progress has been reviewed by R. Strauss (Chem. Ztg. **59**, 373-5, and Fettchem. Umsch. **42**, 190-3, 219-28), A. Foulon (Fettchem. Umsch. **42**, 11-3), A. van der Werth (Allgem. Oel- u. Fett-Ztg. **32**, 57-61), C. H. Keutgen (Chem. Ztg. **59**, 34-7), and R. Furness (Indus. Chemist 11, 21-4).

Rendering methods for lard production are described in a series of papers by C. R. Moulton (Meat **2**, Nos. 7, 8, 9, and 10) and by T. Ruemele (Allgem. Oel- u. Fett-Ztg. **32**, 6-8). An apparatus for continuous rendering of fats by means of hot water is described in the patents of T. Hinko (Ger. 608,200, Cl. 23a; Aust. 137,205). An apparatus for use in extracting fish oils was invented by H. S. Hansen (Brit. 426,000). In the warm extraction of this material A. Middlemass (Brit. 414,717) finds that adding glacial acetic acid, to bring pH to about 4.6 or less, aids in the extraction.

In this country both the expeller and the hydraulic types of mills are used for pressing cottonseed. Data presented by J. M. Newbold (Oil and Soap **12**, 166-7) show that the crude oil obtained from the hydraulic mill is decidedly better than that from the expeller mill, and this difference is progressively greater as the moisture content of the seeds increases. A. Goldovskii (Masloboino Zhirovoe Delo **10**, No. 12, 24-8) finds that the most favorable texture in sunflower seed pulp for pressing is obtained with a moisture content between 17% and 18%, and increased extraction efficiency is obtained if the pulp is heated during the kneading and addition of water. G. Vuigovskii and coworkers (Masloboino Zhirovoe Delo **11**, 299-301) obtain good yields by adding 16-17% of sodium chloride solution to the sunflower seed mash to be extracted. When sunflower seed pulp is heated prior to extraction, the changes in the oil produced as per I. Kolpakov (Masloboino Zhirovoe Delo **10**, No. 4, 32-4) are a decrease in acidity and increase in iodine value, these being respectively 5.1—12 units lower and 7.7—10.4 units higher on leaving the press than in the crude pulp; R. Heublyum (Mat. grasses **26**, 10315-7) finds that no difficulty is experienced in extracting to a residual fat content of about 1% when the seed pulp is preheated.

Mustard oil produced by the use of newer presses has not been equal in pungency to the oil produced by the use of native wood rotary mills. J. A. H. Dale (J. Sci. Tech. Indian **1**, 103-5) has removed this disadvantage of the modern means by pretreating in cooking kettles containing an upper compartment where the milled seed is first treated with 3-4% of water; it is then passed into a lower compartment and heated at 40° for 45 min. to develop the required odor by enzymic action.

According to E. R. Ragsdale (U. S. 1,985,426), it is profitable to return the foots filtered from crude oil into oil bearing material that is to be pressed.

The patent issued to E. V. Breitenbach (U. S. 2,015,213) describes apparatus for pressing oil out of seeds in a continuous manner. The apparatus of Fried. Krupp Grusonwerk A.-G (Ger. 610, 127, Cl.23a) combines a rendering with a pressing method for use in production of palm oil; i.e., the material is boiled with water and the water is skimmed; during the same time the settled residue is continually removed and subjected to pressing.

Descriptions of some existing countercurrent extraction processes are presented. T. R. Richert (OIL AND SOAP **12**, 148-52) describes the process used by the Hansa mills of Hamburg, Germany; A. A. Horvath (Food Industries **7**, 387-8) describes the Boehm system and H. Joyce (OIL AND SOAP **12**, 61-9) describes the method and the recent modification as used and developed by the "Edison Institute of Technology." K. Sohler patented (Brit. 422,530) a new apparatus which uses the countercurrent principle in several chambers through which the oil containing material is forced by conveyors, while the solvent flows in the opposite direction and is removed by specially constructed filtering means from the compartment which also receives the fresh unextracted material.

There are numerous solvents used in the commercial extraction of oils; the superiority of any one over another depends on the ease of handling, the type of seed, the conditions under which the extraction takes place, and the quality of product and by-products desired. With the alcohol extraction method the best condition for technical purposes, according to M. Sato, T. Inaba and K. Kitagawa (J. Soc. Chem. Ind. Japan **37**, 718-21B, ibid. **38**, 50B) is an alcohol concentration of about 92% by weight and a 78° operating temperature. Under these conditions it is claimed that the oil and crude meal produced are superior to gasoline extracted products, the oil being light in color, low in moisture and protein content, and almost free from fat acids. The authors also present experimental data for several oils. The results of E. Li, P. King, and S. Lin (Chinese Industry 1 No. **1**, 115-28) favor the use of a combination of benzine and alcohol in a 2 to 1 ratio, respectively, for extracting soybeans. With this solvent a better yield is claimed than with chloroform, ether, carbon disulfide, carbon tetrachlorid, or benzine. M. Nakamura patented (Japan 109,730) the use of a mixture of alcohols and chlorinated hydrocarbons as solvents in the method by which after extraction, the solvent separates into two layers; the lower one contains the pure oil, while the upper contains the alcohol and impurities. A subsequent patent (Japan 109,731) by the same inventor claims the use of alcohol in combination with carbon bisulfide in the same manner of operating. A patent (Ger. 612,716 Cl. 23a) assigned to Harburger Oelwerke claims ethylene dichloride is a suitable fat solvent for extracting moist animal matter. The investigations published by U. Toko (Repts. Imp. Ind. Res. Inst. Osaka **15**, No. 9, 1-49) favor the use of benzene extraction for commercial purposes from the standpoint of the quality of product obtained. H. E. J. Peake's patent (Brit. 421,049) describes a method of extracting dry oil or fat containing material by treating with 15% oil solvent not miscible with water and 30% hot water based on oil bearing material, followed by removing the mixture of solvent and oil that rises to the surface. W. S. Butterfield (Can. 353,348) obtains advantages in oil extraction by pulping the material and drying in vacuum before submitting to extraction solvent.

The Beckmann biochemical method has formerly been suggested for extracting fats and oils. This method is applicable only to a very few materials. L. M. Horwitz-Wlassawa and N. W. Nowotelnow (Allgem. Oel- u. Fett-Ztg. **32**, 315-21) have investigated this method for the possibility of improving it for those materials for which it can be used and for extending its use to other materials. They found that by the method 88.2, 79.8, 78.2, 16.5 and 16% of oil were extracted from copra seed, walnut, cedar nut, pistachio nut, and sunflower seed respectively. From other seeds, i.e., hemp, castor bean, cotton, apricot kernel, corn germ, etc., no oil was extracted. The addition of glucose improved the extraction only in the case of sunflower seeds and apricot kernels, which yielded 55 and 25.9% respectively of their total oil; all other modifications gave negative results. The oil extracted by the Beckmann method has a higher acid and a lower iodine value than the ether extracted oil from the same seed.

Because of the price spread between edible and inedible oils and fats there was a greater justification for refining oils. J. P. Harris (Nat'l Prov. **93**, No. 26, 9, 29) describes simple equipment for refining tallow, with a discussion of savings that have been obtained by its use. Reviews on newer methods have been published by C. H. Keutgen (Chem. Ztg. **59**, 34-7), R. Heublyum (Mat. grasses **27**, 10463, 10482-3) and R. Dieterle (Seifensieder Ztg. **62**, 160-1). The latter paper deals with whale oil, while the former is concerned with oils and fats in general.

Patents for improvements obtained with new combinations of compounds in the refining of oils by chemical treatment have continued to appear. Fritz Schmid (Ger. 591,767 Cl. 22h) obtains sufficient refinement of oils for paint making by treatment with zinc oxide, zinc hydroxide or other basic compounds of zinc at room temperature for several days, followed by filtration. A patent issued to Metallgesellschaft A.-G. (Ger. 605,064, Cl. 23a) recommends refining with dilute hydrochloric acid, and aqueous calcium chloride solution. Patents assigned to the last named firm are relative to refining with alkali followed by removal of soap and other impurities with alcohol solution. The first patents (Ger. 614,898 and Brit. 427,680) describe refining by treatment of oil with concentrated solutions of alkali metal salts in mixtures of water and alcohol which dissolve the soaps and remove impurities. Foaming during the removal of alcohol by distillation is obviated according to a subsequent patent (Brit. 430,381) by addition of sulfuric acid or other similar acid just prior to the distillation. M. Bauman and coworkers (Masloboino Zhirovoe Delo **11**, 303-4) find ammonium chloride and sulfuric acid suitable for coagulating and settling the albuminous matter in oils.

Several suggestions have been

made in regard to the continuous chemical refining with the use of centrifuges. A. Schmidt and O. Mikhailovskaya (Masloboino Zhirovoe Delo **11,** 255-8) present data for such a method using a De Laval centrifugal apparatus and find best separation is obtained at 85-90° with addition of water or sodium chloride solution. Noblee and Törl G.m.b.H. (Ger. 615,791, Cl. 53i) claim a better separation is obtained with soybean oil if the oil previous to centrifuging is mixed with anhydrous glycerol containing sufficient dry sugar to bring the specific gravity to 1.36-1.39. According to method described by T. A. Buckley and J. L. Greig (Malay. Agr. J. **23,** 362-8) palm oil (33% water) direct from the extractor is refined in a continuous process by the use of a Titan sludge separator which is a centrifugal machine capable of delivering refined oil of good grade of purity at the rate of 200 gallons per hour with no appreciable loss of oil in the water discharge. The continuous method of B. Clayton (Brit. 417,996) uses an apparatus by which proper proportion of alkali is continually added to oil flowing through a pipe, the rate of flow being great enough to cause mixing by turbulent flow, and separation of impurities is accomplished by a continuous centrifuge.

Distillation in presence of alkali compounds, according to W. J. Hund and L. Rosenstein (Fr. 771,338), recovers free alkylolamines from the compounds which they form with the fat acids or from material containing the compounds. This should create a substantial saving for those using alkylolamine refining.

The method for deodorizing by passing oil over a series of superposed inclined planes under vacuum was improved by the N. V. Machinerieenen Apparaten Falbricken (Fr. 770,269; Ger. 620,703, Cl. 23a) by modifying the ends of the planes so that the oil passing over them forms either thin filaments or drops, thus exposing more surface. In addition, when these drops or filaments fall on the next plane they are broken by the collision and any retained gases are liberated. The improvement in the batch method of deodorizing with superheated steam by H. Lambert and F. Fuchs (Fr. 769,181) deals with a method of dispersing into finely divided condition the steam blown through the oil. A bacterial method for deodorizing animal greases, according to W. Kelle and F. Carlsson (Brit. 432,771) is carried out by treatment in water bath at 25° to 29.5° with fungi of the *Saccharomyces* type together with such bacteria as are contained in wheat and rye flour.

In the conclusion of a discussion on theories of adsorption and bleaching, H. Odeen and H. D. Slosson (OIL AND SOAP **12,** 211 - 5) present the following notes: When refined fatty material is bleached in open kettle, 15 to 20 minutes of contact at maximum temperature will be sufficient. Some clays will exert their maximum effect below 200° F.; whereas, others will function at 20° or 30° higher. The presence of soap beyond small traces gives rise to free fat acids. Most good bleaching earths reduce free fat acids slightly. The decolorizing material should be added to the oil in a single dose. If the oil is to be hydrogenated, the optimum dosage of adsorbent should be such that all traces of soap and catalyzer poison are removed. As an addition to this there is the work of T. Yamada (J. Soc. Chem. Ind. Japan **38,** 120-3B), which shows that when oil is heated with acid earth a dehydrating action takes place with reduction of acetyl value.

Activated charcoal gives best results for purification of oils and is superior in this respect to decolorizing clays, according to the data presented by A. Laptev and E. Erzyutova (Masloboino Zhirovoe Delo **10,** No. 11, 18-21). They find 0.5% charcoal gives results comparable to 2% of the best clays; this difference compensates in part for higher cost of the former. P. Smit (Oil and Colour Trade J. **87,** 392-3; Allgem. Oel- u. Fett-Ztg. **31,** 473-81, and Mat. grasses **27,** 10403-4, 10431-3) recommends using mixtures of carbon and earth for the same purpose, and presents the proportions of the adsorbents in the mixtures that give best results. These proportions vary between 1 to 20 and 1-40, depending on the oil to be treated. Hsuin-Tai Yu (Nanking J. **1,** 213-19) paper presents similar information with special reference to bleaching of tea seed oil. Papers by S. Yushkevich (Trudui VNIIZh. **1934,** No. 3, 53-65) and M. Bauman and coworkers (ibid. 37-52) present decolorizing test data on activated bleaching earths obtained from various parts of Russia. An earth from Zekeyev was found exceptionally potent. A patent assigned to Harburger Ölwerke (Ger. 617,520, Cl. 23a) combines decolorization with the solvent extracting process by adding bleaching earth to the oil containing material before extraction. William Gensecke (U. S. 2,003,076) obtains satisfactory bleaching by subjecting oils to a temperature of about 280°; and allowing the acids formed to distill off. Calcium hypochlorite method of bleaching received consideration in the way of improvement by B. E. Reuter (U. S. 2,022,738 and Fr. 778,882), whose process consists of adding cold calcium hypochlorite in successive small amounts with alternate cooling, agitation and settling until the oil is sufficiently bleached; and before the final settling and cooling the oil is heated to above 160° F.

Current methods for preparing fat acids are reviewed by R. Strauss (Chem.-Ztg. **58,** 977-9). Data on the resistance of several oils to Twitchell reagent and darkening of the mixed acids prepared with the reagent are presented by K. Nishizawa and coworkers (J. Soc. Chem. Ind. Japan **37,** 596-9B). E. Schlutius' experiments (J. prakt. chem. **142,** 49-78) on this reagent are relative to determining the structure and the chemical behavior. He presents several reactions of the reagent with other compounds and submits evidence indicating that the SO_3H group is in beta-position. A. Rabinovich and V. Muromtzeva (Masloboino Zhirovoe Delo **10,** No. 9 and 10, 6-7) recommend the tar produced by acid refining of petroleum for fat splitting. This material is similar to the Twitchell reagent and should be used in two stages in order to obtain a higher yield of glycerol solutions that are less contaminated with impurities. The optimum proportion of tar is about 2.5% for each stage, to which should also be added 0.3% of sulfuric acid.

Several hydrolyzing catalysts were tested for their activity by D. Nakae and coworkers (J. Soc. Chem. Ind. Japan **37,** 583-6B, ibid. **38,** 7-8). At pressure of 8 atmospheres, with 3% water and 1% catalyst, the fatty material obtained with zinc oxide is lighter than that obtained with calcium or magnesium oxides. Lead oxide is also a good catalyst and gives very pale products. Among the alkalies, sodium compounds are more effective than the potassium compounds. In preparing magnesium oxide fat-splitting catalyst the activity increased with increased calcining temperatures up to 800° and decreased above this temperature. Below 800° the activity increased with time of heating, while above 800° there was a reversal of this power with duration of heating. Suggestions are also presented for preparing the zinc oxide catalyst.

Recent literature indicates a trend toward purification of fat acids by distillation. L. M. Tolman and S. Goranflo (Oil and Soap **12**, 26-9) have presented results on distillation of fat acids from several oils by their patented process (U. S. 1,951,241). The outstanding feature of the process is the distillation of fat acids from oils of high iodine value without appreciable change and with a final yield of 90.8%. The apparatus was modified (U.S. 2,006,491) by the former inventor so that the extent of contact of the steam employed in the distilling process is substantially increased, thus increasing the efficiency. Another method of distilling fat acids is described by G. Knigge (Seifensieder Ztg. **61**, 668-9). According to this process the preheated material is spread over a large vertical surface and the heat of vaporization quickly supplied, partly by superheated steam and partly by radiation from the surface of the heated oil, whose temperature can be readily controlled, thus avoiding overheating. C. Bergell (Ger. 601,866, Cl. 23d) accomplishes distillation by passing the fat acids in thin films under heat rays; direct heat is also applied at the same time. The patent assigned to Volkmar Hanig & Co. (Ger. 611,220, Cl. 23d) pertains to an improved construction of the heating vessel of a fat acid distillation apparatus; i.e., into the heating vessel a cylinder of slightly smaller diameter is inserted so that during the heating which takes place on the side of the vessel, thin layers of material pass continually over the heated surface.

In consequence of the development of improved methods for obtaining pure fat acids there were some attempts to prepare synthetic fats by reesterification. Sei-ichi Ueno (J. Soc. Chem. Ind. Japan **38**, 237-41B) prepared synthetic butter from fat acids derived from hydrogenated fish oils and butyric acid and claims the product was satisfactory for cooking and table use. F. Wittka (Allgem. Oel- u. Fett-Ztg. **32**, 282-6) discusses the possibilities of such a process and gives an unfavorable comment. Synthetic oils made to resemble olive oil differ from the natural product in that they have a greater viscosity, lack taste, and are less stable. The method he presents for identifying or detecting adulteration by means of the synthetic fat depends on measuring the amount of solid unsaturated fat acids, i.e., iso-oleic acid, present in the oils.

For the separation of the saturated from the unsaturated constituents of fat acids Edeleanu G.m.b.H. (Fr. 775,700) patented the use of solvents at temperatures that cause precipitation of the saturated constituents. Some of the solvents mentioned are liquid sulfur dioxide, carbon tetrachloride, acetone, carbon disulfide, etc. E. A. Mauersberger (U. S. 2,012,106) effects a separation of stearic from oleic acid in fat acid mixtures, such as Twitchell bone acids, by dissolving them in a hydrocarbon solvent, colloidally dispersing or emulsifying water into the solution and cooling. The saturated constituents crystallize during the cooling. B. S. Tedotov (Russ. 35,308) recovers oleic acid from spent soap solutions by passing chlorine into the solution to effect separation of the acid. Methods and reviews on production of stearin, stearic acid, and oleic acid were published by H. Briske (Seifensieder-Ztg. **62**, 383-4) and T. Egupov (Masloboino Zhirovoe Delo **11**, 226-8).

For the production of lecithin B. Rewald (Ger. 602,637, Cl. 53i) washes the aqueous phosphatide emulsion from soy beans with alcohol and evaporates the filtered alcoholic solution. A. Schwieger's invention (Ger. 602,933, Cl. 53i) differs from the preceding in that dibenzoyl peroxide is used. By the process of S. O. Sorenson and G. F. Beal (U. S. 2,024,398) the lecithin is obtained from hexane-extracted soy bean oil by coagulation with superheated steam and filtering. The product by this method is said to be free of the bitter materials contained in the original beans.

Papers dealing with the selectivity of the hydrogenating process have continued to appear. F. Charnley (Prog. Rept. Pacific Fisheries Expt. Sta. No. **19**, 7-10) followed the hydrogenation course of pilchard oil with interesting results. Compounds forming insoluble tetrabromides disappear somewhere between iodine values of 120 and 60. There was practically no increase in percentage of saturated acids until the iodine value fell to 120, thus indicating that the reaction is highly selective. Over the interval between iodine values 120 and 60 the last traces of fat acids containing 3 or more double bonds as well as practically all those containing 2 double bonds disappear. Similar data are presented by M. Takano and coworkers (J. Soc. Chem. Ind. Japan **38**, 252-4B, 302-4B). Their results show compounds with 3 or more double bonds disappear at iodine value 111. Tests on mixtures of ethyl esters of fat acids each containing one double bond showed that hydrogenation proceeded selectively, the lower molecular weight acids being hydrogenated most easily. The work of T. Christopoulos and A. Koasta (Praktika, Akad. Athenon **9**, 26-30) with olive oil also indicates that the most unsaturated are hydrogenated first and that formation of stearic acid takes place after the formation of oleic acid from linoleic is complete.

The above papers do not take into account the variation produced by mechanical conditions and those variations indicated by T. P. Hilditch (Sci. J. Roy. Coll. Sci. **5**, 63-9, and Proc. 5th Pacific Sci. Congr. **5**, 3647-61) which are due to configuration of the glycerides; that is, an unsaturated acid in the beta-position is hydrogenated more slowly than the same in the alpha-position.

M. G. Barrdas (U. S. 2,014,999) obtains a better degree of selectivity by maintaining an inert gas space above the oil and introducing the hydrogen directly into the inert gas. According to M. Zaayer (Chem. Weekblad **32**, 393) in hydrogenating peanut oil an active catalyst is not always less selective in its action than one less active.

In order to obtain information on the formation of iso-oleic acids, A. Zinov'ev and coworkers (Trudui VNIIZh. **1934**, No. 3, 3-15, and Masloboino Zhirovoe Delo. **11**, 308-12) followed the hydrogenation course from this standpoint and concluded that these acids are not formed by double bond shifts, but by gradual and perhaps selective saturation of double bonds during the initial stages of hydrogenation. In samples of sunflower seed oil the maximum amount of iso-oleic acid obtained is equal to one-half of the original amount of linoleic acid in the oil, thus suggesting that for each part of the latter acid converted into oleic acid another equal part is converted into iso-oleic. Such a relation is not wholly in agreement with current opinions and the latest paper by S. Ueno (J. Soc. Chem. Ind. Japan **37,** 457-8B), who finds that high temperatures and application of a large amount of catalyst retard the formation of iso-oleic acid.

Current methods and recent progress in hydrogenation of oil are reviewed by W. Norman (Chem.-Ztg. **59,** 253-6). According to I. Seto (J. Soc. Chem. Ind. Japan **38,** 85-6) the application of an alternating current during the hardening is conducive to the production of an odorless oil without polymerization, and also permits using the same catalyst as often as 38 times before its activity diminishes.

The patents assigned to I. G. Farbenind, A.-G. (Holl. 35,986 and Ger. 615,148) describe a considerable departure from the usual methods of hydrogenating. The catalysts here used are the sulfides of heavy metals with hydrogenation pressures between 50 and 200 atmospheres. A later patent (Ger. 617,236) assigned to the same firm pertains to the preparation and recovery of the catalyst used in the process.

For the production of an edible fat from fish oils, M. P. Belopol'skii and O. B. Maksimov (Bull. Far Eastern Branch Acad. Sci. U.S.S.R. No. **9,** 111-15), recommend hydrogenation of the solid fractions filtered from oil at 8 to 10°. F. Pinsher (Masloboino Zhirovoe Delo. **11,** 157-9) obtains good hardening results with such oils, using 0.33% nickel at 200° for about 3 hours. S. Ueno and coworkers (J. Soc. Chem. Ind. Japan **38,** 357-61, 398-400B) and A. Sergeev (Masloboino Zhirovoe Delo. **11,** 79-81) present analytical data on hydrogenated marine oils hardened to various melting points and under various conditions.

Refining and removing the "catalyst taste" from hydrogenated oils can be carried out, according to D. Hildisch (Ger. 589,001, Cl. 53h), by treatment with a gas-evolving reagent, i.e., ammonium carbonate, steam, etc., at a high temperature; while S. Ueno and coworkers (J. Soc. Chem. Ind. Japan **38,** 357-61B) recommend a combination of caustic refining and the above method. The tendency of hydrogenated sesame oil to develop a pink color on heating is obviated as per G. W. Phelps and R. Bradley (U. S. 2,022,361) by washing with caustic solution after the hardening process.

Judging from the number of papers on preparation of catalyst by Russian investigators, it seems the greatest attention has been drawn to improving this phase of the hardening process. I. Petryaev (Masloboino Zhirovoe Delo. **11,** 221-2), Shcherbakov *et al.* (ibid. 244-6), E. Etinburg *et al.* (ibid. 246-7), and B. Malaeva (ibid. 247-9) present the methods used for preparing nickel formate catalyst and operating data of the respective plants with which they are associated. V. Yashchenko (Masloboino Zhirovoe Delo. **10,** 22-3) states that the most active catalyst is prepared from the formate by reducing in a well refined oil with gradual increases in temperatures, i.e., progressively heating from 170 to 220° in the first 2 hours, to 420° in the next 2 hours, and holding at 420° for 1 hour. A. Sinowjew and coworkers published a series of papers (Trudui VNIIZh. **1934** No. 3, 3-5, 16-23, 24-29) on the production of catalyst by reducing various nickel compounds in oil. Nickel formate gave the most recommendable result. It is decomposed in oil at 240-250°, but in presence of kieselguhr a temperature of 270-280° is required. Under the latter conditions a more active catalyst is obtained. Nickel hydroxide or carbonate is reduced in oil suspension at 240-260°; in the presence of kieselguhr carrier, reduction takes place at about 290°. When the hydroxide or the carbonate is pretreated by oxidation with bromine, the oil suspension-reduced-catalyst derived therefrom is as potent as those obtained from nickel formate. This result is considered to have an important bearing upon the regeneration of spent catalyst. Nickel oxalate can not be decomposed in oil by heating to temperatures as high as 360°. E. Etinburg (Masloboino Zhirovoe Delo. **10,** No. 9-10, 45-7) described his method for preparing catalyst in oil suspension from nickel carbonate. The experiments of A. Maschkin and K. Kasakowa (Masloboino Zhirovoe Delo. **11,** 81-2) demonstrated advantages of precipitating nickel carbonate with ammonium carbonate, which when obtained from the nitrate, required no washing, and when derived from the sulfate required only one washing. A catalyst prepared from 9 parts of nickel and 1 part copper can be reduced in oil at 200° and gives hydrogenation results similar to those obtained from nickel formate. C. B. Jackson (U. S. 1,991,096) has patented a new method for preparing catalyst. Nickel chromate is converted to the chromite with selenium or tellurium oxide and then reduced to the metal with hydrogen at high temperatures.

A very intensive study on polymerization is presented by A. Steger and J. van Loon (Rec. trav. chim. **54,** 387-95, 428-33, 433-42, 750-6 and 757-9). They demonstrated that on polymerization of ethyl linolenate both slightly dispersed and highly dispersed constituents are formed, the former being polymers and the latter cyclic isomers of linolenic acid. Both reactions occur simultaneously until no linolenate remains, thus explaining why linolenic acid cannot be completely converted into highly polymerized constituents. In their last publication they state that polymerization deals with chemical and not with physical changes of molecules. A review of the subject is presented by the latter author (Chem. Weekblad **31,** 419-20). E. Fonrobert and F. Wachholtz (Farben Ztg. **40,** 477-9) studied polymerization from the standpoint of the amount of heat given off. This is found to increase as the temperature of treatment is raised. The reaction is monomolecular. In addition to polymerization there is an interchanging esterifying process. K. Kino (Sci. papers Inst. Phys. Chem. Research Tokyo **26,** 91-7) submitted evidence in support of the contention that polymerization may take place without a shift in the double linkages, and such a shift with formation of a conjugated system is not always necessary for intramolecular polymerization of oils. E. Karsten (Farben-Ztg. **40,** 77-9) investigated polymerized linseed oil by determining the iodine absorbed by a series of samples produced by treatment at various temperatures. In spite of the difference in treatment all oils absorbed an amount of iodine equivalent to iodine value of 156-162. No relation was discovered between the tendency of an oil to gel with zinc oxide and the amount of halogen absorbed.

A usual method of following the course of polymerization in theory studies is to hydrogenate and then analyze the product. For this purpose a hydrogenating method as described by H. I. Waterman and E. van Vloprop (Chem. Weekblad **31,** 420-2) is useful, because less additional polymerization takes place than would be the case with usual methods. The process is carried out at 70°, with special platinum or palladium catalyst.

Literature on the technical aspects of the drying oils is as abundant as or probably more so than that on the theoretical phase. H. Tchang and C. Ling (J. Chem. Eng. China **2,** 21-30) tabulated the optimum conditions; i.e., temperature and duration of action, for obtaining the best results on tung oil with 18 common driers; these tables are useful for the reason that optimum conditions vary with the drier used. A. M. Khomutov (J. Applied Chem. U.S.S.R. **7,** 960-6) recommends intermittent heating for more rapidly increasing the viscosity of perilla oil.

Several patents claiming discoveries of new polymerization catalysts have appeared. M. N. Kozlov (Russ. 34,669) recommends diphenylguanidine and mercaptobenzothiazole with or without calcium resinate. W. Krumbhaar (U. S. 2,024,103) electrically disperses heavy metals in the oil. H. A. Gardner (U. S. 1,986,571) obtains good results with sulfur or selenium, which process requires removal of the sulfur or the selenium, by reacting with oxides of copper, zinc, lead or iron.

A patent assigned to I. G. Farbenind. A.-G (Ger. 610,600) claims improvements of drying oils by adding about 10% oxidized paraffin oil. Better polymerized products of drying oils are obtained, according to A. Hill and E. E. Walker (Brit. 422,941), if the polymerization is followed by vacuum distillation of the volatile constituents. A modification of this process (Brit. 428,868 and Fr. 781,293) includes, in addition to the above, the esterification with glycerol of any remaining free fat acids. The volatilized byproduct obtained by these methods is used for soap making. The patents of M. Luther and K. Goetze (U. S. 2,015,347) and E. Asser (Ger. 609,300) deal with improved blowing technic. A. Kufferath (Paint Varnish Production Mgr. **13,** No. 9, 30-1) recommends using ozone air mixtures as rapid drying agents for paint and varnish films.

The crystallization and frosting of tung oil that is attributed to presence of unpolymerized elaeostearins is prevented, according to H. Ulrich (Peint, Pig. Ver. **21,** 96, 113), by heating with glycerol and a catalyst. That heating to 300° gives like results is claimed by H. L. Plummer and L. F. Stone (U. S. 2,011,908).

For preparation of oil suitable for making printing inks from soy bean oil, H. Chang and T. Chang (Chemistry [China] **2,** 296-301) obtain optimum results by blowing with a slow current of air at temperatures between 130 and 140° for 42 to 48 hours.

Outlets for fish oils are gradually being developed. F. Ohl (Farbe u. Lack **1935,** 99-100) prepares a satisfactory partial substitute for linseed oil from fish oils by air blowing at 200-250° after removal of the saturated components by freezing. Good results are also claimed by K. Kino (J. Soc. Chem. Ind. **38,** 77-9) with polymerization followed by removal of nondrying constituents by extracting with acetone. Y. V. Branke and F. S. Shavskii (Za Lakokrosochmuju Ind. **1935,** No. 2, 19-24) add 20% resin to sardine oil after the removal of the saturated portion and heat at 550° for 4-5 hours to obtain a product which when added to 80% of its weight of turpentine results in a satisfactory lacquer. O. F. Denstedt (Prog. Rept. of Pacific Biol. Sta. **1935,** No. 34, 3-5) succeeded in producing lacquer from pilchard oil. He polymerizes the oil, then steam distills off the nondrying components; and before the residue gels, it is poured into a suitable solvent such as turpentine. K. Masumori (J. Soc. Chem. Ind. Japan **38,** 51-2B) demonstrates that the effect of either alkali- or acid-clay refining on polymerization of fish oils is negligible.

The manufacture of gasoline may become a future outlet for waste or cheap oils and fats. A process for this purpose as patented by L. Maurin (Fr. 770,706) is carried out by treating the oil with a complex system of catalysts, playing the part of oxidizing, hydrogenating and dehydrating agents. Y. Shinozaki and H. Kubo (J. Soc. Chem. Ind. Japan **37,** 677-8B, 678-9B, and ibid. **38,** 21B) obtained a 70% yield of gasoline (sp. gr. 0.74) from soy bean oil by hydrogenating it with a copper-chromium catalyst at about 450°. An intermediate reaction is the formation of alcohols at about 350°. Y. Yendo (Bull. Inst. Phys. Chem. Res. Japan **13,** 1373-93) obtained 60 to 70% yields of light oil (sp. gr. 0.7) from fish oil by a similar method. K. Ping (J. Chinese Chem. Soc. **3,** 95-102, 281-7) cracked cottonseed, castor, perilla, soy bean, tung, peanut, and several other oils in the presence of aluminium chloride and obtained yields from 23 to 32% by volume of light oil with boiling point up to 250°. E.-K. Li and S.-C. Chow (J. Chem. Eng. China **1,** 1327-34) and K. G. Chang and H. Y. Chang (J. Chem. Eng. China **2,** 32-7, 211-5) produce gasoline by destructive distillation of the calcium soaps of the fat acids. In addition to the gasoline they recover glycerine and combustible gases.

A patent by A. Languasco (Fr. 782,459) concerns a method of preparing lubricating oil from fatty oils by heating them under reflux in presence of metal chlorides, oxides, or silicates as catalysts.

The usual method of rendering castor oil soluble in mineral oil in the preparation of a mixed lubricant is to heat the mixture at high temperature. An improvement in this process, according to I. Davidsohn and R. Strauss (Ger. 608,973, Cl. 23c), is obtained by additions of small amounts of chlorinated high molecular weight hydrocarbons. The improvement by P. Perucca (Ger. 621,443) deals with the removal of free fat acids formed during the heating, by re-esterifying them with alcohol.

The Relationship of Fats to Their Finished Commercial Products

The creaming and the shortening values are important criteria for judging baking fats. The investigations regarding the relationship of these to the physical and the chemical characteristics by Dr. P. Mabel Nelson and coworkers (Iowa Agr. Expt. Sta. Rept. on Agr. Research **1934,** 147-9) demonstrated that for each fat there is an optimum temperature of creaming which gives best results in cake making; creaming volume is relatively unimportant with regard to the final cake volume or score. There is no apparent relationship between shortening value of lard and iodine value, percentage of free fat acids, or melting point, while with lard substitutes there was some relationship between shortening and iodine value. A patent issued to Procter & Gamble Co. (Fr. 761,280; Brit. 428,048) claims good creaming qualities and better cake volume are obtained if the shortening contains a small amount of free fat acids.

In a general discourse on fats and shortening with regard to bakery products, G. F. Garnatz (OIL AND SOAP **12,** 290-3) stated that up to 6% fat can be used safely in bread with desirable results. This is not in agreement with the opinion more generally prevailing, which considers amounts above 3% of the weight of the flour detrimental to volume, structure, and taste.

Patents dealing with the use of fat acid esters of glycerol, polyglycerol or glycol containing unesterified hydroxyl groups are the most numerous among those on food fats. The claims, in addition to emulsification, are production of good creaming qualities with other baking ingredients, increase in volume of finished pastries, nonspattering margarin and "nonblooming" confections. These patents (U. S. 1,985,496; 2,006,798; 2,022,766; 2,024,355; 2,024,356; Ger. 615,563 Cl. 23c; Brit. 414,981; 425,981; 425,982; Fr. 781,842; 782,222, and Japan 109,441) differ in the hydroxyl component used (i.e. glycerol, glycol, etc.), in the qualities claimed (i.e. emulsifying, creaming, etc.), or in the products into which the esters are incorporated. The patents (U. S. 2,015,606; 2,009,796; 2,022,493; 2,022,494; 2,023,388; 2,025,684; Brit. 421,063; 421,284) asserting discovery of new methods of preparing the above-mentioned compounds show no outstanding differences except that they either describe a method of partial saponification or a method of reacting glycerol, polyglycerol or glycol with fat in the presence of an alkali compound as a catalyst.

The practice of improving butter aroma by increasing the diacetyl content is claimed to be advancing in use. Such practice as increasing the amount above the maximum ordinarily found in natural butter is considered adulteration in several countries (Schweiz. Milchztg. **60,** 567, and Ann. fals. **28,** 278-80). A method for extracting this flavoring constituent from starter by steam distillation is described by H. A. Ruehe and R. J. Ramsey (Milk Plant Monthly **24,** No. 2, 40).

W. Mohr and Ahrens (Molkerei-Ztg. **49,** 104-5) issue recommendations for standardizing and adding color to butter. The paper by H. Herz (Milch. Zentr. **63,** 349-50) treats butter from the standpoint of the physical properties and presents methods for preparing winter butter of favorable consistency by control conditions of kneading, washing, etc.

Suggestions for improving margarin and the manufacturing technic are presented in several publications. G. Klein and N. Chanpalova (Masloboino Zhirovoe Delo **11,** 222-3) describe most suitable conditions of mechanical processing for preparation of margarin from hydrogenated oils. Patents issued to M. C. Reynolds (U. S. 2,022,924) and A. D. Joyce (U. S. 2,024,647) describe manufacturing technic according to which the melted fat is partially cooled and the butter flavor producing material is then emulsified into it. R. Kaufman (Aust. 141,513) recommends taking the fat in two portions of different melting points; the lower melting portion is emulsified with milk, cooled to about 0°, and the higher melting fraction is then added.

Several emulsifiers for margarin are reported. D. Hildisch (Fr. 783,388) recommends mixing glycerol with the fat, at the same time adding gelatin with the aqueous material. B. R. Harris (U. S. 2,024,357 and Can. 342,364) claims use of sulfated fat acids. I. Sandomirskii and B. Semenova (Masloboino Zhirovoe Delo **9,** 20-1) finds 1-1.5% molasses gives better results than egg yolk, and even better results are obtained by using 0.75% molasses in conjunction with 0.07-1% egg yolk. Noblee and Thörl G.m.b.H. (Ger. 621,327) use the glycerin and lecithin-oil mixtures as produced according to some other patents (Ger. 599,639 and 602,935) issued to them. In a similar manner, Akt. Ges. Medizinische Produkte (Ger. 615,027 Cl. 53h) use the lecithin and cholesterol mixture as obtained by their patented process (Ger. 560,146). The papers by V. Ivanowa (Trudui VNIIZh. **1934,** No. 3, 98-103), K. Popov. (Masloboino Zhirovoe Delo **11,** 250-1), and M. Bauman and I. Dvinyaninova (Masloboino Zhirovoe Delo **11,** 251-4) report that about 0.4% oxidized oil produces suitable margarin emulsification and they present directions for preparing the emulsifier.

Addition of tributyrin to margarin for improving flavor has been a failure until recently because of the bitter taste. D. W. Stewart (Analyst **60,** 172-3) obtains the improved flavor and aroma without the bitter taste of tributyrin by heating the fat mixtures either with butyric acid or its triglyceride. This results in the formation of monobutyric triglycerides by substitution or interchange. F. Bloemen (Ger. 612,027 Cl. 53h) improves the flavor by adding to the milk in the manufacture of margarin, during or immediately before souring, a small proportion of ethyl lactate or substances that yield ethyl alcohol upon souring. Subsequent patents (Ger. 613,222 Cl. 53h and 620,988 Cl. 53h) by the same inventors deal with the use of synthetic nutrient solutions containing lactose and yeast in place of milk or in conjunction with milk.

Other papers on emulsifiers deal with lecithin. A. Hughes (Biochem. J. **29,** 430-5) reports a fall in the surface potential of unimolecular films of lecithin and lysolecithin between pH 3 and 6, and pH 2 and 5 respectively. Lecithin is more rapidly oxidized by dilute potassium permanganate solutions than triolein or lysolecithin. H. Bollman (Ger. 581,763 Cl. 23c) improves stability of vegetable lecithin emulsions by adding alkalies. This is also recommended by B. Rewald (J. Soc. Leather trade chemist **19,** 220-5), who finds that treatment with a mixture of 50 parts lecithin, 50 parts water, and 1 part sodium carbonate before adding the neatsfoot oil is a suitable practice in leather processing. I. Inaba and coworkers (J. Soc. Chem. Ind. Japan **37,** 595B) present data on oil-water mixtures with special reference to the use of soy bean lecithin or lecithin soap as an emulsifier.

An organized scheme for analyzing five different types of emulsions is presented by F. W. Biffen and F. D. Snell (Ind. and Eng. Chem. Anal. Ed. **7**, 316-9). These methods are modifications and combinations of old methods. A means of evaluating stability of emulsions by employing microprojection equipment for determining dispersed droplet size was tested by S. Berkman (J. Phys. Chem. **39**, 527-39). Favorable results are reported. G. Meszaros (Z. Untersuch. Lebensm. **69**, 318-30) proposes expressing the emulsifying power of fats in "E-Nos." The "E-No." is defined as the milligrams of fat that will emulsify in 100 grams of water without emulsifiers. "E-Nos." for several fats are tabulated in the original publication.

Deterioration of Fats and Oils

The subject of fat spoilage is reviewed by D. de Prat (Mat. grasses **26**, 10348-50; ibid. **27**, 10372, 10404-5, 10429-30), C. C. Price (Can. Chem. and Met. **19**, 134-5), T. A. Wieshahn (Food Indus. **7**, 222-3, 275-6), L. M. Horowitz-Wlassowa *et al.* (Z. Untersuch. Lebensm. **69**, 409-21), and K. Taufel (Fettchem. Umsch. **42**, 164-7). The last named author compares the process of oxidative spoilage with the oxidation of fats in the animal body and presents some analogies. A review by W. Riedel (Deut. Molkerei-Ztg. **56**, 221-5) is limited to defects and spoilage of butter.

The Kreis test is modified by M. Pyke (Analyst **60**, 515-9) so that the color produced is measured by a Lovibond tintometer.

Modifications of the Swift's accelerated oxidizability test are presented by H. H. Sommers (Oil and Soap **12**, 201-2) and by E. Freyer (Oil and Soap **12**, 139-46). The first named extends the exhaust tubes from the fat into test tubes containing methyl red indicator solution. After the induction period is completed, the indicator turns dark red. The latter suggests accelerating the test by means of light. In addition, Freyer presents data to show that the rate of air flow had no bearing on the acceleration. This is substantiated by L. B. Kilgore and D. H. Wheeler (Oil and Soap **12**, 178-80). An irradiation technic for accelerating oxidative tests was developed by L. H. Lampitt, N. D. Sylvester and P. Bilham (Biochem. J. **29**, 1167-74). This is standardized so that measurements made in a position other than that of the sample have been correlated with intensity in absolute units of the light incident on the fat. These authors followed the oxidative changes by chemical tests.

R. Neu (Pharm. Zentralhalle **76**, 65-70) reports investigations on the mechanism of rancidification of fats. Attention is directed to the similarity in transformation of maleic to fumaric acid and that of oleic to elaidic acid. The degradation of oleic and elaidic acids into two isomeric dihydroxystearic acids by oxidative action is discussed in the light of previous investigations (Allgem. Oel- u. Fett-Ztg. **30**, 583-8) with the conclusion that oleic acid possesses the cis-configuration while the elaidic acid represents the trans-configuration. During the spoilage of fats and oils, no rearrangement of butendiol occurs, but rather a direct splitting off of carbon monoxide, thus

$$(:CH.CH\,O)_2 - CO = CH_2\,CH\,CH\,O.$$

H. Schmalfuss, H. Werner and A. Gehrke (Margarin Ind. **27**, 79-81) showed that aldehydic reactions can appear without microorganisms when saturated fat acid esters are radiated with a mercury lamp. According to other papers, the same authors and associates (Oesterr. Chem. Ztg. **37**, 162 and Margarin Ind. **27**, 93-5) find that soy bean oil is rapidly ketonized by light of wave lengths up to 410 *mu.* Hard and soft Rontgen rays or short electromagnetic rays did not cause the oil to form ketones. Unsaturated fats form ketones more readily than saturated. Oxygen, water, and nitrogen compounds are not necessary for the process, but they accelerate it.

J. M. Aas (Fettchem. Umsch. **42**, 71-5) studied the oxidation of several oils by determining the change in iodine value as a function of the variation in weight of sample. Graphical representation of the data shows that during the early stages of oxidation of oils the decrease of iodine value is directly proportional to the weight gained, except in the case of linseed oil. During the oxidation there is a distinct tendency for the weight of the oil to pass through a maximum and then decrease. A large portion of the double bonds remain unchanged. The double bonds attacked are 40 to 60% of the total in animal oils, and 15-50% in vegetable oils. In spite of the unsaturated character of linseed oil, only up to about 30% of the double bonds are affected; this is attributed to polymerization.

The phenomenon of gaseous evolution during heating of rancid oil has escaped with only slight notice until the work of J. T. R. Andrews (Oil and Soap **12**, 104-5). A 490 gram sample of refined cottonseed oil was allowed to become rancid by oxidation at room temperature for fifteen months. By heating at 85° for one week this oil evolved 156.6 cc. of gases consisting of carbon dioxide 0.71, carbon monoxide 2.63, hydrogen 66.73, nitrogen 26.4, oxygen 3.34, and $C_n\,H_{2n+2}$ 0.35%.

R. B. French, H. S. Olcott and H. A. Mattill (Ind. & Eng. Chem. **27**, 724-8) report experiments on the study of antioxidants and autoxidation. The apparatus used was a modification of that described by Greenbank and Holm (Ind. & Eng. Chem. **17**, 625). With several natural antioxidants and phenolic compounds protection is fairly proportional to the amount added. At the end of the induction period, the level of peroxide in mixtures is fairly uniform. In the case of one antioxidant derived from the unsaponifiable lipids of wheat germ oil, the effectiveness varied inversely with the amount of peroxides in the fat mixtures whether these had accumulated slowly or were added in the form of an oil of high peroxide content.

The antioxidants patented during the year are as follows: E. W. J. Mardles and W. Helmore (Brit. 423,938), acyl derivatives of mono alkyl or mono-aryl hydrazines; F. Kuhrmann (Ger. 614,605, Cl. 23b, and 612,717), perylene and perylene derivatives; Wm. Calcott, W. A. Douglass and H. W. Walker (U. S. 1,993,771), *p-p'*-dihydroxybiphenyl; Wm. Calcott, W. A. Douglas, and H. W. Walker (U. S. 1,987,321), *p-p'*-diethoxydiphenylamine; J. Davidsohn (Ger. 619,928), aliphatic high molecular weight halogenated hydrocarbon; A. S. Richardson *et al.* (U. S. 1,993,181), phosphoric acid, sulfuric acid, or their salts; E. W. Eckey (U. S. 1,993,152), phosphoric acid, sulfuric acid or their salts; and D. P. Grettie and R. C. Newton (Brit. 415,205), crude cottonseed oil.

Antioxidants were also reported in literature other than the patent literature. R. Strauss (Seifensieder-Ztg. **62**, 238) recommends chlorinated paraffin for soap and cosmetic preparations. K. Stephan (Chem.-Ztg. **59**, 416-7) discloses that several oils to which 0.2% camphor was added showed no Taufel-Thaler reaction after one year while control samples were all strongly rancid. The camphor may be removed by passing steam through the oil or washing with 90% alcohol. S. Musher (Food Ind. **7**, 167-8) claims good antioxygenic effects are obtained in lard by adding soy bean flour, crushed sesame seed or oat flour. The effect persists even when the flour is filtered from the melted lard, but is greater if the flour is allowed to remain in the fat. H. G. Miller (Oil and Soap **12**, 51-2) asserts that cottonseed meal, in addition to being a good stabilizer for cod-liver oil, functions also as a preservative for the vitamin content. E. I. Evans (Ind. & Eng. Chem. **27**, 329-31) demonstrated that vegetable lecithin possesses antioxidant properties in cottonseed oil when the autoxidation is catalyzed by cobaltic oleate. This property is lost by heating to temperatures above 65°.

Methods other than addition of antioxidants, for stabilization of oils are described in patents issued to S. Schmidt-Nielson (Brit. 426,752) and Elact. Ges. electrische Apparatus G. m. b. H. (Brit. 420,471 and Fr. 766,739) The first patent pertains to the stabilization of marine oils by heating in closed container at 250° for at least 48 hours; while the latter claims good stabilization by passing an electric current through the oil or fat.

M. R. Coe and J. A. Le Clerc (Oil and Soap **12**, 231-3) continue their research of the preceding year by supplying evidence confirming a superiority of the green light protection method to those using antioxidants. The work of W. L. Morgan (Ind. & Eng. Chem. **27**, 1287-90) confuses our knowledge of protective wrappers since it does not agree with reports of other investigators. Morgan demonstrated that blue and invisible ultraviolet light materially accelerate development of rancidity; whereas, other visible light, such as red and yellow, have very little effect and he suggests, as a consequence, that rancidity-retarding wrappers may be of any visible color except blue. As a result of the work he has developed a highly protective yellow transparent cellulose film for use in packaging such materials as potato chips, crackers, cake, butter, nuts, etc.

F. R. Robertson and J. C. Campbell (Oil and Soap **12**, 234-6) studied the effect of six months' storage of cottonseed oil in containers made of several commercial samples of metals and alloys. The changes in free fat acids, refining losses and color are tabulated. No definite conclusions are drawn except that copper and copper alloys should not be used in contact with cottonseed oil.

The method for recovering rancid fats by treatment with semicarbazide and filtering was investigated by K. Stephan (Chem.-Ztg. **59**, 416-7). A rancid fat treated with one gram semicarbazide and four tenths sodium stearate for each hundred grams of fat showed no Taufel-Thaler or Kreis reaction. The reagent can be recovered from the precipitate by boiling with acid.

The tendency of butter toward fishiness, tallowiness and other oxidative defects was investigated by W. Ritter and M. Christen (Schweiz Milchztg. **61**, 23-4, 31-2, 61-2; 69-70). It was found that the use of cream containing .01-8 mg. copper or 0.5-16 mg. of iron is conducive to formation of the above named defects. Hydroquinone and hydrogen peroxide oppose the process. Vitamin C, maleic acid and aldehydes are inactive. The living *reducto-bacteria frigidum* neutrale, as well as other alkali formers, prevent the tallowiness due to metals. According to G. Van B. Gilmour and P. S. Arup (Ice & Cold Storage **38**, 120) butters of high flavor and high pH (above 6.7) keep well in storage.

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

ANTIOXIDANTS AND THE AUTOXIDATION OF FATS IV. LECITHIN AS AN ANTIOXIDANT

By H. S. OLCOTT and H. A. MATTILL

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AMONG the many substances that have more recently been suggested for delaying the progress of rancidity in fats, vegetable lecithin is probably one of the first (2). It is somewhat surprising that in the past ten years so little information of an experimental nature has been published to support the claims of this substance as an inhibitor and to explain the manner of its action.

In a list of inhibitors and their effect on commercial oleic acid, Trusler (15) found lecithin practically ineffective. Royce (12) included lecithin among the inhibitors which he studied by the methylene blue test. His data showed that in a concentration of 0.2 per cent in finished cottonseed oil, at a temperature of 70° C., lecithin gave an antioxygenic index[1] of 2 by the oven test (organoleptic) and of 3 by the methylene blue method[2]; with hydrogenated shortening 0.1 per cent gave an index of 1.5 by the oven test and 8.3(?) by the methylene blue method; this method gave irregular results with hydrogenated shortening.

Sollmann (13), using the Warburg apparatus for the oxygen-absorption method, reported without supporting data that lecithin inhibited the oxidation of cottonseed oil catalyzed by cobaltic oleate, and that when exposed to oxygen at temperatures above 65° C. for one-half hour it no longer exhibited antioxygenic properties.

Kochenderfer and Smith (8) measured the induction period of the oxidation of lard by the oven test and by the oxygen absorption method, as influenced by two commercial samples of soy-bean lecithin. They obtained indices of 1.7—1.8 by the former method and somewhat smaller figures by the latter. Results obtained from these lecithins after reprecipitation by acetone were variable, and this is not surprising, since by the nature of its prepara-