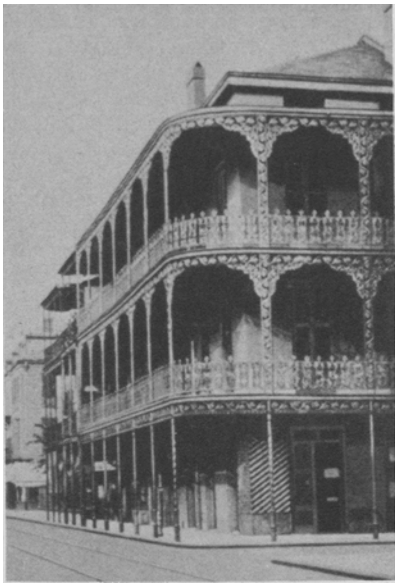
General view of typical mining operation at Grand Ecaille.

cover on visiting the plant, it is not such a simple operation as the layman might suppose. The hot water must, of course, be super hot, and it must be available by the millions of gallons, since the mining operation ordinarily uses 3,000,000 gallons each 24 hours.

The water goes out from a control station, is pumped down the outer space of the pipe-within-pipe-within-pipe well. It escapes through the perforated bottom section of the outer pipe—from 900 to 1,500 feet below the surface—and rises through the porous limestone caprock of the salt dome, fusing the sulphur as it goes.

The sulphur sinks to the bottom of the well hose and is brought to the surface in the "middle" pipe, by air pressure coming down the innermost line. The hot water flowing downward outside the sulphur line keeps the molten "S" thoroughly liquid all the way to the surface.

Following the visit through the mine, a lunch will be served and the trip back to New Orleans started, with a promise of not later than five p. m. in your hotel.



A striking characteristic of the architecture of New Orleans' Vieux Carre ("French Quarter") is the myriad patterns in wrought and cast iron.

REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1937

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THE total production of fats and oils for the year 1937 was greater than that for the preceding year. This factor, even though consumption and business activity were improved, led to a gradual reduction in prices. According to "Chem. & Met. Eng." price analysis, the average prices at the end of the year were 30 per cent lower than the average at the beginning; however, due to the high prices during the first half of the year, the monthly average prices for 1937 were about 6 per cent higher than during 1936.

Although the general price trend was downward, some foreign drying oils were more expensive because there was an increase in the consumption of these oils and a decreased wood oil production because of the strife in the producing country. Among the more common edible fats and oils, lard production was low because of the decrease in hog slaughter. However, the increased production of cottonseed and soy bean oils compensated for this deficiency.

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The international commerce in fats was influenced by trade agreements and the continued efforts of several nations to strengthen their military defense.

In the United States, oils of the coconut type from South America are replacing the usual coconut oil, which is now heavily taxed. Margaret J. Hausman [*Soap* **13**, No. 2, 28-32, 37, 73] described several oils and fats that are interchangeable with cocoanut oil for soap manufacture. The patent literature of drying oil substitute was reviewed by A. W. Van Heuckeroth. [*Natl. Paint, Varnish and Lacquer Assn. Circ.* 531]. G. S. Jamieson and R. S. McKinney [OIL & SOAP **13**, 202] suggested that American black walnut oil could be used in paint and varnish along with a strong drying oil. It could also be used as a cooking oil when refined.

Mineral oil, coal tar distillates, soap, fillers and inorganic substitutes for fats and oils in soap making, and casein, resins and other developments in the paint industry were given wide publicity as fat and oil conservers in the German literature of recent years. Although active research was very productive, these substitutes have not been able to fulfill the need for the natural products. For this reason the German industries have increased their whaling fleet and the production of marine oils. The literature contains several monographs giving the possibilities of various materials as German fat sources. W. Ludorff [*Fette u. Seifen* **44**, 416-20] treated the herring oil industry. H. P. Kaufman and H. Fiedler [*Fette u. Seifen* **44**, 286-9, 420-3] discussed the safflower and grape marc as oil sources. E. Schilling's [*Fette u. Seifen* **44**, 275-80] report dealt with the flax plant. Soy bean oil production was discussed by G. Sessous [*Fette u. Seifen* **44**, 175-8] and B. Schmidt [*Fette u. Seifen* **44**, 178-9. Wegener [*Fette u. Seifen* **44**, 86-95] reviewed the German fat supply and government plans relating to the problem. An investigation of plant breeding research led W. Rudorf [*Fette u. Seifen* **44**, 129-36] to the conclusion that increasing the amounts of vegetable oils produced by breeding without disturbing other crops would not yield sufficient fats to supply the total German requirements.

Also in connection with fats, Germany was conserving her supply of glycerine. Legislation there prohibits the manufacture of cold process soaps because in these the glycerine was not recovered. Some necessary process changes in shifting to fat acids as raw products for making the legal soaps were described by Hermada [*Seifensieder—Ztg.* **63**, 898-900].

Oils obtained from wood in the paper industries, so-called tall-oils, now seem to be established commercial products. Both J. A. Wallach [*Soap* **13**, *No.* 3, 31-3, 73] and H. Reinert [*Farbe u. Lack* **1936**, 461-2] published monographs on its production, character and use in the paint industry. Wallach also listed many other products in which the oil could be interchanged with other oils. J. Hojka [*Cs Mydear a Vonavkár* **14**, 101] obtained from wood a grease capable of being saponified by passing a definite mixture of carbon dioxide and carbon monoxide into wood cellulose solution under pressure at a high temperature and in the presence of a catalyst.

Another possible source of fat which as yet is only of experimental importance is the synthesis by means of fungi, bacteria and enzymes. Reviews on this subject were issued by W. Schwartz [*Angew. Chem.* **50**, 294-6] and by H. Fink, H. Haehn and W. Hoerburger [*Chem. Ztg.* **61**, 689-93, 723-6, 744-7]. Fink and coworkers [*Z. Spiritusind.* **60**, 74, 76-7, 81-2] reported their results on fat formation by 50 strains of *Oidium lactis*. Whey was used primarily as medium and the nitrogen for the bacteria was supplied by ammonium sulfate. The economic aspect of the work was discussed. Characteristics of the fat from mold (*Citromyces spec.*) and yeast (*Saccharomyces spec.*) were determined by K. Täufel and coworkers [*Fette u. Seifen* **44**, 34-8. *Z. Untersuch Lebensm* **72**, 394-404]; these will be tabulated in the latter part of this review. E. Sym [*Polish Agr. Forrest Ann* **40**, 406-8] synthesized fats and cholesterol esters by means of animal lipase in organic substrates dispersed in carbon tetrachloride and benzene. A patent which deals with the production of fats by enzymes was issued to K. Lüdecke [*Ger.* 647, 219 *Cl.* 53 *h* 1.01]. Carbohydrate solutions, i.e., starch, sugar, or sugar produced from wood, are treated with seeds or seed capsules of oleaginous plants in alkaline solution for one to two months to yield fats.

Statistical data have been treated editorially in several trade journals of the industry. Original and authoritative sources of this information emanated from government bureaus. Among these, Anne Dewees [*U. S. Dept. Agr. Statistical Bull.* 59] compiled figures on production, prices, trade and disappearance of fats, oils and oleaginous raw materials for the years 1912-35 and the available data for earlier years. H. J. Zimmerman [*U. S. Dept. of Commerce, Bureau of Census*] tabulated production, consumption, imports, exports, and stocks for years 1932 to 1936. Periodic press releases by the Department of Commerce, Bureau of the Census, gave data on quarterly production and consumption of various fats which included figures on the products prepared from the fats and oils. Another government bulletin [*U. S. Dept. Bureau Ag. Economics F. O. S.*—3] discussed the economic situation regarding drying oils. It is interesting to note that the consumption of drying oils in industry has risen from a low point of 475 million pounds in 1932 to 790 million pounds in 1936. Of these oils used in the United States during 1934-1936, 64 per cent was linseed oil, 17 per cent tung oil, 9 per cent perilla oil, 6 per cent fish oil, 2 per cent soy bean oil and 2 per cent of all others. These varied only slightly during the four years reviewed in the paper, thus indicating that the paint industry demand for the various drying oils was in about the same ratio each year. D. H. Killeffer [*Ind. Eng. Chem.* **29**, 1365-6] also reviewed drying oils, giving data on production and imports of the five important oils and their uses in the three important divisions of the industry. Developments and interchangeability were briefly discussed.

For a brief review of statistics the following data were obtained from a report by C. E. Lund [*U. S. Dept. of Commerce, Bull. on Fat and Oil Trade in* 1937, *February*, 1938]:

(All data in million pounds)

U. S. Production of Fats and Oils:	1936	1937
Lard	1,063	900
Tallow	578	507
Lard substitutes	1,586	1,568
Butter (creamery)	1,629	1,611
Oleomargarine	393	394
Cottonseed oil	1,247	1,625
Whale oil (by U. S. Whalers)	31	69
Soybean oil	225	194
Linseed oil (from both foreign and domestic seeds)	456	665
Peanut oil	70	51
U. S. Imports of Fats and Oils:		
Vegetable oils	1,410	1,651
Oil equivalent of oil seeds.	732	1,025
Animal and fish oils	193	153
U. S. Exports of Fats and Oils:		
Vegetable oils	54	42
Oil equivalent of oil seeds.	17	14
Animal oils, fats and greases	147	147
Factory and Warehouse Stocks—Dec. 31:		
Vegetable oils	1,062	1,450
Fish oils	216	201
Animal fats	402	262
Greases	60	75
Other oils	213	261
Oil seeds (reduced to oil).	525	708

The above data for 1937 were partly estimated. The final figures will in most cases be a few per cent higher.

COMMERCIAL TREATMENT

The materials of construction for fat, oil and soap process equipment received a little attention in the literature devoted to fats. Acid-proof stone linings were fostered by L. Kögel [*Seifensieder-Ztg.* **64**, 467-8] and K. Dietz [*Fette u. Seifen* **44**, 302-3]. Acid-proof and rust-proof steels were treated by H. Hougardy [*Fette u. Seifen* **44**, 230-4, *and Allgem. Oel. u. Fett-Ztg.* **34**, 260-5], T. Hinko [*Öle, Fette, Wachse, Seife, Kosmetik* **1937**, *No.* 5, 7-9] and E. Baerlecken [*Fette u. Seifen* **44**, 228-9]. Properties of chromium, chromium-molybdenum, chromium-nickel and chromium-manganese alloy steels were given with special consideration to their use in autoclaves for fat splitting and for the processing and handling of soaps.

Whaling activity was spurred on by several European nations. This industry was the subject of a monograph by C. H. Hudtwalcker [*Walfang-Verlagsgesellschaft Dr. Holm*

& Co., Bremerhaven]. The historical development of the industry and the complete operations of hunting, handling and processing at sea were described. Mechanical apparatus for comminuting whale was patented by P. L. Fauth [*Ger.* 641,018 *and* 642,920 *Cl.* 50c 4.10]. Storing whale flesh and blubber was accomplished according to patent of D. Hildisch [*Norw.* 57,059] by preserving in solutions of hydrochloric, sulfuric, phosphoric or formic acid of pH less than 5, particularly 1 to 3. Rendering means were patented by A/S Myrens Verksted [*Norw.* 57,042] and L. Larsen [*Norw.* 55,338]. The former boiled the blubber in water and in the passage through a tubular boiler it was comminuted at one or more points. Larsen boiled the raw material in a strainer drum. The material passing through the strainer was separated into oil, glue, water and suspended solids by another part of the apparatus.

The combined rendering and refining apparatus recently patented in the United States by C. B. Upton [*U. S.* 2,075,070] was reported in last year's review from the Canadian patent on the same apparatus. Descriptions of apparatus for rendering tallow, as developed by T. Hinko [*Öle, Fette, Wachse, Seife, Kosmetik* **1936,** *No.* 14, 6-7; **1937,** *No.* 4, 7-8; *No.* 9, 7-9; *No.* 12, 1-2], were published throughout the year.

The major portion of the information on expressing oils deals with the pretreatment of the raw material. According to patent of T. J. Harrell and C. W. McMath [*U. S.* 2,064,158], cottonseed oil, of less than 0.5% acetone-insoluble, was produced by crushing the seeds, heating to 190° F., raising the water content to 11-20%, heating to 222-235° F., to reduce water content to 5.5-7.5% before pressing. R. B. Taylor [*Chem. & Met. Eng.* **44,** 478-81] recommended cooking cottonseed meats under pressure at temperatures above 270° F. before pressing. Higher yields without loss in quality were claimed. M. K. Thornton, Jr. [Oil & Soap **14,** 151-2] obtained lowest refining losses and best color by cooking the cottonseeds at a low temperature, raising the temperature to 190-200° F., adding hot water and allowing the stock to settle at 110° F. before pressing. For use in an expeller, R. T. Anderson [*U. S.* 2,065,848] heated cottonseeds, castor beans, copra or other raw material to 105-125°, then cooled it to 60-80°, adjusting the operations so that the final moisture content was below 4 per cent, and the material was then passed through a continuous expeller. P. Ammann [Brit. 452,892] preferred reducing the moisture content of oil-bearing vegetable material to 3 per cent without roasting. Laboratory investigations on optimum conditions for hydraulic pressing of cottonseed oils were conducted by E. C. Koo et al. [*Ind. Research* (*China*) **6,** 9-14; *J. Chem. Eng.* (*China*) **4,** 15-20]. Effects of temperature, pressure, and moisture content of cottonseeds on the oil yields were reported. Optimum moisture content was between 5 and 11 per cent. Experiments on the treatment of seed by Skipin's method were reported on cottonseed by A. I. Skipin *et al.* [*Masloboino Zhirovoe Delo* **12,** 379-81, 433-5], on sunflower seeds by A. Tyakin [*ibid.* 481-2], and A. M. Goldovskii and V. Nassonov [*ibid.* 569], and on linseed by A. I. Skipin [*ibid.* 473-4]. Optimum conditions for sunflower seeds were 8.5 per cent moisture in the ground seeds, steaming at 80 to 85° C. and roasting at 115 to 120°. With linseed, roasting should be at 47 to 51° and the hulls should be mixed with the partly extracted meal for further roasting and extraction. R. T. Anderson [Oil & Soap **14,** 149] has shown that with the increased capacity of modern expellers there results a darker color in crude soybean oil because of the heat developed in the equipment. He therefore recommended spraying oil over the barrel of the expeller to control the temperature.

Brief notes on extraction of grape seed oil were presented by R. de Vita [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** *No.* 10, 16-7]. A method of removing seeds from wine-making pressed residues comprised separation by a series of four sieves and then blowing with air.

A report by F. Gogolev [*Masloboino Zhirovoe Delo* **12,** 492-3] regarding effect of drying seeds on the acidity of the oil produced, is of importance from the standpoint of seed storage. The acid increases with increasing moisture content and may be decreased to a definite minimum by drying. Drying sunflower seeds from 13.1 to 7.96 per cent moisture content reduced the acid number of the oil derived therefrom, from 1.51 to 0.86; increasing the moisture content of the seeds restored the acid number. Moldy seeds of 25 per cent moisture content had an oil acidity of 29.6, which decreased to 23.7 on drying. The author postulated that the effect was due to microbiological changes.

Patents on pressing equipment were issued to A. Nyrop [*Dan.* 53,328] and N. V. Oliefabriken "Het Hart" en "de Zwaan" vorbeen Adriaan Honig [*Ger.* 648,315 *Cl.* 23a. 1 *and Brit.* 456,088]. The latter invention was a device for applying cloths to molds of cake for pressing with a hydraulic press. Nyrop invented an extraction apparatus which included equipment for finely dividing the material, a heater for quick heating, a pressure pump, a vessel where cooking takes place under pressure, means of removing the material from the pressure vessel so that it is subjected to a sudden reduction of pressure and then means of separating the material into its components.

M. Singer [*Seifensieder-Ztg.* **64,** 863-5, 881-2], W. E. Meyerweissflog [Oil & Soap **14,** 10-14], R. H. Lamping [Oil & Soap **14,** 315-7] and M. Bonotto [Oil & Soap **14,** 310-1] contributed persuasive communications on the advantages of solvent extraction over pressure methods for the production of oils. Economy of the solvent method was emphasized. Safety in solvent extraction was discussed by M. Bonotto [Oil & Soap **14,** 30-3]. Among the precautions mentioned are: all piping should be welded; differences in voltage between sections should be avoided; compressed air should not be used in lines; metallic moving parts should be of brass, bronze or copper to prevent sparks; sewers should be trapped several times; pipes handling solvents should have no U bends; and spilled solvents should be diluted with carbon tetrachloride from bottles distributed about the plant for that purpose.

Continuous solvent extraction has still continued as a subject for considerable inventive ingenuity, as shown by patents issued to W. J. O'Brien and R. C. Brett [*U. S.* 2,074,988], M. Bonotto [*U. S.* 2,-086,181], H. H. Bighouse [*U. S.* 2,096,728], Hansa-Mühle A. G. [*Ger.* 646,189 *Cl.* 23a.2 *and Fr.* 810,462], W. Lill [*Ger.* 636,093 *Cl.* 23a. 2], W. J. Podbielniak [*Fr.* 802,701] and Etablissment Rocca, Tassy et de Roux [*Fr.* 802,597]. Inventors of Gesellschaft zur Verwertung Fauthscher Patente m. b. H. [*Brit.* 459,763 *and Fr.* 806.493] improved the economy of their solvent extraction system by altering the apparatus so that the grinding and the roller mills are submerged in the solvent.

C. S. Boruff and D. Miller [Oil & Soap **14,** 312-3] developed a process of extracting corn oil from distillery grains rather than from the incoming corn. Better efficiency and feeds of good quality were reported by carrying out the process according to their method.

General chemistry, composition and properties of extraction naphthas were presented by A. E. MacGee [Oil & Soap **14,** 322-4, 324-7]. A patent was issued to the Standard Oil Development Company [*Fr.* 806,674] on using hydrocarbon solvents containing two to four carbon atoms; the solvent was separated from the dissolved material by reducing the pressure. Chlorinated hydrocarbons received considerable attention in this field. A. Chernukhin [*Masloboino Zhirovoe Delo* **13,** *No.* 3, 7-8] showed by comparative tests that the results obtained in oil extraction by dichloroethane exceeded those obtained with benzine, petroleum ether or diethyl ether. F. Sallusto [*Ann. ist super agrar Portici* **7,** 47-51] similarly showed that trichloroethylene had many advantages over other solvents. Halogenated hydrocarbons were used in the processes invented by H. Wielrath [*Ger.* 646,922 *Cl.* 53g. 4.02] and F. W. Nitardy and W. S. Jones [*U. S.* 2,067,279]. The latter invention pertained to obtaining vitaminiferous oils by cooking livers, at the same time adjusting the ratio of water to dry liver between 2:1 and 4:1 and then solvent extracting. Wielrath both dried and removed oil from fish by boiling in halogenated hydrocarbons of boiling point greater than water and immiscible with water, until the boiling point of the charge reached that of the solvent, followed by filtering and distilling the solvent.

S. Igarashi and Y. Ishida [*J. Soc. Chem. Ind. Japan* **40,** 271-2] reported improvements in yield of soy bean oil in the extraction with alcohol when small percentages of calcium acetate, acetic acid, calcium chloride, sodium soap of soy bean oil or several other salts were added.

Fish liver oils were extracted by C. Nielsen [*U. S.* 2,078,404] by steaming at temperatures of about 100° C.; the liquid was discarded and the residue was extracted with diethyl ether as a solvent, all operations being effected while the material was protected from the oxidizing influence of air. K. Kawi [*Brit.* 465,547] extracted fish livers with oil for the production of medicinal oils. H. N. Brocklesby and K. Green [*Progress Repts. Pacific Biol. Sta. & Pacific Fisheries Exptl. Sta.* **1937,** *No.* 33, 7] recommended a counter flow system of extraction with oil for preparing vitaminiferous oils from halibut liver oil wash water. A large amount of vitamin A had been retained in the original wash water because the liver oils, due to autolysis in the livers before extraction, contained considerable free acids. The large amount of soap formed therefrom on alkali refining emulsified a considerable portion of the vitamin constituents in the wash water.

An apparatus for the continuous distillation of oils or fats and solvents was invented by P. L. Fauth [*U. S.* 2,078,841].

By-products of certain oil pressing processes are a valuable source of income or even may be considered the main product of the industry. For instance, to obtain seed flour containing enzymes a patent issued to Standard Brands, Inc. [*Brit.* 466,882] claimed use of solvent extraction at temperatures below 70°. M. Bonotto [*U. S.* 2,086,180] designed an apparatus for removing solvents from soybean residues. Steam is injected into superposed zones of material at successive intervals of time, the amount being increased for each zone, and injection is continued until all have been steam treated. The solvent is carried off by the steam. Method of preparing both flour and oil from peanut kernels was described by P. Ammann [*Brit.* 461,760]. The peanuts are first pressed, the residue rubbed, winnowed, mulled, and finally solvent extracted to remove the remaining oil. By-products for animal and poultry feeds from the various types of oil extraction equipment differ in their nutritive value. J. W. Hayward [Oil & Soap **14,** 317-21] and the same author with coworkers [*Poultry Sci.* **16,** 3-14] reported optimum temperature treatment before and during the extraction for the production of the best quality soy bean oil meal. High temperature expressing, i. e., 140 to 150° C. for 2.5 minutes during expelling, or cooking at 140 to 150° for 90 minutes for hydraulic press and solvent extraction yielded good quality meals.

Another type of by-product emanating from the oil industry is the phosphatides. Good monographs on this branch of the industry were prepared by G. A. Wiesehahn [Oil & Soap **14,** 119-22], B. Rewald [*Chemical Industries* **41,** 253-4] and A. A. Horvath [*J. Chem. Ed.* **14,** 424-6]. Phosphatides were removed from soy bean oil by H. R. Kraybill [*U. S.* 2,069,187] by washing with alcohol and water. B. H. Thurman [*U. S.* 2,078,428] patented the use of soap and ethyl acetate to precipitate the phosphatides from oils which are to be used for technical purposes. G. E. Halliday [Oil & Soap **14,** 103-4] showed that during the storage of soy bean oils, the phosphatides slowly settle to the bottom layer of oil. In carloads of oil stored 3 to 112 days the lecithin content of the top oil varied from 0.72 to 1.35 per cent, the middle oil 0.65 to 1.45 per cent, and that of the bottom oil 1.45 to 22.35 per cent. G. Wolff [*Ann. fals* **29,** 537-8] suggested that since most of the phosphatides of oils are lost during the refining, means should be developed for reincorporating these constituents. Commercial lecithin preparations were patented by C. H. Buer [*U. S.* 2,064,727] and A. A. Lund [*U. S.* 2,090,537]. Buer added 5 to 6 per cent alcohol to dry lecithin and pressed it into tablets. Lund converted the lecithin into lecithin hydrate by mixing lecithin with water and alcohol and then removed the alcohol, thus yielding a lecithin preparation having a water vehicle.

According to Y. Iwasa [*J. Agr. Chem. Soc. Japan* **13,** 225-35], sugar, saponin, and alcohol may be derived as by-products in the preparation of soybean oil by alcohol extraction. As is known, on cooling the mixture of alcohol and soybeans, two layers are formed, an oily layer and a sirupy layer containing the meal, alcohol and water. The filtered sirup, after removal of alcohol, contained 70 per cent carbohydrates. Glucose, fructose, galactose, and stachyose were found in the sirup. Saponin was precipitated by the addition of sulfuric acid to the sirup. The sirup freed from saponin was inoculated with various alcohol fermentation microorganisms. The alcohol production by *Saccharomyces ellipsoideus* with 0.1 per cent addition of cobalt chloride to the charge was superior.

Several miscellaneous general papers on the refining of fats appeared during the year; F. Wittka [*Chem. Ztg.* **61,** 56-7] and C. Kerkhoven [*Ole, Fette, Wachse, Seife, Kosmetik* **1937,** *No.* 1, 6-7] briefly described current methods; O. Gerhardt [*Seifensieder-Ztg.* **64,** 393-5] discussed tallow refining, K. Schneider [*Allgem. Oel-u. Fett-Ztg.* **34,** 252-5] described the Bamag-Meguin A.-G. and the "Wecker" processes, and H. Schmalfuss [*Fette u. Seifen* **44,** 292-6] pointed out that some of the drastic methods now used destroy and remove vitamins and other valuable minor components.

The simplest means of refining is by sedimentation. S. Z. Rakuts [*Masloboino Zhirovoe Delo* **12,** 387] recommended precooling linseed oil to 0° and then settling at 18 to 20°

as most practical. A preliminary heating was said to retard the sedimentation rate. G. P. Solovev [*Masloboino Zhirovoe Delo* **12,** 533], however, reported that the volume of sediment and the corresponding linseed oil lost in sedimentation were reduced considerably by the presence of 0.75 per cent water and preheating to 45° for 15 minutes.

The manner of use and the type of caustic employed in refining was the much discussed problem of caustic refining. F. Wittka [*Allgem. Oel-u. Fett-Ztg.* **33,** 563-9] recommended 2 to 7° Bé caustic. If the emulsion does not break with usual salt treatment he recommended treatment with sulfuric acid and repetition of the deacidification. With expensive and slightly acid oils, the use of dilute lyes was said to be most economical. R. Dieterle [*Seifensieder-Ztg.* **64,** 632-3] listed coconut and babassu fats, good palm fat, sesame and peanut and some types of whale oil as being more economically refined with 2 to 6° Bé caustic and at 98° C. using a caustic factor of 1.1 to 1.4, *i. e.,* the caustic necessary, calculated from free fat acids multiplied by the factors. Poor quality marine oils, soy bean, rape and cottonseed oils require concentrated caustic (10 to 20° Bé), a caustic factor of 2 to 5, and temperatures between 60 and 50°. A. Ryabo [*Masloboino Zhirovoe Delo* **12,** 549] reported that losses in alkali refining were considerably reduced by treating the oils with 5 per cent excess, 27° Bé caustic and 2 per cent salt at 40 to 45° C., for 20 to 25 minutes and separating the soap stock after 12 hours. Experiments on refining several fats and oils according to Russian patent 38,721 were reported by A. A. Zinov'ev and coworkers [*Masloboino Zhirovoe Delo* **12,** 485-8, 543-5, 583-5; **13,** 12-3, 28-9]. A low loss of oil in the soap stock was evident when 1 to 2 per cent of sodium chloride—based on the soap stock—was used during alkali refining. Several other salts that were tried gave poor results. M. Z. Klyachko [*Masloboino Zhirovoe Delo* **13,** *No.* 2, 15-7] claimed that castor oil can be refined with 20° Bé sodium carbonate containing 2 per cent sodium chloride and heating to 62-5°. This manner of operation was time-saving because no emulsion was formed. A solid deacidifying agent for oils was prepared by G. Leot [*Brit.* 451,730] by coating heavy metal particles with alkali; these can be sprinkled uniformly on the surface of the body of oil or melted fat. I. Petryaev [*Masloboino Zhirovoe Delo* **13,** 26-9] cautioned fat refiners to remove all the soap in an oil after alkali refining, because this soap may hydrolyze and develop a high acidity in the oil.

It has been shown that cottonseed oils of high gossypol content undergo the least losses during refining. Because of this, G. W. Owen [Oil & Soap **14,** 149-51] recommended mixing 30 per cent expeller oils with hydraulic press cottonseed oil. The high gossypol content of the expeller oil improves the type of soap stock produced with less loss of oil. Since gossypol is a polyphenol, M. S. Elgart and N. V. Ionova [*Masloboino Zhirovoe Delo* **12,** 546-9] reasoned that other phenols should create the same refining effect. Phenol was found to be most effective in reducing the refining losses; the phenol was removed during subsequent bleaching and washing.

Patents issued to B. Clayton *et al.* [*U. S.* 2,100,274; 2,100,275 *and* 2,100,276] dealt with apparatus for continuous refining whereby proportioned oil and caustic flows through a conduit in which mixing and heating occurs, and the soap stock is removed from the oil by centrifuges.

Several novel systems of refining were introduced. A. O. Fischer [*U. S.* 2,090,738 *and Fr.* 809,527] removed free fatty acids and other impurities from oil by stirring it with furfural and then allowing it to separate into two layers. The bottom layer contained an emulsion of furfural free fatty acids, amines and other impurities. W. Ekhard [*Brit.* 452,682 *and* 465,111] treated the oil with a fermentable substratum inoculated with microorganisms which produce lactic, propionic and butyric acids. After fermentation ceased the oil was removed from the products of fermentation and other impurities. W. Fuchs [*Ger.* 630,790 *Cl.* 23a 3] emulsified the fats with readily separable material and refining was accomplished in an electroösmosis apparatus. Iron was removed from the oleic acid for use in manufacture of leather cleaning soap by precipitation with tannic acid according to patent by W. J. Yates [*U. S.* 2,064,285].

Edible oil deodorizing equipment and methods were reviewed by A. P. Lee and W. G. King, Jr. [Oil & Soap **14,** 263-9]. They emphasized the current trend toward continuous processes with automatic control. A new apparatus for continuous refining was patented by A. W. Ayres and N. Brewer [*U. S.* 2,068,971]. The deodorization of tung oil was investigated by H-L. Tchang and Y-C. Wang [*Natl. Acad. Peiping* **2,** 23-9]. Steam or wet gas treated oils reverted to their original odor in a few days. Dry carbon dioxide or air gave better results; only a weak odor reappeared. The exclusion of moisture was emphasized in removing the odor and maintaining a product of only weak odor. According to a patent issued to Eastman Kodak Company [*Fr.* 809,700], subjecting an oil to high vacuum distillation removes protein substance and products causing rancidity.

A description of a method of bleaching fats with hydrogen peroxide was published by A. Jordan [*Öle, Fette, Wachse, Seife, Kosmetik* **1936,** *No.* 13, 14-5].

Physical bleaching was treated in the fat literature from different viewpoints. Activated carbon in oil and fat purification was discussed by E. A. Sigworth [*Soap* **13,** *No.* 8, 24-7, 113]. I. and A. Davidsohn [*Ind. Chemist.* **13,** 281-3] similarly considered bleaching earths. C.-Y. Lin and J. O. Wilson [*J. Chem. Eng. China* **3,** 325-30] reported discovery of four clays which were said to be much more efficient than fuller's earth. S.-I. Ueno and Y. Hayashi [*J. Soc. Chem. Ind. Japan* **40,** 66-73B] compared the stability of carbon and clay treated oils with the original unrefined oils. The loss of stability was illustrated diagrammatically by curves showing acid number and Kreis red units as a function of time for 25 oils. As a means of evaluating active earths, A. Berczeller [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** *No.* 7, 3-5] proposed the measurement of the exothermic reaction between turpentine and the earth. A simple apparatus for this purpose was described. During the test the turpentine polymerizes and thus produces changes in some characteristics which also may be used as criteria in the test. The presence of moisture adversely affects the test. E. Erdheim [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** *No.* 2, 24-7 *and Mat. grasses* **29,** *No.* 349, 114-17] maintained that the order of activity of bleaching earths varies with the oil. He recommended preparation of bleaching curves for each earth and on each oil, such curves being used as a guide to practice and selection of earths. A steam jacketed filtering apparatus containing bleaching earth as a filtering medium was invented by A. G. Geirnaert [*Belg.* 417,392].

A review of patents on restoring bleaching earths was compiled by H. Goette [*Allgem. Oel- u. Fett Ztg.*

34, 256-9]. New methods were described by A. Eisenstein [*Austrian* 147,701 Cl 23a.], V. Ruff [*Masloboino Zhirovoe Delo* **12,** 552-5] and E. W. Zublin [*U. S.* 2,090,741]. The latter used treatment with superheated steam; Ruff reactivated carbon by heating at 800-890° for 3 hours in a retort in absence of air, and Eisenstein treated the used earths with alkali solutions.

A very advantageous practice in the industry would include recovering of oil from spent bleaching material and hydrogenation catalyst. Apparatus and methods for accomplishing this task were described by H. Sieck [*Oil & Soap* **14,** 314-5], I. Taussky [*Öle, Fette, Wachse, Seife, Kosmetik* **1936,** *No.* 14, 1-2] and A. S. Slashchev [*Masloboino Zhirovoe Delo* **13,** *No.* 2, 17].

Various means of splitting fats were patented. Patents issued to Procter & Gamble Company [*Can.* 365,544 *and Brit.* 446,597, *and Brit.* 466,596] and to Henkel & Cie G.m.b. H [*Fr.* 808,069] describe methods of passing water and oil countercurrently at high temperatures and under high pressures. A glycerol and water mixture was obtained at one end of each apparatus and the fat acids at the other end. S. M. Konstantinow [*Russ.* 48,962] split one half of his fats with acid and the other half with alkali and combined both charges, thus obtaining separation of fat acids and a neutral glycerin water. According to a patent of J. R. Moore and E. K. Wallace [*U. S.* 2,065,145] catalytic splitting was carried out while the fat was dissolved in a water miscible solvent such as acetone, diethyl ketone or ethylene glycol. The solvent was distilled off and the glycerol-water solution was separated from a top layer of fat acids. Enzymes for splitting fats were obtained by E. Takamiya [*U. S.* 2,102,101, *Fr.* 802,772, *and Brit.* 467,618] by treating seeds or plant material containing them with a 0.6 to 1.2 normal solution of acid. The amount of solution used was sufficient to form a soft mass. The enzyme split off and was recovered. The progress of the splitting reaction of fats in an autoclave with caustic was described by Lascaray [*Seifensieder—Ztg* **64,** 122-4]. The proportion of sodium ion increased in the fat layer as the reaction progressed or as the amount of fat acids increased in the system composed of fat acids and small amounts of sodium hydroxide. In the presence of a large amount of unsaponifiable the separation into two layers was slow and incomplete. Splitting experiments with tallow, palm oil and coconut oil with 0.5 per cent caustic at 36° temperature and 10 atmospheres pressure gave 92 per cent reaction after 6 hours and 97-8 per cent after an additional 2 hours. The glycerol water separated quickly and contained 0.06 per cent combined sodium hydroxide and .1 to 2 per cent fat acids. Results of a series of splitting tests with various ratios of water to fat and additions of catalyst were tabulated by H. P. Kaufmann and M. C. Keller [*Fette u. Seifen* **44,** 42-7]. Small amounts of metal oxides improved both the speed of the reaction and degree of splitting. Increased temperature greatly increased the rate. Under equal conditions the percentage of fat split at various fat: water ratios from 6:1 to 2:1 ranged from 69.6 to 84.7 per cent respectively. In a later report the authors [*Fette u. Seifen* **44,** 42-7] postulated that because the equilibrium constant of the fat-splitting reaction was independent of temperature, and for various other reasons, its heat of reaction must be substantially zero. Investigation by J. Hetzer [*Fette u. Seifen* **43,** 257-8] indicated that the splitting reaction was not selective. Neither enzymes nor partial autoclave hydrolysis reacted so as to liberate fat acids of high molecular weight in preference to those of low molecular weight or the unsaturated acids in preference to the saturated acids.

Recent methods of fat distillation were reviewed by A. Kuckhoff [*Seifensieder-Ztg.* **63,** 833-5], E. Wecker [*Fette u. Seifen* **44,** 222-7] and J. Hetzer [*Seifensieder-Ztg* **64,** 449-50, 530, 608-9, 631-2, 664]. The continuous system of fat acid distillation patented by Procter and Gamble Company [*Brit.* 457,624] comprises heating the fat acids under pressure and introducing them continuously into a vacuum chamber wherein the acids are vaporized and they pass into a condensing apparatus.

Several patents issued to Imperial Chemical Industries [*Brit.* 457,120; 457,292; 457,778; 458,117; 458,118 *and* 458,119; *and U. S.* 2,073,327] dealt with the design of apparatus for short path high vacuum distillation by which it has been claimed that natural triglycerides can be distilled. This type of still, according to patents assigned to Imperial Chemical Industries Ltd. [*Brit.* 464,395 *and Fr.* 802,177] and communication by K. C. D. Hickman [*Ind. & Eng. Chem.* **29,** 1107-11] can be used for the concentration of vitamin A. The British patents feature 10 per cent saponification and short-path distillation; the fractions obtained at pressures 10^{-3} to 10^{-4} and temperatures of 200 to 265° C. contained relatively large amounts of vitamin A. According to the French patent the oils were first moderately hydrogenated and then distilled. Hickman distilled cod-liver oil and vitamin A and D concentrates in a molecular still; his results were reported graphically. Single distillations of fish oils effected considerable concentration of the vitamins.

Historical information and a discussion on some problems of fat hardening were presented by W. Normann [*Chem.-Ztg.* **61,** 20-22 *and Fette u. Seifen* **44,** 330-6]. Equipment and methods used for hydrogenation in some Russian plants were described by G. Syrkin and I. Tovbin [*Masloboino Zhirovoe Delo* **13,** 21-6] and by E. Botkovskaya and L. Nikolaeva [*Masloboino Zhirovoe Delo* **12,** 394-7].

The rate and course of the hydrogenation reaction was studied by D. A. Harper [*J. Soc. Chem. Ind.* **56,** 308-10T]. With the rate of hydrogenation from oleic to stearic as unity the rates for other acids and oils were evaluated. Reduction of oleic to stearic, in glycerides, seemed slowest, C_{20} and C_{16} acids with one double bond reduced faster and the C_{20} monethenoid reduced most rapidly. Brücke [*Brit.* 452,887] claimed that favorable selective hydrogenation of train oil fat acids was obtainable by hydrogenating in the presence of a catalyst at 80 to 130° C. and under 25 atmospheres pressure. V. V. Ipatieff, Jr., and I. F. Bogdanov [*J. Gen. Chem.* (*U.S.S.R.*) **6,** 1651-8] hydrogenated a mixture of allyl alcohol and oleic acid dissolved in ether, in the presence of platinum catalyst at 20° C, the hydrogenation of oleic acid began after the entire allyl alcohol was reduced. Y. Shinozaki and S. Kagawa [*J. Agr. Chem. Soc. Japan* **13,** 12-22] demonstrated that there was no reduction of the hydroxy groups of castor oil in presence of copper as a catalyst unless the oil was heated at 250° C. and under about 80 kilograms per square centimeter pressure. Octadecanediol was isolated from the hydrogenation product of castor oil.

Production of isomers during hydrogenation was studied by several investigators. V. M. Puzanov [*Masloboino Zhirovoe Delo* **12,** 444-6] oxidized partially hydrogenated sunflower oil after removal of saturated constituents. Analysis of products indicated that 12-13 isoöleic and isoelaidic acids and 9-10 oleic and elaidic acids had been present. Similar work by Y. Toyama [*J. Soc.*

Chem. Ind. Japan **40,** 283-5B] indicated that several iso-acids having the double bond between 12-13, 14-15, 15-16 or possibly between 16-17 carbons are formed on partial hydrogenation of erucic acid. R. Koyoma [*J. Soc. Chem. Ind. Japan* **40,** 29-30B] hydrogenated sardine oil at low hydrogen pressure. A large production of isoöleic acid began after 3-5 hours, reached a maximum at 4.5 hours and then decreased. Considerable hydrogenation had occurred after 5.5 hours.

An unusual system of hydrogenation is that of heating oils with alcohols. The alcohols supply the hydrogen. Mixtures of 150 parts of sunflower oil with 19 parts of ethyl alcohol and 0.4 to 2 per cent aluminum-nickel, copper-nickel and nickel catalyst were autoclaved at 240-360° and 28-41 atmospheres pressure for 15 minutes by M. F. Belyakov and G. A. Ivanova [*Masloboino Zhirovoe Delo* **12,** 537-9]. The treatment reduced the linolenic acid and increased the oleic acid content of the oil. Best results were obtained with copper-nickel catalyst. V. A. Rush *et al.* [*J. Applied Chem. U.S.S.R.* **10,** 702-8] performed similar experiments except that they used propyl alcohol as the hydrogen donor and a catalyst prepared from nickel formate. The products contained saturated compounds 12.5 to 12.8, oleic acid 50.8 to 54.5, isoöleic acid 33.1 to 27.4 and linoleic acid 3.6 to 5.3 per cent. With use of nickel-kieselguhr catalyst there was less destruction of the aldehydes formed from the propyl alcohol.

Less hydrogen was required for the hydrogenation of polymerized than for oxidized sunflower oil according to tests by A. I. Kal'fe [*Ukrain. Khem. Zhur.* **11,** 483-91]. He therefore suggested that polymerization before hydrogenation would be an economical procedure in preparing hardened oils for technical purposes.

A highly active catalyst was prepared by the reduction of nickel carbonyl at 120 to 145° by H. I. Waterman and coworkers [*Rec. trav. chim.* **55,** 854-8; **56,** 521-5]. They obtained a fat of 60° C. softening point by the hydrogenation of soybean oil at 60° C. and at atmospheric pressure for 1¾ hours. Codliver oil hardened under the same conditions and pressure with this catalyst yielded a product which still showed the Carr-Price reaction. When the activity of this colloidal catalyst decreased by aggregation of the metal particles, they could be separated easily by magnetic methods.

Several Investigators recorded studies on new catalysts. G. Klein *et al.* [*Masloboino Zhirovoe Delo* **13,** *No.* 3, 9], H.-Y. Chang and S.-H. Wang [*J. Chem. Eng. China* **1,** 136-7] and V. Kopeikovskii and T. Lapina [*Masloboino Zhirovoe Delo* **12,** 580-1] described the use of copper-nickel catalyst. The first two papers gave the method of preparation with some hydrogenation results. The latter gave details of recovering the catalyst by dissolving in 9 per cent sulfuric acid and precipitating with sodium carbonate. Nine nickel catalysts containing various amounts of copper, manganese, aluminum oxide, cobalt, and ferric oxide with kieselguhr as a carrier were tested in high pressure hardening tests on several fats by R. Koyama [*J. Soc. Chem. Ind. Japan* **40,** 25-9B]. Those containing large amounts of nickel were more active than those prepared from manganese, cobalt or copper compounds. A patent on the preparation of a highly active catalyst by reduction of a nickel ore containing silica and alumina was issued to M. P. Lysyakov [*Russ.* 42,544].

Nickel formate was reduced to a catalyst according to patents issued to N. V. De Bataafsche Petroleum Maatschappij [*Fr.* 804,479] and E. C. Williams and S. H. McAllister [*U. S.* 2,067,368] by heating a suspension of the salt in isododecane at about 250 to 350° C. Part of the hydrocarbon vapors were used to sweep out the gaseous decomposition products from the system. H. B. Jesperson [*U. S.* 2,084,687] in preparing a catalyst from nickel formate, ground the dehydrated salt with fat or oil and reduced it with hydrogen. In the recovery of catalyst prepared from nickel formate P. A. Artamonov [*Masloboino Zhirovoe Delo* **12,** 537-9] suggested that the loss of activity was due to the presence of water and the aggregation of nickel particles; he therefore recommended discharging the catalyst from the filter press into oil and passing it between rolls. I. Kaplan and S. Yanovskaya [*Masloboino Zhirovoe Delo* **12,** 446-7] showed that dehydrating nickel formate containing up to 35 per cent water at 180° in vacuum does not affect the activity of the catalyst produced.

The catalysts recommended by Rohm and Haas Company [*Fr.* 802,542] for the hydrogenation of oils to alcohols were cobalt and silver or their oxides. The product of the ammoniacal reduction of a chromium nitrogen compound whose oxide is soluble in ammonia was patented by P. L. Salzberg [*U. S.* 2,089,433] for use as a hydrogenation catalyst.

Publications relating to the drying oil industry indicated that the activity in this field was much increased. Both individual and cooperative study of these oils has yielded new information on improving them and also on means of preparing substitutes. The substitutes were resins, improved semi-drying oils and other miscellaneous materials. Reviews and general descriptions of the process for improving oils for paint purposes were submitted by A. Foulon [*Fette u. Seifen* **44,** 252-4], W. V. Lee [*Oil Colour Trades J.* **91,** 833,-835, 837-40], H. W. Chatfield [*Paint Manuf.* **7,** 103-5, 144-5], I. Mellan [*Natl. Paint Bull.* **1,** *No.* 6, 12-3], A. E. Rheineck [*Paint Oil & Chem. Rev.* **99,** *No.* 5, 9-12], R. S. Morrell [*J. Soc. Chem. Ind.* **56,** 795-8] and G. V. Schulz and E. Huseman [*Angew. Chem.* **50,** 767-73]. The last two reviews deal principally with the chemistry of the bodying reactions.

Several papers dealt with changes in characteristics of drying oils during their heat treatment. H. P. Kaufmann *et al.* [*Fette u. Seifen* **44,** 289-92] charted the changes in wood, oiticica and linseed oils during polymerization. Wood and oiticica oil on heating 12 to 16 hours at 180-190° C. showed an initial drop in diene value; however, at gelation this value was still quite high. The thiocyanogen value was not appreciably affected. The iodine value of tung oil decreased. On heating linseed oil, both the iodine and thiocyanogen value decreased, and the small diene number dropped to zero. Oiticica oil heated for 30 hours at 140-150° showed no substantial decrease in diene or thiocyanogen value. W. Leithe [*Fette u. Seifen* **44,** 14] reported that both index of refraction and density of linseed oil increase, and the same characteristics for tung oil decrease, during bodying of the oils. These changes were said to be qualitatively the same, and were therefore thought to indicate that the mechanism of the reactions in the two oils therefore do not differ. Changes in density and viscosity of vegetable oils with various oxidation and polymerization treatments were reported by M. Tachimori [*J. Soc. Chem. Ind.* **39,** 395-6B, 473-5B; **40,** 19-21B] and by V. M. Breitman [*Ind. Eng. Chem.* **29,** 1202-6]. Both investigators developed several equations which represent the effect of time and temperature of heating on the properties of the products.

The lower boiling fractions of the

methyl esters of linseed oil fat acid, heat treated at 290 to 300° C. in a hydrogen atmosphere, were analyzed by K. Kino [*Sci. Papers Inst. Phys. Chem. Research Tokyo* **30,** 244-8, **31,** 244-6]. In the fractions distilling up to boiling point 190° at 3-4 mm. pressure there was slight decrease in the saponification value and an increase in the iodine number with increase in boiling point. The high saponification value of the lower boiling fractions indicated that cracking occurs in the process.

A. J. Currier and I. H. Kagarise [*Ind. Eng. Chem.* **29,** 467-9] recorded data on the rate of oxidation of linseed oil with driers, using the length of the induction period, that is, time required for reaching maximum velocity of oxygen absorption as a criterion. Cobalt and manganese linoleates gave shorter induction periods than lead. Lead phenylpropiolate, salicylate and acetate were poor driers. A study of maleic anhydride—B—eleostearin addition treated with cobalt drier by G. Gee and E. K. Rideal [*J. Chem. Soc.* **1937,** 772-8] by a phase-boundary-potential method showed that the potential of the unoxidized film was unaffected by the catalyst. The potential of the oxidized film containing peroxide decreased when treated with cobalt; which was interpreted to indicate that the polymerization with catalyst involves the formation of a complex with the catalyst while the oxidation of oils does not require this mechanism.

A general discussion of the chemistry of drying films was presented by R. S. Morrell [*Chemistry & Industry* **56,** 795-8]. In nonpolar solution the drying oils have an induction period while in acetic acid the polymerization is rapid. Morrell favored the opinion that in nonpolar solvent molecular aggregates were formed while in acetic acid a peroxide of dimeride character was formed. T. F. Bradley [*Ind. Eng. Chem.* **29,** 440-5, 579-84] applied Carothers' general theory of polymerization to the drying of oils. It was assumed that dried films have chains cross-linked in three dimensional structures and drying therefore consists of converting linear two dimensional structures to three dimensional types. Only one double bond in each radial was said to function as an active center. Substantiation of the theory was attained by the demonstration that saponification of treated oils gives dimeric acid regardless of the extent of polymerization, by geometric structures, by the inability of glycol linoleate to dry, and by the inability of mono- and diglycerides of China wood oils to form films. The report of B. Glassmann and S. Barsutskaya [*Z. Anal. Chem.* **109,** 251-61] also indicated that triglycerides gave the polymers. They reported analytical data on linoxyn; the purified material corresponded to triglycerides while the crude contained both di-glycerides and triglycerides.

Mechanical linking as an explanation of bodying of oils was proposed by E. Rossmann [*Fette u. Seifen* **44,** 189-92, 434-5]. The intramolecular polymerization was said to involve two fat acid radicals of the same fat molecule in the formation of a ring. The mechanical linking of such rings was said to be well in accord with various observations on building up colloidal complexes, on molecular weight and on iodine value. Kurz [*Fette u. Seifen* **44,** 184-5, 434-5] criticized this theory with the suggestion that Rossmann's experiments were on esters containing a mixture of fat acids and therefore his correlations between molecular weights and the type of compounds formed would be in error. He recommended that the problem of the mechanism of bodied oils be studied with pure chemical compounds.

The diene value of oil served to substantiate the view that during boiling of oil conjugated double bonds were formed. M. Goswani and A. Saha [*J. Indian Chem. Soc.* **14,** 116-7] demonstrated this with linseed oil of zero diene value which acquired a diene value on boiling. K. Kino [*Sci. Papers Inst. Phys. Chem. Research Tokyo* **30,** 244-8] refused to accept the proof that conjugated double bonds were formed as explained formerly on the basis of increase in iodine value and claimed that a large amount of hydrogen can be added to the compound formed without much effect on the iodine value.

The mechanism of drying and continued autoxidation of dried drying-oil films was reviewed by H. Behrer [*Farbe u. Lack* **1937,** 425-6]. The drying of films was studied by electron diffraction by H. Clewell [*Ind. Eng. Chem.* **29,** 650-3]. Distinct refraction patterns indicated that an unoxidized oil probably contains few polar products. The carbon chains orient normally to the film surface during drying. L. Auer [*Paint Bull.* **1,** June, 8-9; July 8-11] experimented with drying of oils in desiccators in air pressure of 16 mm. of mercury. He found that the oils dried but required a longer time. The films dried even in the presence of less oxygen than was necessary to satisfy the autoxidation theory.

Various groups of the Natl. Paint, Varnish, Lacquer Assoc. have published material on heat bodying of oils. The Baltimore Club [*Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect. Circ.* **523,** 315-22] recommended that equipment be designed so that acids do not condense and return to the charge because the dominant factor which caused "livering" between linseed oil and pigments was the acid value. The Cincinnati-Dayton-Indianapolis-Columbus Club [*Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect. Circ.* **523,** 355-64] found no appreciable difference in varnish prepared from wood oil treated at various temperatures between the limits 232 and 288° providing the treatment was carried out in a manner to obtain the same body. The New York Club [*Natl. Paint, Varnish, Lacquer Association, Sci. Circ.* **523,** 409-37 *and* 1-100S] reported commercial scale bodying of linseed oil in air and in vacuum with the physical properties of the products. Other information recorded the relationship between viscosity of linseed oil and presence of acetone insoluble, behavior with other paint constituents and behavior when used for grinding.

The methods of preparing stand oils by heating in vacuum and by polymerizing the oil followed by removal of the low molecular compounds by selective solvents called "Tekaolization" was described by E. Rossmann [*Fette u. Seifen* **44,** 59-60, *and Angew. Chemie* **50,** 246-8]. A still for removing the unpolymerized constituents from polymerized oils was designed by D. Oosterhot and H. I. Waterman [*U. S.* 2,065,-728]. The oil in the apparatus flows over heated surfaces which are in close proximity to cooled surfaces for condensing, and at the same time it is submitted to high vacuum. A method of polymerizing oils by subjecting to heat and pressures to 3000 atmospheres was patented by E. W. Fawcett *et al.* [*Brit.* 452,039; *Fr.* 801,916]. H. V. A. Briscoe [*Brit.* 452,653] recommended passing a current of inert gas through the charge during cooking of oils at atmospheric pressure and temperatures of 300° in large lots. A. M. Collins [*U. S.* 2,078,194] polymerized China wood oil in the presence of a polymerizable open-chain acetylene polymer to give a product that forms hard films of good flexibility.

A patent issued to Standard Oil Development Company [*Fr.* 805,-775] claimed the use of boron fluoride catalyst for the polymerization of oils when diluted with hydrocarbons. H. I. Waterman and C. van

Vlodrop [*J. Soc. Chem. Ind.* **55**, 333-4T] reported that the polymerization of linseed oil was catalyzed by sulfur dioxide and by gaseous hydrochloric acid. The resultant products were of better quality than those of uncatalyzed heat polymerization. According to R. Jürgen [*Farben Ztg.* **42**, 85] an economical linoleate drier can be prepared from foots produced by the alkali refining of linseed oil. A. I. Svetlov [*Russian* 50,396] patented the polymerization or oxidation of oils in the presence of glycerol. To obviate the effect of a too rapid dryer R. L. Sibely [*U. S.* 2,090,936 *and* 2,090,937] patented the addition of compounds comprising reaction products of ketones and aromatic amines or a condensation product of an aldehyde and an amine.

For prevention of wrinkling of films during drying U. J. Koenig [*U. S.* 2,100,484] patented the volatilization of non oxidized material and A. Chwala [*Fr.* 809,885] for the same purpose adds a small amount of a carboxylic acid having a triple bond.

Many publications dealt with linseed oil. Refining of the oil for paint purposes was described by I. Osnos *et al.* [*Masloboino Zhirovoe Delo* **13**, No. 3, 13-16]; bodying treatments were described or discussed by I. Mellan [*Natl. Paint Bull.* **1**, 8-9, 10-11, 12-3, 13-4, 15-6], F. Fritz [*Öle, Fette Wachse, Seife, Kosmetik* **1936**, *No.* 14, 4-5], E. Asser [*Paint, Varnish Production Mgr.* **16**, 14-20] and H. C. Cohen [*Verfkroniek* **9**, 140]. H. Wolff and G. Zeidler [*Verfkroniek* **10**, 33-4] and K. Vettewinkel [*Verfkroniek* **10**, 186-8] discussed the use of variously treated linseed oils from the standpoint of the qualities that they impart to coating materials and Margaret J. Hausman [*Am. Ink Maker* **15**, *No.* 7, 16-9] dealt with the oil from the standpoint of preparation for manufacture of printing ink. A monograph giving information on production, refining, and bodying of oil was issued by U. S. Department of Commerce, Bureau of Standards (T1BM-44).

Methods of improving linseed oil were reported. According to a patent issued to Springer & Moller A.-G. [*Ger.* 635,926 *Cl.* 22h 2] stand oils of wood oil character can be produced from linseed oil by adding an unsaturated dicarboxylic acid and heating to over 200°. A patent of R. D. Bonney and W. S. Egge [*U. S.* 2,072,151] used the same ingredients with the addition of ester gum resin and a drier and instead of just heating, the mix was aerated at about 80°. A. V. Blom [*Fette u. Seifen* **44**, 107-11] reported that undesirable side reactions were suppressed by treating the linseed oils at high temperatures and rapidly cooling the charge at the end of the heating cycle ("Bisol" process). This oil was said to have a drying curve similar to linseed stand oil containing tung oil, compatibility with nitrocellulose or chlorinated rubber and good wetting power for pigments. Characteristics of cooked mixtures of blown linseed oils and several resins were reported by E. Stock [*Farben-Ztg.* **41**, 1259-6, 1283-4]. The selection of some commercial resins to replace the tung oil used with blown linseed oil varnish was said to be possible.

In using resins with linseed oil one must be aware of the fact that some of the resins are antioxidants and will increase the induction period of the oil. Data on the extent of this effect by six phenol-formaldehyde resins and mixtures of these with ester gum on pure linseed oil was reported by C. C. Vernon and W. W. Rinne [*Ind. Eng. Chem.* **29**, 1393-5].

Among the general papers on tung oil C. C. Concannon [*Am. Paint J.* **21**, Apr. 26, 54-8; Oct. 26, 7-9, 53, 56-8, 60-2] reviewed the progress and economic position of the American tung oil industry and H.-H. Wen [*Chemistry China* **3**, 550-70, 729-45] surveyed the oils of the Wan-Hsien and Chung-Ching districts of China giving production, trade, transportation and methods of refining.

Apparatus for the treatment of tung oil was patented by J. P. Ward and F. Pelton [*U. S.* 2,090,586] and by B. Lystad [*Norw.* 57,364]. The first apparatus was for a continuous process in which the oil was passed over superposed compartments that contained means of maintaining progressively higher temperatures in succeeding portions of the upper channels and a constant temperature in the lower channel. Lystad's apparatus comprised a container on a heating element, the container being provided with hinges so that when the oil has received the desired heat-treatment it can be quickly cooled by pouring into cold oil or other varnish ingredients. T. H. Geiger and L. M. Burgess [*U. S.* 2,084,137] heat-treated tung oil together with a removable diluent such as high-flash coal-tar naptha and then removed the solvent from the thickened oil. To render the oil compatible with ingredients of a nitro-cellulose lacquer, L. A. Donovan and E. A. Daniels [*U. S.* 2,094,590] added a small amount of sulfur before heating, which prevented it from jelling.

J. Rinse and W. H. G. Wiebols [*Ind. Eng. Chem.* **29**, 1149-54] compared the action of water on several linseed oil, tung oil, and other oil films. Linseed oil films absorbed more water when lead driers were present, less with manganese and least with cobalt driers. The influence of the driers on tung, oiticica and synourin oil films was just the reverse order. This difference was postulated to be due to the two principal processes during drying—polymerization and oxidation.

The characteristics of the new drying oil—oiticica oil—are being disseminated by means of both trade and scientific publications. M. E. Marvin [*Am. Paint J.* **21**, 54, 56, 58; *Drugs, Oils & Paints* **51**, 520-522], Margaret J. Hausman [*Am. Ink Maker* **15**, *No.* 1, 16-19], C. P. Holdt [*Natl. Paint Bull.* **1**, *No.* 3, 10-11, 18] and A. D. Little, Inc. [*Drugs, Oils & Paints* **51**, 247] published brief communications on oiticica oil which in most cases covered production, properties, bodying, formulas, applications, and economic discussions. The publications of E. Stock [*Farben-Chem.* **7**, 365-7; *Farbe u. Lack* **1937**, 449-50, 463-4] tabulated the color, the hardness-elasticity properties and resistance to five per cent acetic acid and five per cent soda solutions of oiticica oil cooked with 16 commercial oil-soluble resins.

Other drying oils that received brief descriptions as to their position in the industry were perilla, stillingia, and po-yok. C. W. A. Mundy [*Oil, Colour, Trades J.* **91**, 917-20] wrote a monograph on perilla oil; T-H Shen [*Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem.* **3**, 17-26] in his description of stillingia oil evaluated it as being intermediate between linseed and tung oil, while A. E. Rheineck [*Paint, Oil, Chem. Rev.* **99**, *No.* 9, 7-8] indicated that po-yok oil was similar to oiticica.

Many communications on the substitution of semi-drying or non-drying oils, resins and other materials for drying oils were instigated by both local lack of drying oil and by excess supply of other oils of poor edible quality. A list of patents on substitutes for the drying oils issued between 1863 and 1936 was compiled by A. W. Van Heuckeroth [*Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect. Circ. No.* **531**, 123-55]. The American literature on the subject was reviewed for a Russian publication by A. Y. Drinberg [*Org. Chem. Ind. U.S.S.R.* **2**, 210-3]. In

Germany, J. Scheiber [*Farbe u. Lack* **1937,** 137-8] reviewed the substitutes. Utilization of soy bean oil in paints was fostered by J. Heberer [*Oil & Soap* **14,** 15-6] and W. F. Taggart [*16th Ann. Meeting Am. Soybean Assoc.* **1936,** 47-8]; fish oils were fostered by L. J. Reizenstein [*Drug, Oils & Paints* **52,** 328, 330], E. Flood [*Tek. Ukeblad* **82,** 342], H. Powelzik [*Fette u. Seifen* **44,** 254-6], B. Scheifele [*Farben-Ztg.* **42,** 669-70, 694-5] and Ohl [*Allgem. Öel-u. Fett-Ztg.* **34,** 183-9].

R. Erastova and K. Roganova [*Org. Chem. Ind. U.S.S.R.* **3,** 554-7] rechecked the methods proposed in the literature for processing fish oils for use in paints. The method of polymerization and steam distillation according to two German patents [*Ger.* 272,465 & 273,347] yielded the best results. P. V. Serbserbin and A. M. Livshits [*Masloboino Zhirovoe Delo* **13,** 29] reported that dolphin oil could be used in film-forming mixtures when it was mixed with an equal part of linseed oil and heat-treated with cobalt drier. G. R. Henshall [*Can.* 368,-873] improved the fish oil for use in paint by heating with aluminum compounds and tin chloride at 257 to 265°, cooling, adding chromic acid, chromium sulfate, and chromium hydroxide solution and evaporating the water.

Polymerized tobacco seed oil was claimed to give satisfactory results in varnish making according to M. Brambilla and G. Balbi [*Chimica e industria (Italy)* **19,** 373-7]. Castor oil was converted into a drying oil by T.-P. Jen [*Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem.* **3,** 36-9] by distilling in a current of carbon dioxide at temperatures below 315°.

L. A. Mikeska and A. H. Gleason [*U. S.* 2,092,889] prepared drying oils from gasoline boiling up to 400° F. by cooling to —70° F. and bubbling boron fluoride through it for about 15 minutes followed by distilling the product to a temperature of 400° F.

The information on resins which are also used for drying oil economy will be reported in the following division of this review.

PRODUCTS DERIVED FROM FATS AND OILS

Much of the information in this section of the review could be classed among the subjects already reviewed; however, this division contains material on butter, and other products derived from fats, except detergents.

Some Pacific Coast packers have been merchandising lard containing Angostura. According to a report by Allied Research Laboratories [*Natl. Provisioner* **96,** *No.* 6, 27] the effect of this condiment on lard is an enhancement of physical properties and the addition of an agreeable flavor.

Treatments to influence the physical state of plastic fats were invented. Patents assigned to Girdler Corp. [*U. S.* 2,063,065 *and* 2,063,-066] describe chilling apparatus for fats, comprising two refrigerating chambers containing agitators and wall scrapers, and means of flowing the fat from one chamber to the other. Cooling in the second chamber was at a slow rate to obtain desirable physical properties. T. M. Godfrey and V. Serbell [*U. S.* 2,-101,496] chilled shortening until semisolid, aerated it and passed it through a texturizing orifice. In H. A. Keck's modification of this process [*U. S.* 2,101,501] added advantages were claimed by repeating passage through an orifice. "Graininess" in shortening was inhibited by A. W. Ralston and V. Conquest [*U. S.* 2,079,336] with the addition of small quantities of ammonium soaps. T. Hinko [*Öle, Fette, Wachse, Seife, Kosmetik* **1937,** *No.* 6, 6-8] presented notes on compounding high melting fats with oils in order to obtain definite melting range. Better information in this practice was obtainable from the cooling curves of the fats than from the plain melting points.

A comparison by A. W. Harvey [*Ind. Eng. Chem.* **25,** 1171] of the shortening properties of plastic fats indicated a lack of correlation between the relative breaking strength of plain pastry and evaluation by subjective eating tests. He recommended eating tests as a better criterion for evaluating shortenings. A comparison of hydrogenated cottonseed oil shortening and lard for cake baking in like recipes favored the hydrogenated shortening. However, with changes in ratio of cake ingredients and manner of mixing, Dorothy G. Berrigan [*Cereal Chem.* **14,** 525-31] demonstrated that comparable products can be obtained with each.

Modern aspects of butter-making problems such as preparation of pure bacterial cultures, churning, washing, aroma, color and storage were presented by W. Mohr [*Fette u. Seifen* **44,** 375-83]. Notes on the manufacture of butter were prepared by R. W. Brown [*Can. Dairy and Ice Cream J.* **16,** *No.* 4, 21-4, 46-8], D. R. Theophilus [*Proc. 10th Ann. State Coll. Wash. Inst. Dairying* **1937,** 7-11], H. C. Raven [*Proc. 10th Ann. State Coll. Wash. Inst. Dairying* **1937,** 12-13], S. T. Coulter and W. B. Combs [*Minn. Agr. Expt. Sta. Tech. Bull.* **115,** 39 pp.] and J. Keay [*Can. Dairy and Ice Cream J.* **16,** *No.* 8, 25-8, 68]. In these papers sticky butter was associated with products of fall and winter months, churning and over-working at high temperatures. A firm texture was associated with low temperature churning and washing with cold water. The papers emphasize temperature control in all butter operations and adjustments in churning details to produce a uniform grade of butter during all seasons.

There are two different theories of the mechanism involved in the churning of butter. According to one, churning causes a reversal of oil-in-water to a water-in-oil emulsion. The other theory involves aeration or frothing with consequent accumulation of milk proteins at the air-liquid interface with breaking of emulsion. Evidence to support the latter view was developed by W. Clayton and J. F. Morse [*Nature* **139,** 717]. When milk proteins were prevented from accumulating in the froth, where surface denaturation occurs, churning did not yield butter. Tests with special surface-active materials such as saponin and bile salts which are preferentially absorbed in the froth, proved them excellent anti-churning agents. Egg albumen delayed butter formation until surface denaturation of this colloid allowed the accumulation of milk protein at the air-liquid interface.

Discussions on butter flavors centered principally around the acetylmethylcarbinol and diacetyl content of the butter. Tests by W. L. Slatter [*Natl. Butter and Cheese J.* **27,** *No.* 20, 20-4; *No.* 21, 18-26] and W. L. Slatter and B. W. Hammer [*Iowa Ag. Expt. Sta. Res. Bull.* **211,** 42-54] showed that in unsalted butter the amount of the above constituents decreased during the first few days of holding and in some cases the decrease was followed by an increase. The use of citric acid-fermentation streptococci with butter culture appeared to be associated with an increase in diacetyl on holding. The use of salt in butter retarded the production of these flavoring ingredients during holding. C. R. Barnicoat [*J. Dairy Res.* **8,** 15-30] reported that the diacetyl content of butter remained fairly constant during storage at 14° F. for 3½ months. A report on analysis of market butter by C. Brioux and E. Jouis [*Compt. rend.* **205,** 526-8] showed that 76.3 per cent contained amounts of diacetyl ranging from a trace to 0.5 milligrams per kilogram; the remaining samples ranged from 0.51 to 1.5 milligrams per kilogram with one exception which contained 2.5 milligrams. These authors reported considerable decrease in the amount of diacetyl in butter on standing. One sample which contained 1.5 milligrams per kilogram on the day of churning contained only .05 milligrams 26 days later. Methods of developing and incorporating diacetyl in butter and information on the stability of the flavor in butter were presented by W. L. Davis [*Dairy Ind.* **1**, 165-7] and H. A. Ruehe [*Natl. Butter, Cheese J.* **28**, *No.* 4, 20-2].

A butter having certain therapeutic properties was patented by G. Erhard and G. Schaefer [*Ger.* 637,243 *Cl* 30*h* 2]. The product was treated with radium emanations during its production.

A butter substitute prepared by H. D. Wendt [*U. S.* 2,085,134] from milk or cream to which had been added 0.1 to 0.3 per cent citrate salt and a small amount of gelatine was manufactured by centrifuging to a fat concentration of over 65 per cent butter fat.

A new method of emulsification for preparation of margarine was patented by R. C. Newton, W. F. Bollens and L. C. Brown [*U. S.* 2,098,010]. A fine degree of moisture dispersion throughout the fat was obtained by super cooling melted fat with the aqueous liquid and immediately agitating. According to H. Schow [*Brit.* 461,615] the physical characteristics of butter were induced in margarine by improving the dispersion of liquid constituents to the point where the margarine in the molten state at 50° C. has a viscosity at least 15 per cent higher than the viscosity of the original oil-fat mixture.

Biochemical tests on some margarines by S. N. Matsko [*Z. Untersuch. Lebensm* **72**, 76-7, 143-8] indicated that these products were poor in vitamins. Enrichment with carotene extracted from either carrots or sting nettle was recommended. A. A. Scheunert [*Ernahrung* **2**, 45-55] recommended the use of fish liver oils as efficient vitamin A and D supplements to margarine. The addition of vitamins to margarine was incorporated in an Act of Parliament in Denmark [*Am. J. Pub. Health* **27**, 1221]. The product should contain 14 International Units Vitamin A and 0.1 Unit of D per gram. The vitamin A should be in the form of carotin and vitamin A, half the effect being from each.

New patents on processes for preparing emulsions were reviewed by A. Foulon [*Fette u. Seifen* **44**, 435-7]. Methods for emulsifying mayonnaise preparations were investigated by N. I. Kozin *et al* [*Voprosy Pitaniya* **5**, *No.* 6, 3-6; *Masloboino Zhirovoe Delo* **13**, *No.* 3, 28-30]. The chief emulsifying agent recommended was egg yolk powder; this could be supplemented with casein, sour cream, egg albumen, or potato starch.

New patents were issued for the use of polyalcohol esters of fat acids as emulsifiers. One of the original patents by H. Schrader [*U. S.* 1,826,900] was reissued [*U. S. Reissue* 20,361]. The esterification of fat acids and glycerol was carried out in phenol solution in the presence of camphor-B-sulfonic acid by T. P. Hilditch and J. A. Riggs [*U. S.* 2,073,797] in order to yield a product in which mono-glycerides predominated. Several patents on the use of mono- and di-glycerides in the preparation of emulsions were assigned to Procter and Gamble Company [*U. S.* 2,091,886; 2,091,887; *Brit.* 454,566]. L. C. Brown, D. P. Grettie and R. C. Newton [*Brit.* 458,581; 458,582] prepared the mono- and di-glycerides from hydrogenated soybean oils so that the product in addition to having the usual surface activity, would enhance the keeping qualities of the fats with which it was mixed. The method of preparing polyglycerol esters as described in patent issued to The Emulsol Corp. [*Brit.* 452,138] comprised polymerizing glycerol and esterifying the product with fat acids by an alkaline catalyst and heat to 225 to 230° C. A. K. Epstein and B. R. Harris [*U. S.* 2,089,470] patented the use of mixtures of lecithin and mono- and di-glycerides as emulsifiers for margarine. W. Schrauth [*U. S.* 2,086,479] used sulfonated alcohols in combination with mono- and/or di-glycerides for emulsification.

The purification of mono- and diglycerides was the subject of two patents; E. W. Eckey and C. C. Clark [*U. S.* 2,065,520] removed the soap catalyst from the finished product by treatment with strong acids, addition of filter aids—kieselguhr—, evaporation of water and filtering out the coagulated and dried precipitate. R. Furness [*U. S.* 2,071,459] purified the crude product by agitating with aqueous solutions of sodium sulfate to cause the esters containing the free hydroxyl groups to dissolve in the aqueous solution and separating the latter from the undissolved esters.

Other emulsifying processes that were patented are: the use of condensation products of fat acids and alkylolamines by W. Kritchevsky [*U. S.* 2,089,212]; a mixture of agar-agar, gelatin and pectin for water-oil emulsions by H. Preiser [*Ger.* 646,503 *Cl.* 23*c* 2], sapogenin such as ursolic acid, oleanolic acid or betulin by C. E. Sando [*U. S.* 2,076,794], fat alcohols for emulsifying spray oils by W. J. Yates [*U. S.* 2,091,062] and calcium soaps with an aminophenol for lubricating greases by W. P. Hilliker [*U. S.* 2,065,857]. A survey of methods for using oil and fat emulsions in the textile industry for impregnating textiles with drying oils or mineral oils was prepared by A. Foulon [*Allgem. Oel-u. Fett-Ztg.* **34**, 451-3].

Suggestions were made as to the use of certain oils. A. Bourdin [*Fr.* 808,217] prepared a substitute for petroleum jelly from horse fat by crystallization and then centrifuging at 28° C. The product had a melting point of 25° C. For use as ointment base in place of petroleum jelly G. W. Fiero [*J. Am. Pharm. Assoc.* **25**, 862-3] recommended hydrogenated castor oil. The method of using tallow-lard mixtures for extracting volatile oils by enfleurage was described by T. Hinko [*Öle, Fette, Wachse, Seife, Kosmetik* **1937**, *No.* 10, 13-4].

Means of processing castor oil so that it becomes compatible with mineral oils for use as a motor lubricant were described by Y. Kwei [*Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem.* **3**, 77-9] and K. T. Steik [*U. S.* 2,068,088]. Kwei heated the castor oil with aluminum oxide as a catalyst while blowing with carbon dioxide for agitation and prevention of oxidation. Steik heated a mixture of castor oil and naphthenic acid to temperatures above 100° C. The product was soluble in mineral oil and could be used either alone or as a mutual solvent for castor and mineral oil. Mixtures of phosphoric acid esters of castor oil, and vegetable, animal and mineral oils for use in high-pressure lubrication were patented by N. V. de Bataafsche Petroleum Maatschappij [*Ger.* 641,887 *Cl.* 23*c* 1]. The high temperature lubricant patented by I. R. Valentine [*U. S.* 2,088,452] was prepared by heating a mixture of vegetable oil, caustic, and ethyl ether of diethylene glycol to a temperature of about 280° C. and adding a large proportion of mineral lubricating oil. The Standard Oil Development Company [*Fr.*

810,094] and I. G. Farbenindustrie A.-G. [*Brit.* 463,890; 463,932] were assigned patents on preparing mineral-oil-soluble polymerized products of vegetable and animal oils. The first mentioned used sulfur and the other boron fluoride as catalysts for the polymerization. The products increased the viscosity of the mineral oil lubricants to which they were added.

An important contribution to the blending of mineral oil lubricants with vegetable oils was made by A. Balada [*Öle, Fette, Wachse, Seife, Kosmetik* **1937**, *No.* 10, 1-8, *No.* 11, 1-16]. Carbonization tests on the lubricants were of no value, because the values were all small while practical tests in motors gave abundant carbon formation. Parts from motors in which the vegetable oils were used and parts from motors in which only mineral oils were used were illustrated. The vegetable oils caused carbon formation in the explosion chambers, and gum formation and corrosion in other parts. An automobile motor lubricated with mineral oil containing 10 per cent rape oil required general repairing after traveling 10,000 kilometers. No investigation on castor oil was reported by this author.

Formulas for lubricating greases containing fats and metallic soaps were presented by G. Ritter [*Chem.-Ztg.* **61**, 908-10]. J. K. Drysdale [*Brit.* 451,988] thickened oils to a grease consistency by adding 25 to 45 pounds of dehydrated soap to each ton of oil, heating to 295° C. and allowing to cool. C. O. Greenlee [*U. S.* 2,083,015] manufactured grease from lubricating oil and calcium soap by heating the mixture to 230° F., and cooling with agitation while adding water. O. P. Puryear [*U. S.* 2,072,824] prepared a castor oil soap for use in manufacture of lubricating grease. The soap was made mineral oil soluble by heating at about 500° F. until at least 4 per cent was lost by evaporation.

C. J. Boner [*Ind. Eng. Chem.* **29**, 58-60] prepared metallic soaps of 18 metals with two fat acids of different titers and combined each of these under similar conditions with two mineral oils to form greases. Soaps of the metals of lowest atomic weights yielded greases of best transparency; the more basic metals produced the softest greases, and consistency was heaviest and the drop point highest in greases made from the acids of the highest titer. Water was required as an emulsifier only with the calcium and strontiun soaps.

Separation and purification of linoleic and oleic acids was studied by J. B. Brown and coworkers [*J. Am. Chem. Soc.* **59**, 3-6, 6-8]. Crystallization of corn or cottonseed oil fat acids from methyl alcohol, 1 to 1 mixture of ethyl alcohol and petroleum ether, and acetone at —20° C. gave a separation of saturated and unsaturated acids. Fractionation of the unsaturated acids in acetone at —70° C. resulted in a product containing up to 86 per cent linoleic acid. Oleic acid was obtained from the unsaturated portion of the mixed fat acids after removal of the saturated, by crystallizing four times from acetone at —60° and then removing the palmitic acid by crystallization at —35°. H. P. Kaufman and H. E. Mestern [*Ber.* **69B**, 2684-5] separated pure unsaturated acids from mixtures by preparing the bromides, fractionally crystallizing and debrominating. Debromination was accomplished by refluxing one hour in pyridine with pure zinc in a current of indifferent gas. The pyridine was removed with dilute hydrochloric acid, and the product was ether extracted and washed. Synthetic linoleic acid was prepared by C. R. Noller and M. D. Gervin [*J. Am. Chem. Soc.* **59**, 606-8]. First, n — amylvinylcarbinol was prepared from n — amyl magnesium bromide and acrolein and this with phosphorous tribromide was used to prepare a mixture of 1 — bromo-octadecene —2 and 3 bromo-octadecene —1. The mixture of bromides was converted into the Grignard reagent condensed with 8, 9—dibromo—9—methoxynonyl chloride and the bromine and methoxy group removed.

New methods of preparing alcohols from fat acids were sought by several investigators. W. H. McAlister [Oil & Soap **14**, 39-43] obtained products consisting mainly of alcohols with some olefines by electrolyzing with graphite anodes, a soap solution containing inorganic salts and a low molecular weight alcohol. E. I. du Pont de Nemours and Co. [*Fr.* 810,983] and R. J. Rosser and H. Swann [*U. S.* 2,070,318] produced higher alcohols by the action of metallic sodium or other alkali metal on fat acid esters. The latter reacted the materials in xylene solution, the former used an aliphatic ether as the solvent. Methods of producing the higher alcohols from fats and oils by hydrogenation were patented by W. Schrauth and T. Bottler [*U. S. Reissue* 20,447 *of* 2,023,383], W. Normann [*Ger.* 648,510; 639,527 *Cl.* 12o 5.02], W. A. Lazier [*U. S.* 2,094,127; 2,094,611] and Rohm and Haas Co. [*Brit.* 457,358]. The latter used oxides of chromium, manganese, vanadium or molybdenum and an oxide of an alkaline earth metal at temperatures of 190 to 400° C. and pressure of 400 pounds per square inch. Lazier used oxides and chromites of several metals as catalysts with temperatures above 200° and pressures above 10 atmospheres. W. Norman used either finely divided copper or started with copper carbonate as a catalyst.

Higher unsaturated alcohols were also derived from sperm oil. C. O. Henke and R. G. Benner [*U. S.* 2,070,597] and W. Schrauth [*U. S.* 2,075,963] treated the oil with sodium to reduce it to alcohols. Henke and Benner carried on the reaction in presence of an aromatic hydroxy compound and used xylene as an inert solvent. Schrauth used butyl alcohol as a solvent for the reaction mixture.

The higher alcohols are used for the manufacture of wetting agents, in polishing compositions and in cosmetics. New uses for these discovered during the year are as defoaming agents in adhesives patented by Chem. Fab. Stockhausen & Cie and Buch and Landauer A.-G. [*Ger.* 647,324 *Cl.* 22i 2]; as improvers for drying oils per patent of I. G. Farbenindustrie A.-G. [*Ger.* 649,108 *Cl.* 22h 2]; and as coating for medicinal tablets as described by Lucille M. Mills [*J. Am. Pharm. Assoc.* **26**, 479-82].

Many other derivatives were prepared from fats. Several patents did not state definitely the intended use, but gave various general uses such as to prepare other derivatives. Anhydrides of lauric acid and other acids were prepared by H. Gray and T. F. Murray Jr. [*U. S.* 2,087,030] by treating the corresponding chlorides with an aqueous solution of trisodium phosphate at temperatures below 60°. Esters of fat acids and lower monohydric aliphatic alcohols were prepared according to patent of P. Ernst [*Ger.* 642,454 *Cl.* 12o 11] by treating the glycerides with 2 to 3 times the necessary amount of alcohol. Under these conditions the liberated glycerol forms a separate layer and may be withdrawn from the mixture.

Aldehydes were prepared according to patent issued to Armour and Company [*Brit.* 458,391] by reacting fat acids or their esters with formaldehyde vapor in the presence of an oxidising catalyst. The product can be reduced to alcohols or sulfated to produce wetting agents. Ketones were prepared according to other patents assigned to them. [*U. S.* 2,101,559; 2,101,560] by reacting fat acid chlorides with carbazole or substituted carbazoles or thiophenes. These products are waxy solids and may be used in electrical insulation and as polishing or antifoaming compounds.

Methods for the preparation of nitriles from fat acids were given by workers of the Armour and Company Laboratories [*Brit.* 467,043; 467,047; *J. Am. Chem. Soc.* **59**, 986-92]. Nitriles were first prepared from fat acids and ammonia. These were cracked in their vapor phase to produce straight chain hydrocarbons and nitriles of lower molecular weight than the starting materials. According to a later patent to the same group [*U. S.* 2,086,239] these nitrites can be converted to alcohols by preparing the amine and treating it with an alkali metal nitrite. H. F. Oxley and E. B. Thomas [*Brit.* 464,106] prepared fat acid nitriles by heating ammonium salts of the fat acids with a quantity of some of the fat acids in the free state. The nitrile was formed by decomposition of the ammonium salt and was distilled off. Treating the alcohols derived from fat acid, with liquid ammonia in presence of thorium oxide catalyst at high pressure according to Y. Shinozaki and H. Kubo [*J. Agr. Chem. Soc. Japan* **13**, 1-5] yielded amines of high molecular weight. Amides of higher fat acids were prepared by C. O. Henke and W. H. Zartman [*U. S.* 2,058,013] by reacting fats with aliphatic amines in aqueous solution in closed vessels above 100° F.

Coal tar fractions having boiling range of about 432° to 500° C. were reacted with fat acids in the presence of aluminum chloride according to patent issued to A. W. Ralston and C. W. Christensen [*U. S.* 2,077,068]. The products are used as constituents of lubricating oils. The same inventors with G. Josh [OIL & SOAP **14**, 5-7] described a method of killing weeds with products prepared by the action of mercury salts on esters of unsaturated fat acids. A one per cent solution of methyl — 9 — acetoxymercury — 10 — methoxy stearate in kerosene, when sprayed on lawns, destroyed such weeds as dandelions and various other monocotyledonous plants.

According to a patent issued to Continental Oil Company [*Brit.* 459,719] esters of stearic acid and fat alcohols containing two halogen atoms were useful as addition products to hydrocarbon lubricating oils. J. S. Vibar and D. M. Birosel [*Univ. Philippines Natural and Applied Sci. Bull.* 5, 123-8] and E. Q. Yamaguchi and T. Matsushima [*Bull. Waseda Applied Chem. Soc.* 31, 10-3] recorded characteristics of halogenated and dehalogenated oils. Dechlorinated lumbang oil was darker than the untreated oil and its viscosity and index of refraction were greater than those of the chlorinated oil. Estimation of iodine number and chloride content of chlorinated and dechlorinated soy bean oil indicated that 20 per cent polymerization occurs during the processes.

L. Auer [*U. S.* 2,083,550] heated oils at vulcanizing temperatures with sulfur to obtain a product suitable for compounding with latex. The action of sulfur monochloride on fats was investigated by H. P. Kaufmann, J. Baltes, and P. Mardner [*Fette u. Seifen* **44**, 337-40, 390-4]. Vapors of sulfur dioxide on oil films in a vacuum desiccator caused an initial gain in film weight which continued until the weight for each oil became a constant, except for castor oil, which gave no end value for absorption. The amount absorbed was insufficient to account for the unsaturation, which was said to indicate that polymerization renders some of the double bonds inactive. The data presented in the communication should be useful in industries which prepare sulfur monochloride treated oils. General information on the use of sulfur monochloride treated oil in the rubber industry was published by W. Obst [*Allgem. Oel u. Fett-Ztg.* **34**, 175-7].

Recently invented resinous products are allowing more interchange of oils in protective coatings in such a manner as to substitute for expensive drying oils and also to improve the finished products. The economy of the new products and their applications were subjects of communications by F. Zimmer [*Chem.-Ztg.* **61**, 93-6, 115-7] and E. Fonrobert [*Öle, Fette, Wachse, Seife, Kosmetik* **1937**, No. **2**, 11-2]. A review of resin-producing reactions and the physical properties of the resins produced by the reactions was compiled by E. Dreher [*Kunststoffe* **27**, 30-5].

T.-H. Shen and C.-F. Kuo [*Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem.* **3**, 40-51] prepared pentaerythritol, mannitol and phthalic acid derivatives of tung oil. These products were superior to tung oil in alkaline tests and dried more rapidly than the original oil. A paint prepared by W. A. Riddell [*Biol. Board Can. Progress Repts. Pacific Biol. Sta. and Pacific Fisheries Exptl. Sta. No.* 31, 14-5] containing phenolated pilchard oil dissolved in dipentene and cobalt drier, gave protection to submerged wood against marine boring organisms. A lacquer recommended by E. Fonrobert and K. Bruckel [*Fette u. Seifen* **44**, 432-4] for use in tropical countries contained one part phenol resin condensation product, 1.7 parts wood oil, and 1.7 parts linseed oil. The lacquer was especially recommended for withstanding both intense humidity and sun light.

The character of drying of oils and resin formation was investigated by T. F. Bradley and coworkers [*Ind. Eng. Chem.* **29**, 579-84, 1270-6]. With drying acids only, the triglycerides yielded films of the insoluble and infusible type. Polymers prepared from the condensation of glycols and maleic and fumaric acids could be heat treated or oxygen treated to give air drying resins. The products were analogous to certain natural drying oils in molecular structure and effect of polymerization treatment.

Several phthalic acid resin patents were assigned to E. I. du Pont de Nemours & Company [*U. S.* 2,074,782; 2,074,814; 2,086,456; 2,101,227]. These comprised polyhydric alcohol-polybasic acid resins and their reaction products with urea-aldehyde resins and benzoyl peroxide. In the production of polyhydric alcohol-polybasic acid resins invented by I. Rosenblum [*Brit.* 453,228; 457,794; 461,742], ratios of fat acids to polybasic aliphatic acids were specified within certain limits. S. L. M. Saunders [*U. S.* 2,071,312; 2,071,313] prepared a varnish resin by heating a mixture of drying oil, mono-glyceride of a drying oil and phthalic anhydride. A subsequent patent [*U. S.* 2,088,035] included a condensation product of phenol and formaldehyde in the above mixture. C. Ellis [*U. S.* 2,089,196] prepared phthalic acid-nondrying oil resins for use with nitrocellulose in lacquers. H. Hönel [*U. S.* 2,074,509] heated together phthalic anhydride, glycerine, and castor oil for the production of a drying resin. A similar product was prepared by Herbig-Haarhous A. G. [*Brit.* 455,066] by first partly esterifying glycerine with fat acids and then reacting with the polybasic acid. A product prepared by H. A. Bruson [*U. S.* 2,081,266; *Ger.* 637,602; *Cl.* 12*o* 26.02] was produced from castor oil, a fat alcohol and maleic anhydride.

The manufacture of resins from alcohols and polybasic acids was patented by H. L. Bender [*U. S.* 2,064,875], I. G. Farben-industrie A.-G. [*Brit.* 464,276; *Ger.* 647,263; *Cl.* 21*c* 2.15; *Fr.* 806,279]. Another patent issued to the latter [*Fr.* 809,363] was on a resin prepared by the reaction of a urea-formaldehyde resin on a fat acid ester. The Soc. francaise Beckacite [*Fr.* 810,073] in a similar process used a phenol-formaldehyde product instead of urea-formaldehyde resin.

Several reactions were carried out in the varnish oils or other liquid to make a finished coating material. C. Ellis [*U. S.* 2,101,791] heated a polyphenol with tung oil under controlled conditions so as to yield a liquid product. F. B. Root's [*U. S.* 2,082,515] invention dealt with reaction products between a drying oil and formaldehyde. J. B. Rust [*U. S.* 2,069,725] in a similar manner used a resorcinol-acetone resin with the drying oil. J. D. Murray [*U. S.* 2,099,570] combined cellulose esters with drying oils and dissolved the products in a solvent.

E. M. Williams [*U. S.* 2,082,371] prepared a gum which was miscible with oils, by heating and aerating tung oil with large quantities of menhaden oil in the presence of driers.

A fatty oil product suitable for use in nitrocellulose lacquers was prepared by J. S. Long and G. F. Beal [*U. S.* 2,059,260]. The oil was reacted with a phenol in the presence of aluminum chloride and the reaction products were hydrolyzed with weak acids and washed. A tung oil product that is compatible with nitrocellulose was prepared by B. S. Buchmaster [*U. S.* 2,061,829] by heating the oil with sulfur monochloride in a non-oxidizing gas and then passing the inert gas through the product to reduce its sulfur content.

Several fat and oil products were used for moisture proofing textiles and fabrics. The impregnation of the textiles with resinous products derived from fats was patented by I. G. Farbenindustrie A.-G. [*Brit.* 463,300; *Fr.* 809,289] and Bakelite Ltd. [*Brit.* 461,649; 461,650]. Another patent issued to I. G. Farbenindustrie A.-G. [*Brit.* 451,300] describes a method of dispersing fat acid anhydrides with alkylolamines in water for use in waterproofing. L. Auer and P. Stamberger [*U. S.* 2,083,549] partially vulcanized an oil with sulfur and emulsified the product in ammoniacal casein solution to yield a composition suitable for impregnating textiles. The use of fat acid urethanes was patented for the same purpose by I. G. Farbenindustrie A.-G. [*Fr.* 806,944]. A composition suitable for automobile top fabrics, prepared by A. M. Alvarodo [*U. S.* 2,078,921] comprised a mixture of asphalt, wood oil, and an antiwrinkling agent.

Experiments on pyrolysis of fatty oils to hydrocarbons were reported by J. Banzon [*Philippine Agr.* **25,** 817-32], G. Manzella [*Energia ternical* **4,** 92-4], Y.-S. Chao [*J. Chem. Eng. China* **4,** 169-72], F. Michot-Dupont [*Bull. Assoc. Chem.* **54,** 438-48], N. M. Patel and M. S. Patel [*J. Univ. Bombay* **5,** Pt. 2, 114-31], T.-S. Lo and L.-S. Tsai [*J. Chinese Chem. Soc.* **5,** 44-50], E. C. Koo and S.-M. Cheng [*J. Chem. Eng.* (*China*) **3,** 348-53] and M. Friedwald [*Rev. pétrolifère No.* **734,** 597-9]. The papers presented data on the yields of various hydrocarbon fractions from several oils and the method of pyrolysis used. D. Gardner [*Fr.* 801,991] patented the method of manufacture of hydrocarbons from fatty oils by heating in vacuum in the presence of calcium oxide and calcium carbide or calcium silicide. A patent issued to W. Schrauth [*Ger.* 642,590 *Cl.* *23a* 4] concerned the production of hydrocarbons by the hydrogenation of waste fats and separating the product by fractional distillation.

Chrysalis, a waste product of the Chinese silk industry yields about 12 per cent oil on pressing. This oil which was described by S.-C. Chow [*Ind. Research* (*China*) **5,** 475-80] and C.-C. Pan and K.-H. Sun [*Chem. Ind.* (*China*) **11,** No. 2, 1-23] is high in fat acids, impurities and color. It was suggested that the oil be cracked to yield hydrocarbons.

This review will be continued in the May issue.

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

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THE STRUCTURE AND CHEMICAL COMPOSITION OF FATS AND OILS*

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Abstract

This is essentially a general review of progress during the past ten years both in the chemistry of the glycerides of fats and oils and in the chemistry and nature of their constituent fatty acids. Applications of some of the newer research methods are described and discussed.

OVER 120 years ago Chevreul showed that several of the common fats and oils were compounds of fatty acids with glycerol. If this is to be regarded as the beginning of our subject, its further development might be divided for convenience into three periods. During the first of these, from 1815 to about 1900, relatively little of an exact nature was accomplished. This is not intended to imply, of course, that fats and oils were completely neglected scientifically, but rather to point out that fat research during this period was concerned mainly with the generalities of average analytical data. Many of the common fatty acids were discovered. The classic lead soap ether method was first described in 1825. Later two other classic procedures appeared, the saponification number and the iodine number. These two determinations have been of tremendous importance in characterizing fats and oils and in giving us information about their average composition.

During the second period, 1900-1925, we observed a rapidly expanding chemistry of fats and oils. Some attempts were made to actually isolate and identify individual glycerides. Numerous fats and oils were examined, most of them by the accepted proximate methods, and many of them also in an attempt to evaluate quantitatively the composition of their component fatty acids. During this period, too, the chemistry of many of the individual fatty acids was intensively studied; the structures of acids such as oleic, linoleic and lin-

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