Review of Literature on Fats, Oils and Soaps

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Report of the Literature Review Committee

Part II

Deterioration

A comprehensive review of our present knowledge of deterioration in the fat and oil field was presented in a collection of lectures published by the Committee on Food Research of the Office of the Quartermaster General (*Quartermaster Corps Manual 17-7,* 153 pp.). All phases of the deterioration of food fats were treated by various leaders in the field. The subject matter of other review papers were deterioration of flavor of food fats (Robinson and Black—*Ind. Eng. Chem. 37,* 217), oxidative deterioration of fats in cereal products (Triebold—*Oil & Soap 22,* 334), biochemical rancidity (Loury—*Industries corps gras 1,* 14), toxicity of rancid fats (Quackenbush—*Oil & Soap 22,* 336), natural antioxidants of oils (Dubouloz —*Industries corps gras 1,* 68), and a list of antioxidants proposed for the preservation of edible fats (Anon.—*U. S. Dept. Agr., So. Regional Research Lab., AIC-54,* 8 pp.).

Many investigators recommended improvements in the methods of testing for deterioration or evaluating stability of fats and oils. Pool and Prater (*Oil & Soap 22,* 215) standardized the Kreis test procedure so that the color developed could be measured photocolorimetrically. Iselin (*Mitt. Lebensm. Hyg. 35,* 113) cautioned that the fat from tissue intended as the sample for a peroxide test should be maintained under an atmosphere of carbon dioxide during extraction. Stuffins and Weatherall (*Analyst 70,* 403) made the same recommendation for use during determination of the peroxide value. In similar work Lea (*J. Soc. Chem. Ind. 64,* 106) showed that when oxygen was excluded in the Chapman and McFarlane photometric ferric thiocyanate method, the peroxide values were reduced to one-fourth the values from the normal method. A proposed modification of the method, which included the displacement of air with inert gas, gave results 25% those of the normal photometric method. Jasperson *et al.* (*Ibid.* 143) worked on the recently proposed colorimetric tests for oxidation in fats, based on development of a color by α-dicarbonyl compounds. Their spectroscopic observations indicated that the substances responsible for the color developed were not necessarily dicarbonyls.

The work on stability tests characterized, somewhat, the limitations of the tests in current use. According to Nagy *et al.* (*Oil & Soap 22,* 123) the results of the active oxygen stability test on lards containing antioxidants were in most cases unaffected whether the air used was moist or dry. But with ascorbic acid or its derivatives as antioxidants the test showed higher stability in moist than in dry air. In a comparison with storage behavior the results obtained with dry air more reliably predicted the storage life. In similar work Riemenschneider and Speck (*Ibid.* 23) compared storage behavior at 21° with the active oxygen stability test. In many instances there was a general agreement in results, although no constant relationship was found. With the addition of antioxidants the protection indicated by the rapid test was higher than that by actual storage. Riemenschneider *et al.* (*Ibid.* 174) in continuing this work found a fair agreement between the results of the active oxygen, oxygen absorption, and oven test methods. The comparison of antioxidants by means of protection factors was valid only when the same substrate was used. It was interesting to note that McKinney and Jacobson (*Bakers Digest 19,* 97) in a discussion on the active oxygen stability test, recorded the figures 20, 40, 60, and 80 milli-equivalents of peroxide per 100 g. as the respective endpoints in the test for lard, hydrogenated lard, oleo oils, and hydrogenated vegetable fats. These figures were more or less standard in industry but have rarely appeared in widely read journals. Chirgwin (*Oil & Soap 22,* 254) proposed that the endpoint be determined by means of refractive indices. The operation reduces routine manipulation and allows completion of more samples on each apparatus. To

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establish a suitable endpoint a correlation must be made between refractive index and peroxide value for each general type of oil to be tested. Menaker, Shaner, and Triebold (*Ind. Eng. Chem., Anal. Ed. 17,* 518) designed a continuous automatic recording apparatus for testing the fats by the oxygen absorption method. The presence of the operator was not required after the test was started.

Schmidt-Nielsen and Eikeland (*Kgl. Norske Videnskab. Selskab. Forh. 15,* 127) improved the apparatus for the Mackey test, which is used to determine the ignition hazard or stability of oils used in the spinning of textiles. The metal carrier cylinder was replaced with a spiral of lead-free glass, and cellulose wool was used instead of cotton. The improvement depended on elimination of pro-oxidant metals which made many safe oils more susceptible to spontaneous inflammability.

Several investigators recorded observations on rancidifying fats. According to Filer, Mattil, and Longenecker (*Oil & Soap 22,* 196), during the induction period no significant changes occurred; after that time peroxide formation increased appreciably, and linoleic acid, total unsaturation, and the mean length of the carbon chain of the acids decreased. These changes for cottonseed oil and some commercial shortenings, with and without antioxidants, were illustrated graphically. Gunstone and Hilditch (*J. Chem. Soc. 1945,* 836) developed similar information on the autoxidation of methyl oleate, linoleate, and linolenate. The oxidation of the compounds proceeded with increasing rapidity as the temperature was increased. The relative rates of oxidation of the above esters were respectively 1 :12 :about 25.

Holman *et al.* (*J. Am. Chem. Soc. 67,* 1285, 1386, 1390, 1669) prepared a spectrometric characterization of the possible products of fat oxidation. An increase in the absorption at 2750 Å was common to mono-, di-, and tri-unsaturated C_{18} fat acids. Peroxides were not responsible, for their removal did not alter absorption at 2700 Å. An increase of absorption by mono-unsaturated fat acid at 2350 Å was believed to be due to the formation of conjugated dienes. Oxidation of the trienes was also accompanied by decreased absorption at 2600-2800 and increased absorption in the region of 2300 and above 3200 Å. Because the absorption spectra of the acids were not affected by cold alkali, it was postulated that the absorption bands which appeared with autoxidation resulted from oxygen-containing chromophores. The ultraviolet absorption spectra of several ketones, diketones, quinones, and rancid lard were compared. The data suggested that an alcohol-alkali produced color in rancid fats may be due to some extent to compounds derived from unsaturated fat acids which were closely related to compounds obtained by alkali treatment of 5,6-chromanquinone. Dutton and Edwards' (*Ind. Eng. Chem. 37,* 1123) spectrophotometric study of changes in lipids was made on the fat fractions of stored dehydrated eggs. A fluorescing substance that develops in fat of dehydrated eggs during storage was tentatively identified as the reaction product of lipid amines with aldehydes.

Some suggestions were made on the mechanism of some pro-oxidant effects. Ziels and Schmidt (*Oil & Soap 22,* 327) believed that pro-oxidant metals first form metallic soaps. All the metals they tested had a noticeable pro-oxidant effect except aluminum and nickel. In a comprehensive report on palm oil processing by Gruber (*Bull. mat. grasses inst. coloniale Marseille 27,* 175) it was said that chlorophyll was pro-oxidant but this action was hindered by catalase. Carotene was said to absorb two oxygen atoms to change to xanthophyll, which exerts a reducing and stabilizing influence on fats. When an oil is blown with air the carotene adds 12 atoms of oxygen and functions as a transporter of oxygen to fat. In a review on the mechanism of autoxidation of food fat, Täufel (*Fette u. Seifen 50,* 387) suggested that chlorophyll and hemin appear to prevent oxidation at the beginning because of the reducing action of an active hydrogen which was formed.

In a lecture before the American Oil Chemists' Society, Mattill (*Oil & Soap 22,* 1) considerably clarified some of the mechanism of antioxidant action. His suggestions were that (1) with few exceptions the only substances which had primary anti-oxygenic action on fat acids were *o*- and *p*-di- and poly-phenolic compounds or substances having similar electronic configuration, and (2) all other substances which delayed or inhibited the autoxidation of fats should properly be called synergists because they merely reenforce the effect of the phenolic compounds present and have little if any activity apart from them. The activity of the antioxidants was believed to depend upon their oxidation to quinones, whereby hydrogen or electrons or both were released or donated to a fat molecule in the process of being oxidized; the reaction chain being broken at the expense of the oxidation of the more readily oxidizable inhibitor. These views were supported by information from many papers.

Many workers published investigations evaluating antioxidants. On methyl esters as substrates, Stirton *et al.* (*Oil & Soap 22,* 81) found that combinations of citric acid with hydroguaiaretic acid or propyl gallate were the most effective of several compounds tested. Schmidt-Hebbel and Martini (*Anales quim. farm. 1944,* 1) rated 26 antioxidants starting with hydroquinone, pyrogallol, quinhydrone, tannic acid, α-naphthol, guaiac resin, etc., given in descending order of their effectiveness. A similar list prepared from tests on drying oil by Jeu *et al.* (*J. Chinese Chem. Soc. 11,* 25) ran as follows: pyrogallol, *p*-aminophenol, thiourea, catechol, etc. Bucher (*Fishery Market News 7,* No. 7, 17) prepared similar information for the preservation of fish oils. Hydroquinone and α-naphthol were excellent antioxidants. Alkyl gallates had varying protection capacities on different fish oils and were shown some preference because they did not appear toxic to rats. Nair and Ramakrishman (*Current Sci. 13,* 232) preferred using 2 [*o*-(*o*-triacetyl) gallyl] phloroglucinolaldehyde for the preservation of shark-liver oil for they found it more effective than gallic acid. Several other writers preferred special antioxidants for certain products, *i.e.*, nordihydroguaiaretic acid or α-tocopherol was recommended for stabilization of carotene (Bickoff *et al.*—*Oil & Soap 22,* 128), lecithin and soy products were said to be suitable for milled material (Harrel and Brown—*Ibid.* 192), ethyl gallate or ascorbic acid reduced tallowiness in spray dried milk (Findlay and Smith—*J. Dairy Res. 14,* 165), a combination of boric acid and ethyl gallate was recommended for tinned butter (Pont—*J. Council Sci. & Ind. Res. 18,* 53), diacetyl both preserved and improved flavor of mar-

garine (Schmalfuss and Stadie—*Fette u. Seifen 50,* 392) and 3,4-benzopyrene inhibited autoxidation of linoleic and linolenic acids. A dipping process using solutions of antioxidants as the dipping media was suggested as a means of delaying rancidification of bacon (Smith *et al.—Ind. Eng. Chem. 37,* 1206) and fish (Tarr—*Nature 154,* 824; *Prog. Repts., Pacific Coast Stas., No. 64,* 57; Silver—*Food Industries 17,* 1454).

Two papers treated the natural antioxidants in animal tissues. Dubouloz (*Compt. rend. soc. biol. 137,* 457) reported that the unsaponifiable fractions from dog liver, lung, kidney, spleen, nerves, serum, etc., contained substances that inhibited the oxidation of vitamin A. The most concentrated preparation obtained showed maximum ultraviolet absorption at about 270 mμ. Chipault *et al.* (*Arch. Biochem. 8,* 321) determined the concentration of tocopherols of several fats in hogs. The fats of the same hog were quite similar; but the tocopherol contents of the same fats in different hogs varied widely. They believed that the tocopherols were the only appreciable natural inhibitors of oxidation present in normal hogs and that the tocopherols were probably derived solely from the diet.

In recently patented methods for the preservation of fats and oils the following antioxidants were used: 2,3-dimethyl-1,4-bis(3,4-dihydroxyphenol) butane, commonly called nordihydroguaiaretic acid (Lauer—*U. S. 2,373,192*), ascorbyl monoesters of fat acids with or without enhancing compounds such as α-tocopherol, lecithin, or alkalies (Riemenschneider *et al.—U. S. 2,368,435, 2,375,250, 2,383,815-16*), combinations of a compound having an ene-diol group with *p*-aminobenzoic acid, tocopherols, morpholine, and ethanolamines (Norris—*U. S. 2,377,029-31*), hops and a water and an alcohol soluble extract of hops (Lindow and Thompson—*U. S. 2,382,242*), a special halogenated hydrocarbon solvent extract of rice bran (Patterson and Williamson—*U. S. 2,380,546*), salicylal sodium glycinate, salicylal disodium glutamate, salicylal sodium caseinate and like compounds (Downing and Pedersen—*U. S. 2,363,777*), and thiourea (Pedersen —*U. S. 2,373,049*). Some antioxidants were patented especially for rubber, but the patents were broad enough to include their use in fats. These were 6-(*p*-toluidino)-2,2,4-trialkyl 1,2-dihydroquinoline (Paul —*U. S. 2,381,771*), 5-(*p*-toluenesulfonamido)-1-naphthol (Gates—*Can. 423,653*), and a combination of a monomeric 1,3-butadiene hydrocarbon with diamino diphenyl methane (Howland and Paul—*U. S. 2,377,423*). A packaging paper for fatty material contained hydroquinone as an antioxidant (Musher—*U. S. 2,377,359*). A patented method of incorporating gum guaiac into shortening comprised the use of a solution of the gum in partial glycerides of fat acids (Brown—*U. S. 2,377,610*). A steam deodorization in presence of gum guaiac improved the stability character of fats (Phelps and Black—*U. S. 2,374,234*). Treatment of fats with hydrogen rendered active by an electric discharge was said to delay rancidity (Kiefer—*U. S.* 2,347,486). A phenyl-α-naphthylamine and zinc stearate mixture was patented for stabilizing stearate lubricants against oxidation (Morway and Zimmer—*U. S. 2,363,013*). Soap was stabilized against discoloration and rancidity by the presence therein of a biguanide salt of *p*-tertiary amylphenyl phosphoric acid (Cook—*U. S. 2,375,626*), or an alkali metal salt of an organic aminocarboxylic acid containing at least one nitrilodiacetic acid radical (Henderson—*U. S. 2,371,623*).

Attempts were made to prepare an edible shortening from linseed oil. The investigators' aim was to inhibit reversion of the linseed products to a characteristic paint odor and flavor. The attack on the problem by Privett and coworkers (*Oil & Soap 22,* 287) was based on the belief that a derivative of linoleic acid formed during hydrogenation was responsible for the reversion of linseed oil shortening. Their best shortening from the oil was prepared by a polymerization treatment as used in the paint industry, followed by extracting an acetone soluble portion and hydrogenating the extract. The work of Lemon *et al.* (*Can. J. Res. 23F,* 295) on the same problem contained data on the effect of hot and cold pressing, alkali refining, bleaching, hydrogenation at high and low temperatures, blending with other vegetable oils, and use of antioxidants. None of the laboratory or commercially prepared samples examined by the investigators were considered to be satisfactory stable products. Glimm and Nowack (*Fette u. Seifen 50,* 546) believed that the tallowiness of fat was due to a factice type material. Isolation and investigation of the material indicated that oxygen was connected between fat acids to form dioxane rings.

Information on deterioration of fats by enzymes and micro-organisms appeared in very few papers. Olson and Macy (*J. Dairy Sci. 28,* 701) elaborated the effectiveness of propionate treated parchment wrappers for inhibiting mold growth on the surface of butter. A treatment of the parchment with a 5% solution of calcium propionate acidified to a pH of 5.5 with lactic acid was efficient and fully as effective as solutions of higher concentration of the same material. Immersion in water resulted in a loss of effectiveness through leaching of the preservative.

In studies on lipoxidase-oxidized fat by means of the ultraviolet absorption spectra, Holman and Burr (*Arch. Biochem. 7,* 47) observed that the oxidation was similar to the autoxidation of the fats. Another work on enzyme changes in lipids recorded the hydrolysis of phospholipids in cat organs (Fairbairn—*J. Biol. Chem. 157,* 645). The hydrolysis in liver tissue amounted to about 8% in a few minutes; if the liver was ground, hydrolysis increased to about 15%. Suspending the ground tissue in buffer at pH 7.2 for four hours resulted in the hydrolysis of about 40% of the phospholipids.

Biochemistry and Physiology

Past work on evaluation of various fats in nutrition was based on energy value, digestibility, amount and rate of absorption, and content of accessory nutritive essentials, and "unknown factors." The butter versus margarine problem has evolved through the above methods of evaluation into the more pertinent basis of the value of the fats in promoting well-being, growth, and reproduction. A comprehensive review on the subject was prepared by Cowgill (*Physiol. Revs. 25,* 664). Henry *et al.* (*J. Dairy Res. 14,* 45) measured the growth-promoting value of the fats incorporated in liquid skim milk. No differences were observed between butterfat, peanut, cottonseed, or soybean oils. The butterfat was not utilized as well as less saturated oils, but the differences were not

significant. In conclusion, the authors suggested that it was unlikely that butterfat possessed nutritive properties superior to those of other fats and that the saturated fraction of butterfat was certainly not superior in growth-promoting value to that of the more unsaturated fraction or to more unsaturated vegetable oils. The conclusion that the liquid portion of butterfat gave a better growth response also resulted from investigations by Brown and Bloor (*J. Nutr. 29,* 349), and Henderson *et al.* (*Ibid. 30,* 169). In both reports the fat acids of butterfat were fractionated and the fractions were reconstituted into glycerides. Euler *et al.* (*Ernährung 8,* 257) in comparing butter with margarine in diets otherwise nutritionally adequate obtained data slightly favoring butter in one series and favoring margarine in another; however, the differences were not significant. Deuel *et al.* (*J. Nutr. 29,* 237, 309) compared butter and margarine from the standpoint of both growth and reproduction through ten generations of rats. Their conclusion was that a vegetable fat such as that contained in margarine can serve adequately in place of butterfat for reproduction on a diet otherwise nutritionally satisfactory. The comparison by Boutwell *et al.* (*Federation Proc. 4,* 152; *Arch. Biochem. 7,* 143) of fats in combination with the carbohydrates, starch, dextrin, dextri-maltose, sucrose, and mixtures of fructose and glucose showed butter to be superior to corn oil. A diet with a three-fold increase of vitamin B plus liver concentrate to supply an unknown factor was said to give excellent growth with either of the fats. The two fats were comparable when at least half of the carbohydrate was galactose. Zialcita and Mitchell (*J. Nutr. 30,* 147), in work on the effect of fat upon the utilization of galactose, failed to confirm the previously reported influence, but they found that corn oil, not butterfat, decreased the urinary loss of galactose in a diet containing 48% lactose. It was suggested that a nonglyceride constituent of corn oil may be responsible for the effect. In a report on the nutritive value of rapeseed oil products by Beznak *et al.* (*Ernährung 8,* 236) it was said that rapeseed oil margarine permitted weight gains closely approaching those promoted by butter. One commercial rapeseed oil, refined with sulfuric acid, had a toxic action and inhibited growth.

The biological value of fats was tested by Schulte *et al.* (*Ernährung 7,* 305) by refeeding experiments on adult mice which had lost 25% of their weight through underfeeding. The diet contained 10% fat. Animals regained their original weight when the fats used were olive oil, cocoa fat, refined soybean oil, and refined cocoa fat in, respectively, 7, 9, 5, and 13 days. Smaller weight increases were obtained with hardened whale oil, crude soybean oil, and crude and refined sunflower oil.

Two investigators reported favorably on the use of synthetic fats containing saturated acids with odd numbered carbon atom chains. Hock (*Z. ges. exptl. Med. 113,* 245; *Ernährung 6,* 278) found rabbits assimilated fat acids of both even and uneven number of carbon atoms without a clear detectable difference. Kabelitz (*Biochem. Z. 316,* 409; *Pflugers Arch. 247,* 593)from both human and dog experiments noted no effect of natural or synthetic fats on the serum lipase, except when fats were administered in unusually large amounts.

Roy (*Ann. Biochem. Exptl. Med. 4,* 17, 71) prepared data on the effect of thermal treatment and hydrogenation on the absorption of vegetable oils. Heating decreased absorption. Within limits the degree of unsaturation and hydrogenation had no effect. The decreased absorption on thermal treatment was attributed to an increase in viscosity which reduced the activity of emulsifying agents, thereby retarding lipase activity and absorption. The presence in the digestive tract of unsaponifiable matter from normal and heated oils influenced neither rate of hydrolysis of the fat nor its subsequent absorption. Crampton and Mills' (*Can. J. Res. 23E,* 131) tests showed that the nutritive value of hydrogenated fats as measured by the growth of rats decreased as the melting point increased from 45 to 57°. An increase in the fat content of the diet from 4 to 16% resulted in a decline in body weight which was assumed to be due to poor utilization of fat. Killian and Marsh (*Oil & Soap 22,* 250) tested the methods of cooking with fats on gastric evacuation time in human subjects. No significant differences were observed between the action of hydrogenated vegetable fats and butter in potato meals. French fried and lyonnaise potatoes left the stomach as rapidly as boiled potatoes. Excess fat added to potatoes by pan frying to the extent of making the potatoes greasy, prolonged the emptying time beyond the period for boiled potatoes. An investigation on the influence of normal and low-fat diets upon excretion of lipids by Sola (*Rev. asoc. argentina dietol. 2,* 267) revealed no relation between the quantity of lipids ingested and those eliminated or the weight of the dried feces. The results were interpreted to suggest that the lipids excreted were entirely of endogenous origin. Also in connection with fat investigations, it was interesting to note that rats on very high fat diets lost weight (Bergfeld—*Verhandl. deut. Ges. inn. Med. 52,* 412). Other observations on this high fat diet were an increased iodine excretion and a decrease of the iodine content of the thyroid.

The influence of different levels of fat intake on various physiological aspects were reported. Boyd (*Am. J. Diseases Children 67,* 278) found no significant differences in the average rates of progression of caries between two groups of children whose fat ingestion differed by 100%. In work on the influence of fat intake upon milk secretion (Loosli *et al.—Cornell Univ. Agr. Exper. Sta. Memoir 265,* 31 pp.), results indicated that only slightly more milk was produced on feed mixtures containing 4.0% fat than on mixtures containing 2.0%. In presence of corn starch, a low fat grain mixture depressed milk yield; at 5.3% fat in the feed mixture significantly more milk was produced irrespective of the presence or absence of starch. Li *et al.* (*Am. J. Physiol. 145,* 158, 166) reported that rats and dogs on high-fat, low-protein diets were more susceptible to benzene poisoning.

Some communications dealt with the effect of fat in the diet during abnormal conditions. In discussing experimental cancer, Cameron *et al.* (*Can. J. Res. 23E,* 50) pointed out that the information on accelerating skin cancer on mice with high-fat diets cannot be applied to other forms of cancer in mice and other animals. Rusch *et al.* (*Cancer Research 5,* 431) explained this action of fat on the basis of increased caloric intake. MacLachlan and Thacker (*Am. J. Physiol. 143,* 391) recorded that ranges of anoxia in

rats compatible with life did not interfere with absorption of fat. The experiments of Baldwin *et al.* (*Arch. Biochem. 5,* 137) with guinea pigs showed that ascorbic acid deficiency caused no abnormalities in the fat deposited.

Fat deposition and meat quality of chickens were improved by subcutaneous implantation of diethylstilbestrol pellets (Lorenz—*Poultry Sci. 24,* 128).

The parenteral nutrition studies of McKibben *et al.* (*J. Lab. Clin. Med. 30,* 488) showed that oils emulsified with purified phosphatides were most successful. Emulsions prepared with Igepon T, cetylphosphoric acid, or gelatin produced severe or fatal reactions. Baronofsky *et al.* (*Proc. Soc. Exptl. Biol. Med. 59,* 231) associated formation of gastric and/or duodenal erosion or ulcers to fat emboli caused by intravenously ingested fat. In animals sacrificed within one to four days after intravenous injection of fat the incidence of fat emboli in the tissues was lung 91, brain 61, kidney 73.9, and stomach 47.8%. Intra-arterial injection of 3 cc. of 2% croton oil emulsion in equal parts of Ringer's solution and ethanol into a 15-pound dog caused death in 20 hours (Kisch—*Exptl. Med. Surg. 1,* 248). Brown *et al.* (*J. Lab. Clin. Med. 29,* 259) found corn and sesame oils superior to peanut and cottonseed oils as carriers of material for intramuscular injections because they were more quickly absorbed, less antigenic, and less irritating.

Information on intermediary metabolism of fats included a review by Stadie (*Physiol. Revs. 25,* 395). Frazer and coworkers (*Biochem. J. 39,* 122; *J. Physiol. 102,* 24P; *103,* 306, 5P, 6P) recorded new data in support of the partition hypothesis of fat absorption. Observations in the flocculation of emulsions with plasma and lecithinase led to the suggestion that the intestinal emulsion was acid-soap, while that of the chylomicron was, in part at least, phospholipid. A dispersion of fat globules of less than 0.5 μ was necessary for absorption. Even paraffin in this finely emulsified condition was absorbed. *In vitro* experiments over the pH range of 6.0-8.5 showed bile salt emulsions of lipids of fine dispersion were formed only in the combination of bile salts-oleic acid-monoglyceride. *In vitro* and *in vivo* digestion of olive oil with pancreatic lipase produced free fat acids but no free glycerol, thus suggesting that fat acids and mono- or di-glycerides were the only products of lipolysis. With bile salts these formed the effective emulsifying system in the intestine. This partial hydrolysis of glycerides was in accord with the partition hypothesis of fat absorption. It was suggested that lower glycerides may form the basis for the formation of phospholipid at the oil-water interface in the intestinal cell. The better digestibility of mixed glyceride of stearic and oleic acids over that of tristearin and triolein mixtures was interpreted by Mattil and Higgins (*J. Nutr. 29,* 255) as suggesting that either hydrolysis of glycerides or ester interchange precedes absorption.

Studies on metabolism of fats in the liver were considered both on the breakdown and the formation of fat acids. Lehninger (*J. Biol. Chem. 157,* 363; *161,* 437) showed that oxidation of fat acids by liver suspensions could be coupled with a one-step co-oxidation of α-ketoglutarate to succinate; but it was completely independent of such coupled oxidation if adenosine triphosphate was present. This led to the suggestion that the coupled oxidation of other substrates activates fat acid oxidation by providing adenosine triphosphate during the oxidative phosphorylation of adenylic acid. The use of labeled carbon material showed that liver tissue converted butyric acid to ketone bodies mainly by fission into two carbon chains with subsequent recombination (Medes *et al.*—*Ibid. 157,* 35; *158,* 411). Furthermore, labeled acetoacetic acid developed by the condensation of acetic acid indicated that the reaction occurred by coupling of two acetyl groups; 41-45% of the total acetoacetate came from the labeled acetate and the remainder presumably from constituents of the liver. According to Rittenberg and Bloch (*Ibid. 160,* 417) when acetates labeled both with heavy hydrogen and C^{13} were administered to mice both elements appeared in the liver fat acids and cholesterol. This finding was proof that both carbon and hydrogen of acetate were utilized in the synthesis of fats and cholesterol. Hanson (*Ernährung 6,* 273) developed a procedure for the isolation and identification of small amounts of dicarboxylic acids and used it to show that fat acid decomposition by the human organism occurred without appreciable formation of dicarboxylic acids. Annau *et al.* (*Hoppe-Seyler's Z. 279,* 66) recorded the respiratory quotients of surviving rat liver slices in the presence of saturated and unsaturated C_{16} and C_{18} fat acids.

In a search for agents responsible for greater acetylcholine synthesis by frog brain, Torda and Wolff (*Proc. Soc. Biol. Med. 59,* 246) found no modification was obtained by palmitic and stearic acids. Synthesis was increased by butyric, propionic, and caproic acids and decreased by caprylic, capric, lauric, oleic, and linoleic acids.

Many publications on liver and liver diseases dealt with intermediary fat metabolism. Chaikoff and coworkers (*J. Biol. Chem. 158,* 231; *160,* 377, 387, 489) elaborated on the mechanism of action of the antifatty-liver factor of the pancreas. A restoration of plasma choline and prevention of fatty livers in depancreatized dogs maintained on insulin were obtained on administration of small amounts of a certain pancreas extract. The success of methionine for the same purpose was interpreted to support the belief that the antifatty-liver factor of the pancreas was a proteolytic enzyme which liberated bound methionine from dietary protein. Clark *et al.* (*Am. J. Physiol. 144,* 620) confirmed the effect of pancreas extract and methionine and recorded that cystine was inactive. No positive explanation was advanced for the mechanism of the lipotropic action, but it was believed that constituents other than choline, protein, or methionine were involved. The isolation of glycerylphosphorylcholine from beef pancreas by Schmidt *et al.* (*J. Biol. Chem. 161,* 523) should be of interest in connection with plasma choline, since it is associated with the breakdown and synthesis of lecithin, the common carrier of the choline radical. The formation of glycerylphosphorylcholine was believed to be caused by a specific enzyme. In a case report by Browne and Thomas (*Am. J. Digestive Diseases 12,* 250) the Dragstedt lipocaic pancreas extract decreased the size of the liver and restored appetite, weight, and well-being.

Further elaboration on the abnormal deposition of fat in the liver was reported from many laboratories. Wachstein (*Proc. Soc. Exptl. Biol. Med. 59,* 73) in-

tensified the effect of low choline diet by adding 2% cod liver oil. The cod liver oil also caused deposition in the liver of a pigment called ceroid. An investigation of this pathological effect of cod liver oil by Endicott *et al.* (*Ibid. 57,* 330) attributed it to the effect of some constituents present in cod liver oil; several of the common fat acids were not involved. In work by Stetten and Salcedo (*J. Nutr. 29,* 167, 171) the fatty livers of rats on a choline deficient diet were increased markedly as the chain length of the dietary fat acids decreased successively from 18 to 16 to 14 carbon atoms. No severe fatty livers were encountered with fat acids of less than 12 carbon atoms. With ethyl laurate in the diet the rats receiving no choline died from heart failure in three to six days. The prominent part played by the sulfur-containing amino acids, methionine and cystine, stimulated the work of György and Goldblatt (*Science 102,* 451) in which it was found that 0.1% thiouracil was an effective preventive of abnormal livers of dietary origin. Beveridge *et al.* (*J. Biol. Chem. 160,* 505) showed that the lipotropic effect of a diet was determined not only by its content of sulfur-containing amino acids but also by its adequacy in other respects. Some indirect evidence suggested that tyrosin may be involved. A pathological study of the lesions following a choline-deficient diet made by Dutra and McKibben (*J. Lab. Clin. Med. 30,* 301) showed a correlation of morphological changes in the liver with impairment of its function. Kidney and other tissue were not morphologically abnormal. Holman (*J. Exptl. Med. 81,* 399) found that a repeated bleeding of dogs fed a relatively high fat diet resulted in the liver abnormality, whereas bleeding or high fat diet alone produced no changes. Beveridge and Lucas (*J. Biol. Chem. 157,* 311) confirmed in more detail an earlier report that corn oil obliterates the lipotropic action of inositol. Fatty livers resistant to the action of choline were produced by MacFarland and McHenry (*Ibid. 159,* 605) with beef liver extracts in rats maintained on a high carbohydrate fat free diet supplemented with various combinations of vitamins, choline, inositol, and biotin. Jones and Peck (*Arch. Internal Med. 74,* 371) observed that in 581 autopsies on tuberculous patients, fatty livers occurred in 41.9%.

Several papers contained information regarding the amount of choline necessary. Reugamer *et al.* (*Am. J. Physiol. 145,* 23) found 50 mg. of choline per kilo of body weight sufficed for dogs on a high fat ration. Connor *et al.* (*J. Biol. Chem. 159,* 5) in choline balance studies on four subjects found that only 0.53-1.51% of the ingested choline was excreted. In similar work by Luecke and Pearson (*Ibid. 158,* 561) dogs and sheep given excess choline eliminated only 0.7-2.5% of it. The ingestion of additional choline was accompanied by an increase in urinary nitrogen virtually equivalent to the choline nitrogen ingested. Davis and Gross (*Am. J. Physiol. 144,* 444) observed that excess choline fed to human subjects caused a depression of their red blood cell counts during the following 36 hours, succeeded by a subsequent reticulocytosis. A case of choline poisoning in cattle was attributed to feeding wet brewer's grain containing 0.25-0.28% free choline (Bondi and Meyer—*Nature 154,* 551).

Various aspects of fat deposition were investigated. Shorland and coworkers (*J. Agr. Sci. 35,* 33, 39; *Nature 155,* 48) showed that while the diet does affect somewhat the composition of fat deposited, there seemed to be characteristics of each species which could not be significantly altered by diet. They confirmed the presence of C_{20} unsaturated acids in the depot fat of pigs and suggested that these may be of physiological importance or interest. Stewart and Sinclair (*Arch. Biochem. 8,* 7) found that rats on a diet containing 48.4% castor oil deposited fat containing 7% ricinoleic acid. The fact that only 1-2% of the ricinoleic acid absorbed was deposited was evidence that the rats metabolized the hydroxy acid.

The effect of food fat on milk fat of dairy animals was revealed in some researches. Moore *et al.* (*J. Dairy Sci. 28,* 161) depressed the milk fat production of cows and increased the iodine number of the fat by feeding 5-6 ounces of cod liver oil in one feeding each day; when the oil was fed in 12 feedings each day the effects did not occur. Analyses by Hilditch and Jasperson (*J. Soc. Chem. Ind. 64,* 109) on the unsaturated fat acids of milk and grass fats were made in preliminary work on deposition of unsaturated C_{18} acids in milk fat. Kaufmann and Shaw's work (*J. Dairy Sci. 28,* 467) with carbohydrate diets suggested to them that carbohydrates provided the precursors for the synthesis of the lower fat acids of milk fat.

Effect of age on the depot fat was the subject of some work. The iodine value, refractive index, and color of the body fats of laying pullets were materially the same as those of older hens (Buckner *et al.*—*Poultry Sci. 24,* 126). An investigation into the composition of the fat during development of the black shark from ovary eggs to embryo showed considerable alteration of fat which was interpreted as metabolic; new fat and squalene formation occurs during the development of the embryo (Schmidt-Nielsen and Sundsvold—*Kgl. Norske Videnskab, Selskab. Forh. 15,* 157, 169). The lipid changes with growth and age of rats reported by Williams *et al.* (*J. Biol. Chem. 161,* 463, 475) were an increase in cephalin common to all tissues, increase in cerebrosides in testes and skeletal muscle and decrease in cardiac muscle, a decrease in free cholesterol and sphingomyelin in both skeletal and cardiac muscle and an increase in sphingomyelin in kidney, lung, and spleen.

In work on essential fat acids, Jurgens *et al.* (*Helv. Physiol. Pharmacol. Acta 3,* 41) reported that vitamins of the B group could not cure the acrodynia produced in rats on fat free diets.

In the work on fat soluble vitamins many analytical data were developed. In regard to vitamin A in butter, published information showed the potency in various geographical regions, its seasonal variation, and effect of dairy animal feeds (Krauss *et al.*—*Bimonthly Bull., Ohio Agr. Exper. Sta. 30,* 157; Theophilus *et al.*—*Univ. Ida. Agr. Exper. Sta. Circ. 102,* 4 pp.; Bird and Ferguson—*Farm Sci. Reptr. 6,* No. 2, 13; Jenness and Palmer—*J. Dairy Sci. 28,* 473; Herrington—*Farm Res. 11,* No. 4, 1; Lord—*Biochem. J. 39,* 372; Karmakar—*Indian Med. Gaz. 79,* 535; Sarkar and Sen—*Ind. J. Vet. Sci. 13,* No. 3, 219). The content of vitamin A and its seasonal variation was part of the text of most of the publications on fish oils. Some of these references will appear in the charts on characteristics of oils. However, some references contained only data on the

vitamin content (Weeber—*Biochem. J. 39,* 264; Pugsley *et al.—Can. J. Res. 23F,* 243). In two other analytical reports, one showed that the distribution of vitamin A in various sections of fish livers may vary as much as 25% (Bucher *et al.—Fishery Market News 7,* No. 1, 6); the other recorded that 95% of the vitamin in fish liver oils and distilled concentrates was present as esters. The vitamin A contents of 32 samples of palm oil were also recorded (Poe and Fehlmann—*Food Research 9,* 500). Deuel *et al.* (*Arch. Biochem. 7,* 247) determined the activity of various forms of carotene.

New suggestions were made in regard to analytical methods for vitamin A. Callison and Orent-Keiles (*Ind. Eng. Chem., Anal. Ed. 17,* 378) proposed that pure β-carotene be used as a standard for both biological and spectrophotometric methods. Kreider (*Ibid.* 694) recommended 2-phenylazo-*p*-cresol as a photometric standard. Work on effect of light on the Carr-Price color in the determination of vitamin A led to issuing the precaution of employing low incident light to reduce fading of the blue color (Caldwell and Parrish—*J. Biol. Chem. 158,* 181). Sobel and Werbin (*Ibid. 159,* 681) proposed 1,3-dichlorohydrin as a color reagent to replace antimony trichloride. The color developed by the new reagent was more stable and permitted absorption measurement with ease. Some analysts modified current methods by a chromatographic step which separated the active material from nonactive pigments (Wilkie and de Witt—*J. Assoc. Official Agr. Chem. 28,* 174; Heimann—*Z. Untersuch. Lebensm. 85,* 502; Cooley *et al.* —*Ind. Eng. Chem., Anal. Ed. 17,* 689). Methods of sampling (Bucher *et al.—Fishery Market News 7,* No. 1, 2) and calculating (Sanford—*Ibid.* 6) for use in vitamin A determination in fish livers were issued.

Some observations were recorded on metabolism of vitamins A and D. The toxic effect of excess vitamin A was attributed to an acceleration of metabolism to the point where it caused diarrhea (Wheeler—*Nature 156,* 238). The lower utilization of carotene in foods as compared with carotene in oil was believed to result from the protection of the carotene by oil from the action of destructive enzymes. In two communications on utilization of carotene, the authors believed that utilization depended respectively on tocopherol content (Rao—*Ibid.* 234) and phosphatide content (Slanetz and Scharf—*J. Nutr. 30,* 239) of the diet. Supplementing of mothers' diets with fish liver oil during pregnancy for the purpose of fortifying human milk with vitamin D for infants was considered impractical (Poleskin *et al.—Ibid.* 451).

Information on the tocopherols with vitamin E activity and their physiological effect indicated that their role in nutrition was not yet well defined. Menschik (*Edinburgh Med. J. 51,* 486) observed that rats do not deposit fat on vitamin E deficient diets.

Milhorat and Bartels (*Science 101,* 93) reported that dystrophic animals have a physiological defect which hinders utilization of tocopherol, and that the monoether of inositol and tocopherol was effective in the dystrophic patient. Hove and Harris (*Federation Proc. 4,* 156) increased the effectiveness of methyl linoleate in curing essential fat acid deficiency by supplementing the rations with tocopherols. Dam and Granados (*Science 102,* 327) attributed a color effect on dental tissues to vitamin E and essential fat acids. Highly unsaturated fat acids in absence of vitamin E were believed to act on the dental enamel organ in such a way as to inhibit the deposition of the normal iron-containing layer, resulting in a white appearance of the enamel surface. Willman *et al.* (*J. Animal Sci. 4,* 128) attributed a "stiff-lamb" disease to lack of vitamin E. Levin (*Am. J. Digestive Diseases 12,* 20) reviewed the asserted scientific claims for wheat germ oil and vitamin E preparations and came to the conclusion that discrepancies in observations may be due to differences in types of vitamin E concentrates used. Fisher (*Ind. Eng. Chem., Anal. Ed. 17,* 224) developed a method for determining β- and α-tocopherol in vegetable oils and recorded results on several oils.

Another subject of interest to physiologists was the effect of fat-derived surface active agents on the animal organism. It has already been reported in past reviews that ingested alkyl sulfonates stimulate production of mucus and inactivate pepsin. Block *et al.* (*Gastroenterology 3,* 45) reported that the enzyme effect was abolished *in vivo,* possibly by lipids. Freeman *et al.* (*Ibid 4,* 332), *in vitro* studies, showed that the effects of alkyl aryl sulfonates were not of sufficient magnitude to influence growth or reproduction. In human subjects daily ingestion of 100 mg. for four months produced no change in cellular composition and hemoglobin of the blood nor any demonstrable effect on the kidney function. According to Bischoff (*Am. J. Physiol. 145,* 123) subcutaneous injections of sodium lauryl sulfate produced an edematous area which could be used in delaying resorption of gonadotropins. Insulin under the conditions was partially destroyed.

Characteristics and Composition

Data on characteristics and composition of fats and oils appeared in communications on various subjects. The literature on new oils, processing, deterioration, biochemistry, etc., contained such new data. In most cases where the reference was included in another section it is not repeated in this one. References containing information suitable for tabulation are found in the charts appended to this section. A report by Adriaens (*Bull. Agr. congr. Congo Belge 34,* 3) contained descriptive information of the oil plants and the oils of Belgian Congo but was only available in short abstract form. Brief reviews on processing grape-seed oils containing data on composition were prepared by Rubio (*Farm. nueva 8,* 15, 68, 141, 211) and Flanzy and Reingpach (*Ann. agron. 13,* 60). The Oil Characteristics Committee of the American Oil Chemists' Society (Lauro—*Oil & Soap 22,* 160) recorded standard values for constants of neatsfoot oil, beef tallow, North American lard, babassu palm-kernel oil, Patua palm oil, and Chinese vegetable tallow.

A review of the effects of environment, evolution, maturity stage, length of growing period, and vegetative vigor upon vegetable oil production and oil composition was compiled by McNair (*Botan. Rev. 11,* 1). In selection of rapeseed for production of oil for lubricant manufacture, André and Charles (*Compt. rend. 215,* 587) found the varieties with the largest seeds best. These seeds were richest in oil and the oil had the lowest iodine value. Anderson and Aitken's (*Can. Grain Res. Lab., Winnipeg, Ann. Rept. 18,* 36) analyses showed that the oil content, iodine value, and acid value of sprouted rapeseeds were no greater than

CHARACTERISTICS OF FATS AND OILS REPORTED DURING 1945

Oil or Fat Source	% Oil or Fat	Specific Gravity	Refr. Index	Acid No. or (% free fat-acids)	Sapon. No.	Iodine No.	(SCN) No.	Acetyl No. or ([OH] No.)	R-M No.	Polenske No.	% Unsapon.	Melting Point	Solidification Point	Hexabromide No.
Anda-acu seeds[1]	48	$0.9231^{15.5}$	1.471^{40}	(0.85)	181-3	133.8					0.97			
Buttonweed seed[2]														
Abutilon theophrasti	16-18	0.9227^{25}	1.4730^{25}	(3.41)	193.17	130.7		6.8			1.36			
Cattail seed[3]														
Typha latifolia	17.9		$1.4730^{29.5}$	30.7	186.0	141.6	79.8	10.8			2.52			
Corn-embryo[5]														
from Bulgaria		$0.9237^{20/4}$	1.4748^{20}	12.0	189.6	133.3	75.95	(15.4)			1.2			
from Argentina		$0.9192^{20/4}$	1.4720^{20}	16.6	196.6	109.5	71.20	(10.5)			0.83			
Crab-liver[6]		0.908-0.920[28]	1.485[28]		178-192	90-115						17-19	9-11	
Fish:														
Jacopever[7]														
Sebastichthys capensis														
Liver					177.5	128.0					9.50			
Head					188.4	160.9					1.51			
Body					187.5	156.4					3.30			
Intestines					188.0	145.1					1.86			
Kingklip liver[8]														
Genypterus capensis	30-40				175-200	134-163					1.99-3.46			
Shark liver[9]														
Scoliodon sorra	50	0.9187^{59}	1.466^{52}	0.9	190.9	93.3						36	21	
Stockfish liver[10]														
Merluccius capensis	24.5-33.8				186.1	163.6					2.78			
Tere[11]														
Terre pastenaque		0.9201^{15}		1.28	145									
Garampara nuts[12]	26-30	0.9068^{30}	1.4615^{40}	(13.68)	185.7	72.14		10.42	0.22	0.28	0.93			
Hip seed kernels[14]	9.4	$0.8884^{78/4}$	1.4628^{70}			187		(4.7)	0.8	0.4				
Linden wood[15]	6.7-11.2			64.6	237	64.7	66.3	(84.8)	5.4	2.6	4.3			
Mappia foetida seed[16]	48	0.9319^{27}	1.4781^{27}	3.7	185.4	45.6		5.77	0.68	0.41	0.81			
Milkweed seed[22]														
Asclepias syriaca	22	0.9221^{25}	1.4730^{25}	11.0	191.9	122.8		12.9	0.2	0.0	2.53			0.0
Mimusops elangi seed kernel[23]	25.1			12.74	192.0	80.4-83.6					1.6			
Molinillo seed[24]														
Leonotis nepetaefolia	28.0	0.8984^{25}	1.4673^{20}	11.20	191.2	82.53		4.87	0.29	0.15	3.09			
Niger seed[26]			1.4738^{20}	(0.65)	288.5	140.8								
Ocimum canum seeds[27]		0.9206^{30}	1.4707^{40}	72.2	194.5	179.8		32.1	0.6	0.3	1.25			
Palm kernel (*Eloeis guineensis*)[28]														
from the testa	40.2			(7.7)	229	31.2					0.6			
from the white kernel	53.3			(2.4)	246	12.5					0.2			
Pine-bark[29]		0.9775^{20}	1.4879^{20}	17.8	174.87	123.23		40.55	4.15	0.40	11.92			
Puma (American lion)[30]														
Felix concolor				3.6	173	38.8					1.3	40-45		
Safflower (grown in U.S.A.)[31]	31.5-33.8		1.4749-1.4752^{25}	(0.37-1.82)		147.2-149.8	85.2-86.7				0.5			
Stillingia seed[26]														
Stillingia sebifera		0.9383^{20}	1.4802^{20}	1.82)	188.1	187.8	109.0							
Sudan Mimosoideae seed (7 varieties tested)[32]	2.74-7.89		1.4668-1.4691[40]		185.8-188.6	74.8-102.5	57.3-69.6				2.52-3.86			
Sunflower (grown in U.S.A.)[31]	27.5-30.8		1.4723-1.4738^{25}	0.34-0.97		122.4-136.6	78.4-81.3				0.8			
Tobacco seed[34]	35.1-43.4		1.4738-1.4743^{25}	(0.14-3.76)		139.5-145.9	78.3-81.6							
Wheat germ[35]		0.9268^{25}	1.4737^{30}	8.25	184.0	128.6	82.0				4.04			6.6

FAT ACID COMPOSITION

Oil or Fat Source	Common Saturated Acids			Common Unsaturated Acids			Other Fat Acids
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Buttonweed seed[2] *Abutilon theophrasti*	trace	12.2	0.9	14.1	58.0	trace	C_{16} (−2H) 0.6, C_{18+7} 9.4
Corn[4]	0.1	8.1	2.5	30.1	56.3		C_{16} (−2H) 1.2, C_{18+7} 1.7
Fish:							
Jacopever[7] *Sebastichthys capensis*							
Liver	1.2	11.6	3.9	—(−2.3H)46.3—			C_{20-22} 0.4, C_{14} (−2H) 0.6, C_{16} (−2H) 13.5, C_{20} (−6.3H) 12.7, C_{22} (−8.7H) 7.5, C_{24} (−?H) 2.4
Head	2.6	16.3	2.1	—(−3H)30.3—			C_{20-22} 0.8, C_{14} (−2H) 0.9, C_{16} (−2H) 11.8, C_{20} (−6.8H) 18.8, C_{22} (−9.6H) 15.5
Body	2.6	13.8	1.8	—(−2.4H)28.5—			C_{20-22} 0.2, C_{14} (−2H) 2.3, C_{16} (−2H) 12.4, C_{20} (−7.0H) 21.6, C_{22} (−9.5H) 16.8
Intestines	3.0	14.4	2.2	—(−2.5H)30.6—			C_{20-22} 0.1, C_{14} (−2H) 1.9, C_{16} (−2H) 13.1, C_{20} (−6.9H) 19.7, C_{22} (−9.2H) 12.3, C_{24} (−?H) 2.6
Stockfish liver[10] *Merluccius capensis*	1.4	17.9	1.9	—(−3.3H)32.6—			C_{20-22} 0.5, C_{14} (−2H) 0.4, C_{16} (−2H) 11.8, C_{20}(−7.1H) 18.3, C_{22}(−9H) 12.0, C_{24} (−?H) 2.3
Guinea pig body[13]	5.3	19.4	5.7	36.2	18.8	1.2	C_{12} 1.1, C_{14} (−2H) 0.8, C_{16} (−2H) 2.1, C_{20}(−8H) 2.4, C_{20-22} (−?H) 7.0
Menhaden[15]	6.8	15.5	3.1	15.7	3.6	1.9	C_{14} (−2H) 0.1, C_{16} (−2H) 14.1, C_{16} (−6H) 0.8, C_{18} (−8H) 2.5, C_{20} (−?H) 17.5, C_{22} (−?H) 10.8, C_{24} (−?H) 4.0, C_{26} (−?H) 1.2, C_{26+} (−?H) 2.4
Milk							
Cow[19]	14.65	30.05	10.45	18.69	2.12		C_4 3.52, C_6 1.40, C_8 1.68, C_{10} 2.67, C_{12} 4.54, C_{20} 1.68, C_{10} (−?H) 0.25, C_{12} (−?H) 0.15, C_{14} (−?H) 1.48, C_{16} (−?H) 5.69, C_{20} (−?H) 0.98
Ewe[20]	9.7	23.9	12.6	26.3	5.2		C_4 2.8, C_6 2.6, C_8 2.2, C_{10} 4.8, C_{12} 3.9, C_{20} 1.1, C_{10} (−2H) 0.1, C_{12} (−2H) 0.1, C_{14} (−2H) 0.6, C_{16} (−2H) 2.2, C_{20-22} (−?H) 1.9
Goat[20]	12.3	27.9	6.0	21.1	3.6		C_4 3.0, C_6 2.5, C_8 2.8, C_{10} 10.0, C_{12} 6.0, C_{20} 0.6, C_{10} (−2H) 0.3, C_{12} (−2H) 0.3, C_{14} (−2H) 0.8, C_{16} (−2H)2.6, C_{20-22} (−?H) 0.2
Human[21]		23.6	7.4	33.2	7.1		C_{14} and lower 18.8, C_{16} and lower (−2H) 6.5, C_{20-22} (−?H) 3.4
Mare[20]	7.0	16.1	2.9	18.7	7.6	16.1	C_4 0.4, C_6 0.9, C_8 2.6, C_{10} 5.5, C_{12} 5.6, C_{20} 0.3, C_{10} (−2H) 0.9, C_{12} (−2H) 1.0, C_{14} (−2H) 1.8, C_{16} (−2H) 7.5, C_{20-22} (−?H) 5.1
Molinillo seed[24] *Leonotis nepetaefolia*	1.36	12.57	1.26	67.55	12.39		
Mowrah[25]		19.5	22.5	46.1	11.9		
Niam seed[17] *Lophira alata*		23.2	0.32	8.3	31.5		C_{20} 4.8, C_{22} 4.9, C_{24} 6.9, C_{16} (−2H) 11.7, C_{20} (−2H) 2.1, C_{22} (−2H) 5.6, unsapon. 7.5
Palm kernel (*Elocis guineensis*)[28] from the testa	15.4	12.6	5.5	21.6	5.6		C_{10} 1.0, C_{12} 35.0, C_{20} 3.3
from the white kernel	16.5	7.6	1.7	11.3	1.3		C_8 4.3, C_{10} 4.8, C_{12} 51.3, C_{20} 0.6, C_{16} (−2H) 0.6
Puma (American lion)[30] *Felix concolor*	1.3	22.4	26.9	26.2	2.3		C_{20} 3.7, C_{16} (−2H) 12.6, C_{20} (−?H) 4.6
Tall oil[33]	—— 7 ——			45	48		

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35 S. B. Radlove. *Ibid.* 183.

those encountered in normal samples. In work to determine the importance of bushel weight as a factor in grading sunflower seeds, Sallans *et al.* (*Can. J. Research 23F,* 91) correlated the weight data with percent of oil and nitrogen in seeds, and iodine value, acid value, and index of refraction of the oil. They recommended the weights per bushel of 30, 26, and 22 pounds, respectively, for the first three grades so as to establish appropriate price spreads between the grades.

Several suggestions have been made to improve the accuracy of oil seed analysis. To reduce error in the moisture determination of peanuts due to loss during grinding, two determinations should be made, the first on whole and a second on the ground peanuts (Hoffpauir—*Oil & Soap 22,* 283). In two communications on sampling of soybeans for analysis, increases in size of samples were recommended (Milner *et al.*—*Ibid.* 141; Krober *et al.*—*Ibid.* 194). Work by Collins and Krober (*Ibid.* 307) on the American Oil Chemists' Society method for determining the oil content of soybeans indicated that a finer initial grind of the beans would make unnecessary the regrind after the first extraction. Manley and Wood (*Analyst 70,* 173) encouraged the use of the Bolton apparatus to replace the Soxhlet because the former was more rapid and just as accurate.

Several methods for fat determination were designed for analysis of specific material or class of material. According to Grossfeld and Hess (*Z. Untersuch. Lebensm. 85,* 497) a preliminary hydrochloric acid decomposition was required to completely extract the fat from nutrient yeast. For various foodstuffs, Terrier (*Mitt. Lebensm. Hyg. 35,* 33) extracted repeatedly with alcohol, then repeatedly with ether; the combined solvents were evaporated and the residue was again extracted with ether. The results were slightly higher than those in which an acid treatment was used. In the application of this method to caramels, Terrier and Berner (*Ibid.* 37) broke up the refrigerated samples, heated them with a small amount of water, mixed them with kieselguhr and anhydrous sodium carbonate and extracted. McKee *et al.* (*Fishery Market News 6,* No. 11, 6) issued sampling procedures for fish livers as they are landed at ports.

An American Dairy Science Association committee (Hansen *et al.*—*J. Dairy Sci. 28,* 325) after investigating methods for determination of fat in buttermilk, skim milk, and whey, recommended the three methods commonly known in the industry as the American Association, the Minnesota, and the Pennsylvania methods. A special alkaline butyrometer reagent for the estimation of fat in milk, prepared by Ram and Kothavalla (*Indian J. Vet. Sci. 13,* No. 2, 133) was designed so that need for centrifuging the samples was eliminated. An investigation of the effect of temperature on the accuracy of the Babcock test by Jenness and Herreid (*J. Dairy Sci. 28,* 591) showed that 53.5° for the fatty material fulfills the density conditions under which the bottles are calibrated. Oesting and Kaufman (*Ind. Eng. Chem., Anal. Ed. 17,* 125) applied the Babcock procedure to the determination of fat in meat for control of manufacturing operations.

A method for the determination of neutral fat in a mixture of fat and free fat acids was based on removing the latter chromatographically on alumina (Sylvester *et al.*—*Analyst 70,* 295). Robinson (*J. S. African Chem. Inst. 27,* 19) determined the free fat acids in dark-colored oils by extracting the oils with alcohol and titrating the oil-free alcohol extract. Dubrisay and Goeffroy (*Lait 22,* 209) proposed surface tension measurements by the falling-drop method of benzene solutions into dilute sodium carbonate as a means of determining small amounts of free fat acids in oils and fats.

A method for the determination of monoglycerides in fats and oils depended on an oxidation with periodic acid in which one molecule of periodic acid reacts with one molecule of monoglyceride (Pohle *et al.*—*Oil & Soap 22,* 115). Di- and tri-glycerides were not oxidized by periodic acid under the conditions of the test.

Latest collaborative work on the refining test for grading soybean oils did not result in development of a single method that was applicable to all types of extracted soybean oils (Mitchell *et al.*—*Oil & Soap 22,* 34, 156; King—*Ibid.* 35; Freyer—*Ibid.* 36; Sorenson —*Ibid.* 37). However, the procedures which showed promise were described. Similar work on a bleach test was in progress (Freyer—*Ibid.* 13, 22, 153). The effect of aging of expeller and extracted soybeans on the bleach response by the most recent testing methods was the latest contribution of this group.

New information on testing fats by physical methods has been reported. A new melting point method was based on the temperature at which a disk of fat fused to a glass plate left the plate (Gorchoff—*Soap, Perfumery Cosmetics 18,* 289). The heat transfer medium was a bath containing a solution of calcium chloride. Copley (*J. Am. Pharm. Assoc. 34,* 165) found the U.S.P. method for melting point satisfactory for lard, wool fat, beeswax, and mutton suet, but unsuitable for cacao butter.

The heat capacity data on almost completely hydrogenated cottonseed oil by Oliver and Bailey (*Oil & Soap 22,* 39) was a recent contribution in a series of papers on heat capacities of various cottonseed oils. The information should be of service for the design of heating, cooling, and other processing equipment; and it also characterized the polymorphic nature of oils. Another contribution from this laboratory (Bailey *et al.*—*Ibid.* 10) contained the melting points and x-ray diffraction patterns for cottonseed oil, hydrogenated to an iodine value of one, and tristearin. Four polymorphic forms of hydrogenated cottonseed oil were determined. The x-ray pattern of the lowest form was similar to that of tristearin, but the pattern of the highest melting forms of the oil differed from either tristearin or β-palmito-distearin, the major component of the oil. Similar information on trilaurin, trimyristin, tripalmitin, and tristearin was published by Lutton (*J. Am. Chem. Soc. 67,* 524). Suggestions were made for the association of the x-ray patterns with melting points and the various polymorphic forms. Similar correlations were also determined by Filer *et al.* (*Ibid.* 2085). Similar data on unsaturated glycerides using thermometric measurements only were developed by Daubert and Clarke (*Oil & Soap 22,* 113). No evidence of polymorphism was found in a series of 2-monoglycerides of the even carbon, C_{10}-C_{18}, saturated acids.

Bailey and Singleton (*Oil & Soap 22,* 265, 295), in continuation of earlier work, have prepared new dilatometric curves for a number of pure triglycerides

and commercial fats. A general correspondence was found between expansibilities and specific heats and a close correspondence between the heats of fusion and melting dilations. The dilatometric method was preferred to calorimetric means for determining the composition of fats in terms of liquid and solid phases. The character of solid particles, in addition to the amount, influenced the consistency of the fat; this influence was evident from measurements by a micropenetration method. Frost's (*Fisheries Res. Board Can. Progress Repts. Pacific Stas. No. 63,* 43) dilatometric study of fish oils, principally fish liver oils, was for the purpose of developing a formula to calculate the amount of oil in tanks at inspection temperature.

Several other physical measurements interested fat investigators. An apparatus for analytical control of hydrogenation by Harrington *et al.* (*Oil & Soap 22,* 29) depended on the increase in viscosity during crystallization by cooling for the characterization of the oil. It was considered more efficient than iodine number, congeal point, or Wiley melting point. Volarovich and Stepanenko (*J. Exptl. Theoret. Phys. U.S.S.R. 14,* 313) recorded the dipole moments of linoleic and oleic acids in dioxane solutions of 0 to 1.0 molar concentrations. Ultrasonic velocity data in some vegetable oils were determined by Pancholy *et al.* (*J. Sci. & Ind. Research, India 3,* 111) in order to study the effect of chain length, esterification, viscosity, unsaturation, and addition of heavy atoms to the molecule.

Work on characterizing fats by chemical means included modifying and comparing standard methods and developing new ones. The rapid Hanus method of Norris and Buswell for determination of iodine value was made applicable to castor oil by a preliminary acetylation of the sample (Rosenbusch and Parker—*J. Soc. Chem. Ind. 64,* 211). Tests on stability of Wijs iodine value solution by Child (*Ind. Eng. Chem., Anal. Ed. 17,* 530) indicated that the solution could be kept for 10 months. The solution lost about 1% of its strength per month. Leitao (*Arquiv. inst. biol. exercito, Rio de Janeiro 5,* No. 5, 99)reviewed the six most well known methods of determining iodine value of oils. Platon and Olsson (*Medd. Statens Mejeriförsök No. 8,* 31 pp.) compared the refractive indices and iodine values of Swedish butters with a view of developing data for calculating the iodine value from refractive indices. Very good correlations were obtained. A new characteristic for oils, the oxidation iodine value, was a measure of the oxidation that took place between the fat or oil and sodium dichromate under certain standard conditions (Dji-Bin Hu *et al.*—*J. Chinese Chem. Soc. 10,* 30). Values of over 200, 100-200, and less than 100 were said, respectively, to characterize drying, semidrying, and nondrying oils. Modification in the thiocyanogen reagent and method, of vigorous purification of the individual components, replacement of 25% of the volume of acetic acid with an equal volume of carbon tetrachloride, and the use of finely divided potassium iodide made possible its application to all types of fats and oils (Lambou and Dollear—*Oil & Soap 22,* 226). An American Oil Chemists' Society committee (Mehlenbacher—*Ibid.* 101; *Ind. Eng. Chem., Anal. Ed. 17,* 336) did collaborative work with slight modifications of the standard method in an effort to gain improvements. Aenlle and Pineda (*Ion 5,* 257) designed a bromine absorption procedure for determining the polyunsaturated acids and the total unsaturation of the oil or fat. A new method for determining conjugated unsaturated compounds depended on the intensity of a red color developed by reaction of the oil with tetranitromethane (Kaufmann and Kirsch—*Fette u. Seifen 50,* 314). A new index for evaluating drying oils was a function expressing the relationship between increase in molecular weight to the decrease in iodine value during bodying (Gordon *et al.*—*Am. Paint J. 29,* No. 29, 46). The methods for determining the hydroxyl value by Ogg *et al.* (*Ind. Eng. Chem., Anal. Ed. 17,* 394) included a macroprocedure in which an internal indicator was used, a potentiometric method for colored solutions, and a semimicromethod. Carriere (*Industrial corps gras 1,* 76) did comparative work on the determination of molecular weight, iodine, thiocyanogen, and diene values of blown oils. His conclusion confirmed work published in years past by other investigators.

The literature displayed an increasing activity in the use of the spectrophotometer for the analysis of fats. For this purpose Rusoff *et al.* (*Oil & Soap 22,* 290; *J. Am. Chem. Soc. 67,* 673) tabulated the spectroscopic data on fats, fat acids, and their esters. The effects shown by isomerization, esterification, and number and position of double bonds were given. Brice *et al.* (*J. Optical Soc. Am. 35,* 532; *Oil & Soap 22,* 219) contributed similar data, details for analysis, and established the presence of highly unsaturated conjugated and unconjugated compounds in lards, tallow, and highly purified esters and acids. Tall oil fat acids contained approximately 10% of conjugated diene acids and a small amount of linolenic acid. Hilditch and Riley (*Analyst 70,* 68) developed spectrophotometric technic for determination of linoleic, linolenic, and eleostearic acids and applied the method to the analysis of sunflower seed, niger seed, linseed, and tung oils. Riemenschneider *et al.* (*Oil & Soap 22,* 120) found that the spectrometric determination of linoleic acid in tobacco seed oil gave results 3-5.4% higher than those of the thiocyanometric method. Front and Daubert (*J. Am. Chem. Soc. 67,* 1509) found the method more reliable than the iodine determination for the purity of cholesteryl linoleate appraised in terms of the linoleic acid content. Daubert *et al.* (*Oil & Soap 22,* 180, 299) confirmed the accuracy of the method with the estimation of linoleic and linolenic acid content in synthetic glycerides. Spectroscopic evidence was also obtained to indicate that a double bond acid which resists conjugation on alkali isomerization was produced on partial hydrogenation of methyl linoleate. In work on determination of α-eleostearic acid in freshly extracted tung oil, O'Connor *et al.* (*Ind. Eng. Chem., Anal. Ed. 17,* 467) emphasized that the spectrometric procedure was more direct, simpler, considerably more rapid, and more accurate than chemical means. A spectrophotometric method of differentiating between lard and hydrogenated vegetable oils depended on the presence in lard of a well defined maximum at 3010 and 3160 Å. (Beadle *et al.*—*Oil & Soap 22,* 50).

Many contributions elaborated on methods for determining the composition of fats. Norris and Terry (*Oil & Soap 22,* 41) prepared a description of the distillation equipment and method for this purpose. Baldwin and Longenecker (*Ibid.* 151) tested ester fractionation methods in conjunction with spectro-

photometric determination of the polyunsaturated acids in the fractions from known mixtures and found that the results agreed well with the original composition. Smith and Brown (*Ibid.* 321) analyzed menhaden oil by separating the methyl esters of the acids into saturated, monounsaturated, and polyunsaturated fractions by crystallization from acetone and determining the characteristics of the fractions. Jack and Henderson (*J. Dairy Sci. 28,* 65) used the above procedure for the analysis of milk fat. Hilditch and Riley (*J. Soc. Chem. Ind. 64,* 204) considered the method preferable to lead salt separation. They coupled the method with subsequent esterfractionation and applied it to sunflower seed, sesame, and peanut oils.

Data useful in crystallization technic were the solidification curves of binary mixtures of the C_8 and C_{10} and the C_{10} to C_{34} series of fat acids (Schuette *et al.—Oil & Soap 22,* 107, 238). These curves were a continuation of previous work and complete the data for C_8 to C_{34} fat acids. Other work on binary mixtures of fat acids showed that the solubilities of the acids in organic solvents were directly dependent on the melting point (Ralston and Hoerr—*J. Org. Chem. 10,* 170). The solubilities of the mixtures were between those of the pure compounds. An investigation into the solubility relationship of stearic-palmitic acid mixtures in propane near its critical temperature demonstrated that this means could not give a separation of the two acids (Drew and Hixson—*Trans Am. Inst. Chem. Engr. 40,* 675). Ekwall and Juup (*The Svedberg, Mem. Vol. 1944,* 104) titrated the sodium salts of mixed fat acids potentiometrically with silver nitrate. Definite breaks in the titration curve permitted independent titration of the fat acids if their molecular weight differed by more than two CH_2 groups. Walker (*J. Oil Colour Chem. Assoc. 28,* 119) segregated linseed oil glycerides chromatographically into fractions containing, respectively, seven, six, five, and four double bonds. Kaufmann and Wolf's (*Fette u. Seifen 50,* 519) most recent chromatographic work on fats was the separation of tributyrin from tristearin, and the separation of cis-trans isomers of oleic and erucic acids. Partial glycerides were found adsorbed in the descending order of mono-, di-, and tri.

A very small amount of interest was displayed in ascertaining the glyceride structures in oils. Fish *et al.* (*Oil & Soap 22,* 317) reported liquid-liquid fractionation of coconut oil was unsuccessful. There was some separation, but all fractions contained at least six of the acids present. In analytical work by Venkatarao *et al.* (*J. Indian Chem. Soc. 21,* 249) the composition of tobacco-seed oil was recorded in the form of its original glycerides. Meara (*J. Chem. Soc. 1945,* 22) studied the configuration of glycerides in various fats. In monooleodistearin and in monopalmito di-unsaturated glycerides the mono acid of each was found in the β-position.

Miscellaneous data which should be useful for the analysis of fats were the physical data on synthetic triacid triglycerides (Chen and Daubert—*J. Am. Chem. Soc. 67,* 1256), on mixed synthetic glycerides (Singh—*J. Sci. & Ind. Res. India 2,* 223), and on synthetic monoglycerides (Baer and Fischer—*J. Am. Chem. Soc. 67,* 2031).

Several new uncommon fat acids were recorded during the year. Some C_{20} unsaturated acids were found in pig back fat (DeLaMare and Shorland—*Nature 155,* 48; *Biochem. J. 39,* 246). A sterculic acid from sterculia oil reacted with halogens and thiocyanogen solutions but did not absorb hydrogen on hydrogenation (Steger and van Loon—*Fette u. Seifen 50,* 305). A trienoic C_{16} fat acid was isolated from rape-leaf glycerides (Shorland—*Nature 156,* 269). A new isomer of linolenic acid was found in the seed oil of *Lappula echinata,* Gilb. (Esafov *et al.—J. Applied Chem. U.S.S.R. 18,* 175). Hydnocarpic and chaulmoogric acids were isolated from the oil of *Hydnocarpus wightianna* and their characteristics were recorded Buu-Hoï *et al.*—*Compt. rend. 212,* 577). The branched chain acids, phthioic and mycocerosic, were obtained from the lipids of tubercle bacilli (Ginger and Anderson—*J. Biol. Chem. 157,* 203). Tetracosanoic acid was isolated from carnauba wax (Koonce and Brown—*Oil & Soap 22,* 217). Weitkamp (*J. Am. Chem. Soc. 67,* 447) isolated and identified 32 of the acidic constituents of degras. These included nine C_{10}-C_{26} normal fat acids, two optically active 2-hydroxy acids, C_{14} and C_{16}, ten C_{10}-C_{28} iso-acids and 11 dextrorotatory anteiso acids of C_9-C_{27} and C_{31} chain lengths.

In work on the unsaponifiable of oils, Kirsten (*J. Assoc. Official Agr. Chem. 28,* 289) reported that the standard British method for the determination consistently yielded slightly higher results than the American method. Analyses on shark and skate liver oils by Kini (*J. Indian Chem. Soc., Ind. News Ed. 7,* 32) yielded a maximum value of 26.4% unsaponifiable for Indian oils, whereas Japanese sharks contained up to 90.2%. A variation in glycerol yield from dogfish liver oil, noted by Swain and Morton (*J. Fisheries Research Board Can. 6,* 326) was found inversely related to the content of unsaponifiable which ranged from 7.6 to 34.3%.

The analytical procedures for purity of oils or the detection of adulteration dealt with several oils. The purity of olive was determined by a color produced on addition of trichloracetic acid liquefied with 8% water (Gerona—*Mon. farm. 50,* 363). A gray film developing at the point of contact indicated refined olive oil; a bluish or greenish film indicated pure oil, and a red or violet tone indicated adulteration with residue oil. A method for detecting adulteration of olive oil with cottonseed oil was based on the iodine value of the liquid fat acids—Lutz—*Anais assoc. quim. Brasil 2,* 147). Two methods for detection of olive oil in edible oil mixtures depended on the squalene content (Philippe and Henzi—*Mitt. Lebensm. Hyg. 35,* 94; Fitelson—*J. Assoc. Official Agr. Chem. 28,* 282). According to O'Connor *et al.* (*Oil & Soap 22,* 257) gross adulteration of cottonseed and peanut oils with one another could be detected by a spectrometric estimation of the linoleic acid content. Various investigators used the Bellier test to determine the relative amounts of two oils in a mixture; these mixtures were peanut and cottonseed oils (Riggs and Kirsten—*J. Assoc. Official Agr. Chem. 28,* 293), sesame and peanut oils (Desai and Patel—*Current Sci. 14,* 37), sesame and niger seed oils (Desai and Patel—*Ibid.* 130), and peanut oil with each of the following oils: gingelly, coconut, safflower, niger seed, and mustard seed (Narayanaier—*Ibid.* 177). A technic for assessing the quality of cod oils used for currying and chamoising in the leather industry depended on the physical

properties of the free fat acids (Burton and Robertshaw—*J. Intern. Soc. Leather Trades' Chem. 29,* 28).

Detergents

Practically the only activity on saponifiable stock dealt with the use of rosin in soap. The aim of several investigators was to process the rosin so that it would not oxidize and darken the soap. Van Zile and Borglin (*Oil & Soap 22,* 331) pointed out that this can be accomplished by hydrogenating the rosin. A patented process by Bried (*U. S. 2,383,289*) comprised condensing the rosin with an aldehyde and hydrogenating the condensation product. Another patented process comprised reacting the rosin with *p*-toluenesulfonic acid in the presence of acetic acid (Campbell—*U. S. 2,373,290*). Goday (*Afinidad 20,* 17) issued instructions on soap making with rosin and oil from olive residues. Clayton (*U. S. 2,390,990*) introduced rosin in the form of tall oil into soap stock and refined the mixture by a centrifugal process.

Hirsch (*U. S. 2,391,019*) prepared soap from hydrocarbons by oxidation with alkali persalts, followed by saponification with alkali. Synthetic fat acid soaps were rendered odorless by the presence of a small quantity of an aldehyde, or reducing or oxidizing agents (Henkel & Cie. G.m.b.H. — *Belg. 447,475, 447,483*).

New developments in the mechanics of soap making appeared almost exclusively in the patent literature. Several of the patents were on continuous systems. Trent (*U. S. 2,383,630-1*) devised equipment for continuous saponification of fat acid esters of a lower alkyl monohydric alcohol. Ross (*U. S. 2,381,368*) extruded anhydrous soap in the form of threads into cooled kerosene or other cooling liquids. This method of cooling avoided decomposition and discoloration. Ittner (*U. S. 2,377,424*) produced floating soap in a continuous process by mixing the soap with gas just previous to the cooling step. Jacobs (*U. S. 2,380,650*) improved his continuous anhydrous soap process by standardizing the amount of solvent and the temperature so that when the saponified mass was sprayed the glycerol and diluent evaporated instantaneously. The continuous soap making patents assigned to the Sharples Corp. (*U. S. 2,369,257, 2,369,372; Brit. 559,076*) dealt with reduction of alkali in soap nigre by adding coconut oil acids; the purifying of soap nigre by adding water and centrifuging. The centrifuge used in the soap making forced the soap through a patented exhaust.

Some innovations were suggested in batch soap making processes. Bissinger (*U. S. 2,356,443*) made soap by mixing oil with powdered alkali in the presence of sufficient moisture to cause an exothermic reaction to take place; the soap formed as an intermediate layer. An anhydrous soap manufacturing method by Auer (*U. S. 2,382,530-1*) comprised heating the fats or tall oil with anhydrous sodium carbonate until saponification was complete. Houpt (*U. S. 2,366,334*) made soap from tall oil by anhydrous saponification in organic solvent. The amount of caustic added was just sufficient to neutralize the fat acids. The soap formed in the process precipitated. A floating character was imparted to soap by Kelley (*U. S. 2,371,175*) by boiling soap containing an acid with sodium carbonate; the liberated carbon dioxide formed buoyant cells in the soap.

Several suggestions were made on cooling and molding soaps. The addition of anhydrous sodium sulfate just previous to the cooling of soap aided in the solidification because the sulfate regained its water of crystallization (Savonnerie Couvreur S.P.R.L.—*Belg. 447,840*). Soap chips were converted to granulated soap by addition of water to form a paste. While warm, this was treated with heavy rollers in a vessel till it solidified and was then granulated (Joyce and Linkhardt—*U. S. 2,382,063*). A new apparatus to cool soap into slabs or blocks contained rectangular water-cooled metal cells placed alternately in multiple arrangement with molding frames (Hackett—*U. S. 2,385,134*). New equipment for casting soap in stick form was designed (Walter—*U. S. 2,385,322*). A soap cake forming process, that permitted controlled shrinkage, comprised forming a specially shaped bar which was trimmed after surface cooling (Pease—*U. S. 2,373,593*). The trimming was designed to form localized areas of weakness whereby the shrinkage on cooling was controlled. A new cutting and spacing device for soap bars was also invented (Pease—*U. S. 2,367,310*). A patent on a spray powdered soap process dealt with optimum temperature, pressure, and moisture conditions of operation (Mosher — *U. S. 2,376,499*).

In patented filled soap mixtures the fillers or builders used were special borates (Snell—*U. S. 2,376,096; Brit. 561,294,* clay, plaster, or kieselguhr (I. G. Farbenind. A.-G.—*Belg. 446,970*), and cellulose derived from the hydrolysis of wood and other cellulose derivatives (Phrix-Arbeitsgemeinschaft — *Belg. 446,801;* Soc. anon. Alliance Européenne — *Belg. 446,052;* Schubert — *Belg. 444,156*). Descriptions of processing kaolin for soap making included information for the following methods: elutriating including electrophoresis, buddle processing, flotation, and centrifugal processing (Gerth—*Fette u. Seifen 50,* 324).

Nonsoap detergents, such as the sulfonated fats and fat alcohols, etc., were also prepared in combination with fillers, builders, soap and other material. The admixed materials in these were soap (Safrin—*U. S. 2,388,767*), hydrolyzed proteins (Rust and Spialter—*U. S. 2,373,602-3*), cellulose derivatives (Mehne—*Belg. 446,629;* Backhaus—*Ger. 739,033 Cl. 8i*), glycerol and monoglycerides of the fat acids of coconut oil (Colgate *et al*—*Can. 426,102*), and various inorganic builders (Zellwolle- u. Kunstseide-Ring G.m.b.H. —*Belg. 447,464;* Franklin—*Brit. 559,137;* Hicks and Saunders—*Can. 428,410;* Quimby—*U. S. 2,383,502;* Vitalis—*U. S. 2,373,863*).

Special mixtures of inorganic salts were made for use as soap substitutes (Henkel & Cie. G.m.b.H.—*Belg. 444,304, 445,500; Ger. 744,994 Cl. 18i;* Soc. anon. Savonneries P. Ney—*Belg. 444,310;* van Rumbecke — *Belg. 448,142;* Spiegler — *U. S. 2,367,971;* Meites—*U. S. 2,385,928-9*). Another fat-free detergent was an alkali-pectin preparation (Fischer—*Ger. 739,694 Cl. 8i*).

Many special detergents were patented. The hand cleaning compositions were: mixtures of inorganic soap builders, glycerol, soap, and nonsoap detergents (Morgan and Lowe—*U. S. 2,379,851, 2,383,610*); a paste of water, soap, and bagasse ashes (Compain—*U. S. 2,373,460*); a solution containing *o*-dichlorobenzene, ethylene glycol monobutyl ether, glycol, monoethanolamine oleate, and water (DeVilliers — *U. S. 2,383,114*); and soap interposed between a pair of

sheets of easily disintegrating paper (Muise—*U. S. 2,389,736*). Powdered household cleansers were improved by the addition of calcium silicate to prevent caking (Gunther — *U. S. 2,385,075; Can. 424,535*). Cleansers containing bleaching agents were rendered stable for storage by adding a small amount of oxime of an *o*-hydroxy aromatic aldehyde (Imp. Chem. Industries, Ltd. — *Brit. 555,998*). One metal cleaner contained soap, tar acids, alcohol, sodium dichromate, and water (Gregg—*U. S. 2,386,789*). Another comprised a mixture of coal tar oil, monoethanolamine, oleic acid, ethylene glycol, *o*-toduidine, ethyl silicate, and phosphoric acid (Bowman and Packer—*U. S. 2,356,747*). Some detergents for cleaning tin were special mixtures of inorganic soap builders and zinc sulfate (Schwartz—*U. S. 2,359,587, 2,391,647*). A cleaner for glass contained 2-methyl-2,4-pentane diol and an alkyl sulfonate detergent (Gangloff—*2,386,106*). An investigation of the efficiency of 36 dishwashing compounds showed that the better compounds contained at least 20% phosphorus pentoxide, 30-45 alkali (sodium oxide), eight silicon dioxide, and more than 20 carbon dioxide (Hughes and Bernstein—*Ind. Eng. Chem. 37,* 170). A scrubbing block contained magnesite, clay, magnesium chloride, wood excelsior, and soap (Luse—*U. S. 2,372,838*). Patented detergent briquettes were made from special mixtures of inorganic soap builders (MacMahon—*U. S. 2,382,163-5*). In a review on germicidal soap the use of derivatives of biphenyl, diphenyl sulfide, and diphenylmethane to impart germicidal properties to soaps was emphasized (Gump—*Soap Sanit. Chemicals 21,* No. 3, 36; No. 4, 50).

In a review on surface active agents by Paice (*J. Oil & Colour Chem. Assoc. 27,* 189) applications in textile, fur, tanning, paint, adhesive, rubber, and electroplating industries were mentioned. Some new uses were patented. Among the ingredients of a rubber mold lubricant were turkey red oil and soap (Jones—*U. S. 2,388,153*). A dedusting composition for coal contained hydroscopic salt and a detergent to act as a wetting agent (Miller—*U. S. 2,371,344*). A bar type polishing mixture contained a wax and resin blend mixed with soap and water (Cartwright—*U. S. 2,374,414*). A bating composition for hides and skins comprised an enzymatic agent and sulfonated fat alcohol (Schmitt — *U. S. 2,369,256*). Steigmann (*J. Soc. Chem. Ind. 64,* 88) described methods of using cation wetting agents in making spot test paper for analytical chemistry.

Sisley (*Industries corps gras 1,* 7) reviewed the cation active compounds used in the textile industry. His proposed classification of these contained a division of fat derivatives with 11 subdivisions and a division of non-fat derivatives with six subdivisions.

Physical studies were reported both on crystalline soaps and on soap solutions. Vold and Vold (*J. Phys. Chem. 49,* 32) and Vold (*Ibid.* 315) continued to develop data on the transition points of alkali soaps by a colorimetric method supplemented by dilatometric and microscopic observations. The palmitates of lithium, sodium, potassium, rubidium, and cesium underwent three to six transitions. The smaller number of transitions in some soaps were assumed to be caused by more than one structural change occurring at one temperature. Analogous transitions and transformations among these soaps were pointed out. The work on transitions occurring in sodium stearate was done with great care to obtain consistent results for the transition temperatures of the five phases. Vold and Lyon (*Ind. Eng. Chem. 37,* 497) first applied phase rule studies to commercial soaps. Most soaps appeared to undergo transitions at 43-46° and 63-66°, irrespective of water content or soap stock, contrary to all the published phase diagrams for aqueous soap systems. Several samples also showed transitions at about 52°. Buerger *et al.* (*Proc. Natl. Acad. Sci. U. S. 31,* 226; *J. Phys. Chem. 49,* 417) studied the crystalline forms of soaps by x-ray diffraction analysis. They distinguished seven distinct phases in the examination of the pure sodium soaps of caproic, lauric, myristic, palmitic, stearic, and oleic acids. Explanations were postulated for some disagreeing results of other workers. A phase map for a commercial soap was presented to support the contention that more than three phases exist in the product.

X-ray diffraction studies on potassium laurate solutions by Hughes *et al.* (*J. Chem. Phys. 13,* 131) were to determine the micelle structure and the results were used to interpret some of the mechanisms occurring during polymerization of styrene in soap solution. In this process styrene additions increased a long spacing; on polymerization, the spacing decreased to almost its original value. The micelles then dispersed more styrene, continuing their role in emulsion polymerization. A communication by Dervichian (*Compt. rend. 217,* 299) contained an effort to reconcile the points of view of McBain, Hartley, and Stauff on micelles in soap solutions. It was believed that the properties of the solutions could be accounted for on the basis of a single type of micelle. Snell *et al.* (*Soap Sanit. Chemicals 21,* No. 3, 42) studied micelle formation in the presence of alkali by conductance analysis. Above a relatively low concentration of sodium hydroxide the conductance of a caustic-soap solution was less than that of sodium hydroxide alone at that concentration. It was suggested that decreased ionization and increased micelle formation appeared at lower concentrations of the alkali followed by a sorption at the higher concentrations.

Details of a small number of analytical procedures for soap products were published. A new cutting-wire plastometer suitable for control work in soap making was designed by Lyon and Vold (*Ind. Eng. Chem., Anal. Ed. 17,* 585). The collaborative work of the American Oil Chemists' Society Committee (*Oil & Soap 22,* 62) on analysis of soaps containing synthetic detergents showed satisfactory agreement. Parisot (*Inst. tech. études et recherches corps gras 1944,* 16 pp.) proposed a scheme for complete analysis of soap which may contain various organic and inorganic fillers, and nonsoap detergents in addition to normal soap. According to the outline of the scheme the use of selective solvents was depended upon to yield original separations to which common methods could be applied. Wolff (*Industries corps gras 1,* 36) demonstrated several applications to soap of analytical procedures in which titrations were made in alcohol. In the development of the methods the turning point of many indicators and the neutralization point of acids, bases, and salts used in the soap industry were first determined potentiometrically. A volumetric method for the fat acids in soap was much more rapid than common methods. The soap was dissolved in alcohol treated with excess standard alcoholic solu-

tion of hydrochloric acid and back titrated with alcoholic potassium hydroxide. The amount of fat acids was calculated from the amount of standard alkali required in the titration between the two color changes of thymol blue. The application of volumetric methods of this type to a cosmetic cream containing free fat acid, soap, and triethanolamine was also described. Better and Davidsohn (*Oil & Soap 22,* 325) showed that the Lea method for evaluating the oxidative deterioration of oils could be applied to soap. Blank (*Ibid.* 189) reported tests on the accuracy and precision of the analytical procedures of the American Oil Chemists' Society. Precision and reproducibility improved with the experience of the analyst, rising to a maximum after about one year's experience. The tabulated data from this work should be of interest as a record of the variations in results that occur on the analysis of various components.

Some analytical procedures dealt exclusively with nonsoap detergents. A method by DuBose and Holland (*Am. Dyestuff Reptr. 34,* 321) for determining organically combined sulfuric anhydride in such products depended on extraction with ether from a saturated salt solution, oxidation with perchloric and nitric acids, and precipitation with barium chloride. A method for determining small quantities of sulfonated or sulfated surface active compounds, by Jones (*J. Assoc. Official Agr. Chem. 28,* 398), depended on matching the color formed in the samples with methylene blue against similarly treated standards. Ashton and Stead (*Metallurgia 32,* 53) recommended surface tension measurements to approximate the wetting agent concentration of copper plating solutions.

Comparative evaluations of detergents were based on cleansing, wetting, and water softening action. Heron (*Textile Mfr. 71,* 253) used a modified Rhodes-Brainard washing test to evaluate the washing action of several soaps and commercial nonsoap detergents. Harris and Brown (*Oil & Soap 22,* 3) and Harris (*Rayon Textile Monthly 26,* 77, 142) rated the efficiences of soap builders when used with the commercial detergent, Santomerse. The Launder-o-meter was used as the test equipment and washing was done in synthetic sea water. The wetting properties of sodium lauro-*p*-toluide-3-sulfonate and derivatives of alkoxyanilines and *o*-alkylanilines were evaluated using the Herbig and Congo-Rubin numbers, the Draves test, and the calcium soap dispersing power (Tilak *et al.* —*J. Indian Chem. Soc., Ind. News Ed. 7,* No. 1, 24; *J. Sci. Ind. Research (India) 3,* 193, 290). In general the compounds derived from lauric acid were better wetting agents than those from oleic acid. Melikhov and Tutunov (*Legkaya Prom. 4,* No. 3, 23) determined wetting power by the height of rise on a cotton fabric of a colored aqueous solution of the detergent. Data on several detergents were given. McDonald (*Soap Sanit. Chemicals 21,* No. 12, 41) using foam and cleaning tests compared soaps containing synthetic detergents in hard water. Capacity to foam was not an indication of the cleaning efficiencies of these soaps. The comparison of soaps by Ruff (*Oil & Soap 22,* 125) was based on their water-softening characteristics. Rosin soap was least efficient in water where calcium hardness predominated. Conversely, fat acid soaps were most efficient in calcium hardness and least effective in magnesium hardness water. Matheson (*Chemist Analyst 34,* 63) proposed preparation of a standard hard water for testing soaps. Two communications on dishwashing sanitation were reviews on laboratory technic of evaluating cleaning agents by determining residual bacterial contamination (DuBois—*Soap Sanit. Chemicals 21,* No. 1, 25; No. 2, 42).

There also were miscellaneous characterizations of surface active compounds. Contributions on bactericidal efficiencies were prepared by Flett (*Oil & Soap 22,* 245), Fair *et al.* (*Am. J. Pub. Health 35,* 228), Hoogerheide (*J. Bact. 49,* 277), and Huyck (*J. Am. Pharm. Assoc. 34,* 5). The hemolytic action of detergents was compared with their antibacterial power (Gonzales and Madeiros—*Rev. med. y alimentacion Chile 5,* 232) and with their adsorption by charcoal (Cavier—*Compt. rend. 216,* 255). Some elaboration was made on the structure of compounds formed on denaturation of proteins by synthetic detergents (Bull—*J. Am. Chem. Soc. 67,* 10; Putnam and Neurath—*J. Biol. Chem. 159,* 195; *160,* 397). Balansard and Pelissier (*Compt. rend. soc. biol. 138,* 395) reported that lauryl alcohol sulfate in concentrations of 1:100-1:5000 was toxic to wheat while concentrations of 1:10000-1:100000 accelerated germination.

Many papers on soaps provided information on common practices in the industry or described some of the products. These are most conveniently entered in this review with a mention of the subject treated:

Methods and products: New developments, Davidsohn and Davidsohn—*Ind. Chemist 21,* 414. Plant layout, Thomssen—*Soap Sanit. Chemicals 21,* No. 11, 29. Theoretical aspects of soap manufacture, Davidsohn—*Am. Perfumer 47,* No. 5, 52. U. S. A. wartime soap, Thomssen—*Soap, Perfumery Cosmetics 18,* 564. Toilet soap, Webb—*Ibid. 17,* 830. Shaving soaps, Thomssen—*Drug Cosmetic Ind. 56,* 174. Liquid soap, Boyle—*Mfg. Chemist 15,* 88. Filtration of liquid soap, Kufferath—*Fette u. Seifen 50,* 292. Spray drying, Reavell — *Soap, Perfumery Cosmetics 17,* 816. Spent lye purification, Wigner—*Ibid. 18,* 143.

Raw materials: Substitutes for fats, Stetsenko —*Pishchevaya Prom. 1,* No. 3, 19. Fats from hydrocarbons, Rosendahl — *Z. kompr. flüss. Gase 38,* 25; Wittka—*Seifensieder-Ztg., Allgem. Öl- u. Fett-Ztg. 1943,* 50, 68. Fat acids, Stingley—*Soap Sanit. Chemicals 21,* No. 2, 63. Rosin, Lombard—*Industries corps gras 1,* 72. Wood pulp by-products, Keilen—*Soap Sanit. Chemicals 21,* No. 3, 40; Edwards — *Soap, Perfumery Cosmetics 17,* 667. Lanolin for superfatting, Lesser — *Soap Sanit. Chemicals 21,* No. 4, 41. Water softeners, Lesser—*Ibid.* No. 11, 32.

Properties: Chemical and physical theories of cleaning, Sanders — *Iron Age 155,* No. 15, 62; Dubrisay — *Compt. rend, acad. agr. France 27,* 746; Tomlinson—*Mfg. Chemist 15,* 159; Widaly—*Seifensieder-Ztg. 1944,* 1. Solvent properties of detergent solutions, Tomlinson—*Mfg. Chemist 15,* 198. Toilet soap irritation, Lesser — *Soap Sanit. Chemicals 21,* No. 5, 25.

Nonsoap detergents: Sulfonated peanut oil, Gallent—*Am. Dyestuff Reptr. 33,* 148. Products for textiles, Rey — *Industries corps gras 1,* 45; Borghetty—*Textile Res. J. 15,* 316. New products, Wallersteiner — *Soap, Perfumery Cosmetics 18,*

538. Amine salts of petroleum by-products, Profft —*Petroleum Refiner 23,* 502.

Special cleaners: For hands, Lesser — *Soap Sanit. Chemicals 21,* No. 3, 33. For glass, Lesser— *Ibid.* No. 1, 28; Liddiard—*Chem. Age (London) 51,* 317, 341. For paint and wallpaper, Lesser— *Soap Sanit. Chemicals 21,* No. 12, 37. Abrasives, Lesser—*Ibid.* No. 6, 44. For metals, Harris—*Am. Soc. Testing Materials Bull. 133,* 23; Harris— *Aluminum and Magnesium 1,* No. 7, 28.

Uses: Fatliquoring of leather with nonsoap detergents, Koppenhoefer—*J. Am. Leather Chem. Assoc. 40,* 277; Anon.—*Leather Trades Rev. 78,* 325. Soap in insecticides, Leffingwell and Lesser— *Pests 13,* No. 8, 10.

The patents on nonsoap organic detergents and methods for their manufacture are listed with only partial classification. Most of them are derivatives of fats; those which are not made from the products and by-products of the coal and petroleum industries.

Those patents on compounds that contained sulfur such as the sulfonates, sulfates, and sulfinic acid salts were:

Alien Property Custodian—*U. S. 2,369,612, 2,378,551, 2,383,859.*
Allied Chem. & Dye Corp. — *U. S. 2,347,336, 2,390,295.*
Am. Cyanamid Co.—*U. S. 2,379,535.*
Arkansas Co., Inc.—*U. S. 2,371,284.*
Buffalo Electro Chem. Co.—*Can. 428,953.*
Colgate-Palmolive-Peet Co.—*Can. 425,822.*
E. I. duPont de Nemours & Co.—*U. S. 2,366,738, 2,370,786.*
Eastman Kodak Co.—*U. S. 2,369,443.*
Fuel Research Development Corp. — *U. S. 2,373,793.*
J. R. Geigy A.-G—*Ger. 743,226 Cl. 12q.*
Harvel Corp.—*U. S. 2,377,552.*
Hercules Powder Co.—*U. S. 2,354,774, 2,370,688, 2,373,419, 2,378,436.*
I. G. Farbenind. A.-G.—*Belg. 443,917-8, 445,978.*
Kalle & Co. A.-G.—*Ger. 741,823 Cl. 8i.*
Monsanto Chem. Co.—*U. S. 2,355,592.*
Natl. Oil Products Co.—*U. S. 2,376,381-2.*
Oranienburger Chem. Fabrik A.-G.—*Ger. 737,553 Cl. 8o.*
Procter & Gamble Co.—*U. S. 2,366,133, 2,383,525.*
Sherka Chem. Co., Inc.—*U. S. 2,368,277.*
Soc. anon. Alliance Européenne—*Belg. 446,053.*
Solvay Process Co.—*U. S. 2,373,643, 2,383,120.*
Standard Oil Co.—*U. S. 2,374,193.*
Union Oil Co.—*U. S. 2,381,708.*
Welter—*Belg. 447,710.*

In some cases the sulfur containing products were made by sulfonating or sulfating nitrogen containing organic derivatives such as amines, amides, etc.:

Alien Property Custodian — *U. S. 2,374,934, 2,383,859.*
Allied Chem. & Dye Corp.—*U. S. 2,374,187.*
Am. Cyanamid Co.—*U. S. 2,368,067, 2,383,106, 2,383,130.*
Deut. Hydrierwerke A.-G.—*Belg. 445,151.*
E. I. duPont de Nemours & Co.—*U. S. 2,370,839, 2,374,648.*
General Aniline & Film Corp.—*U. S. 2,366,452.*
Goldschmidt—*Belg. 443,764.*
Hercules Powder Co.—*U. S. 2,379,039.*
Hydronaphthene Corp.—*U. S. 2,355,503.*
I. G. Farbenind. A.-G. — *Belg. 445,946; Ger. 738,811 Cl. 8i.*
Natl. Oil Products Co.—*U. S. 2,367,010, 2,372,786.*
Procter & Gamble Co.—*U. S. 2,383,525-6, 2,383,737-40.*
Schering A.-G.—*Belg. 444,612.*
Swiss Co., Soc. Chem. Ind.—*U. S. 2,376,911.*
U. S. Rubber Co.—*U. S. 2,356,710.*

Many nitrogen containing compounds such as amines, amides, quaternary ammonium compounds, etc., have detergent properties:

Am. Cyanamid Co.—*U. S. 2,349,061, 2,355,442, 2,367,569, 2,375,659, 2,380,697, 2,391,831.*
Emulsol Corp.—*U. S. 2,368,208, 2,371,097, 2,374,213, 2,388,154.*
Martin Dennis Co.—*U. S. 2,387,976.*
E. I. duPont de Nemours & Co.—*U. S. 2,361,185, 2,366,534, 2,377,682, 2,391,267.*
Goldschmidt—*Belg. 446,054.*
Gruenwald—*U. S. 2,374,678.*
Hoffmann-LaRoche, Inc.—*U. S. 2,367,878.*
Imperial Chem. Ind. — *U. S. 2,377,066; Brit. 555,129.*
I. G. Farbenind. A.-G.—*Belg. 445,580, 445,808.*
Monsanto Chem. Co.—*U. S. 2,347,633.*
Natl. Oil Products Co.—*U. S. 2,372,797.*
Röhm & Haas Co.—*U. S. 2,363,386-7.*
Soc. pour l'ind. chim. a Bale—*U. S. 2,355,911, 2,365,871, 2,371,133; Brit. 554,717, 555,443.*
Solvay Process Co.—*U. S. 2,370,518, 2,371,418.*

Several patents were on the preparation of special esters, ethers, and condensation products which had detergent properties or were intermediates for the preparation of detergents:

Alien Property Custodian—*U. S. 2,356,565.*
E. I. duPont de Nemours & Co.—*U. S. 2,366,737, 2,374,236.*
Eastman Kodak Co.—*U. S. 2,364,348.*
Goldschmidt A.-G.—*Belg. 444,625, 447,658.*
Hercules Powder Co.—*U. S. 2,354,775, 2,366,409.*
I. G. Farbenind. A.-G.—*Ger. 740,104 Cl. 12q.*
Monsanto Chem. Co.—*U. S. 2,377,246.*
Richards Chem. Co.—*U. S. 2,379,703.*
Soc. anon. d'innovations chim. dite Sinnova ou Sadic—*Belg. 446,358.*

Newly published information on glycerol was not very abundant. Lenth (*Soap Sanit. Chemicals 21,* No. 2, 33) prepared an economic treatise giving statistics on production and consumption in various industries. Stockman (*Chem. Met. Eng. 52,* No. 4, 100) announced the availability of new distillation equipment which permits increased recovery and elimination of sweet water production. Desnuelle (*Industries corps gras 1,* 4) demonstrated by comparative analyses and tests in the presence of materials that may affect analyses, that the periodate method for determination of glycerol had the greatest specificity. It was not affected by the organic acids, aldehydes, and alcohols usually associated with glycerol in crude samples.

Leffingwell and Lesser (*Am. Dyestuff Reptr. 34,* 123) reviewed the applications of glycerol for textile

processing. Loder (*U. S. 2,388,164*) prepared glycerol ether esters, such as mono- and dimethoxy acetates of glycerol β-methyl ether, for use as intermediates for the manufacture of glycolates.

Several improvements in the manufacture of glycerol by the fermentation process were patented. Fulmer *et al.* (*U. S. 2,388,840*) carried out the fermentation in the presence of sulfite salts. Hodge (*U. S. 2,381,052*) promoted glycerol formation by adding ammonia to the fermentation mash in order to maintain an ammonia content of 0.1-1.0%. Hoyt (*U. S. 2,381,055*) designed a scheme for purification of a 25% glycerol concentrate from distillery slop. Some of the steps involved were digestion with sulfuric acid, treatment with lime paste, precipitation, treatment with adsorbents, and distillation. According to the method of Walmesley (*U. S. 2,389,173*) for recovering glycerol, the fermented liquors were evaporated to about 40% water content, alkaline earth material was added, and the mixture was extracted with alcohol. Wallerstein and Alba (*U. S. 2,366,990*) recovered pure glycerol from fermented carbohydrate solutions by adding formaldehyde, and maintaining the solution alkaline for one hour and then fractionally distilling.

The Composition of Sorghum Grain Oil[1] Andropogon Sorghum var. vulgaris

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STUDIES which involved characterization of the starch in sorghum grain at this station[3] (1) created an interest in the lipid material as well. Sorghum grain is now being processed for starch on a commercial scale, but no oil is being extracted in this operation[4] (2). The volume of sorghum grain produced, which for 1944 was approximately 181,500,000 bushels[5] (3), offers an opportunity for the development of a new source of oil as well as of starch. It therefore seemed desirable to compare the composition of sorghum grain oil with a commercially available oil such as corn oil.

Various analyses for the lipid material in sorghum grain have been reported (1,4,5,6). It was found that in contrast to the clear oil obtained from corn on extraction with ethyl ether, the extract of sorghum grain was a semisolid translucent material. Francis and Friedemann attempted to separate this semisolid material by centrifugation (7). Their characterization of the liquid and sediment fractions indicated that these fractions differed in melting point but not in composition. Yamamoto and Ninomiya (8) believed the liquid fraction to represent the lipid material of the embryo and the sediment fraction the lipid material of the testa or bran; they named the former embryo and the latter testa oil. These fractions were found to exhibit significant differences in the melting point. The embryo oil had a melting point of from —17 to —21° C. and the testa oil from 60 to 62.5° C.

The high melting point of the testa oil indicated that the ethyl ether extract of the hull or bran contained a material not present in the embryo and endosperm. Further evidence for this fact is found in the work of Yamamota *et al.* (5) and Bidwell, Bopst, and Bowling (9). The former were able to isolate high molecular weight alcohols and small quantities of wax from the unsaponifiable fraction of the testa oil. The latter separated the bran and germ of sorghum grain and corn by mechanical means before ether extraction. They found that the amount of ether soluble material obtained from the bran of sorghum grain was almost eight times greater than from corn, but there was no significant difference in the amount of ether soluble material obtained from the germ. The sorghum grain kernel was found to consist of 6.1% bran, 10.0% germ, and 83.9% endosperm which contained 6.8, 31.5, and 0.7% of ether extractable material respectively. Corn was found to consist of 7.4% bran, 11.5% germ, and 81.1% endosperm which contained 0.89, 34.8, and 1.15% of ether extractable material, respectively. Bidwell *et al.* did not characterize these ether-soluble materials. In the present study the lipid material of the hull was separated from the lipid material in the germ and endosperm and each entity characterized.

Experimental

Separation of the Lipid Material in the Bran from the Lipid Material in the Germ: The separation of the lipid material in the bran from the lipid material in the germ and endosperm was accomplished by fractional solvent extraction. The lipid material of the bran was first removed by extracting the unground grain[3] with Skellysolve B under reflux for one hour. Then the grain was ground and the lipid material of the germ and endosperm removed by extracting with Skellysolve F in a large Soxhlet extractor. On evaporation of the Skellysolve B, a white solid residue with a melting point of 78-82° C. was obtained. The Skellysolve F extract yielded a slightly cloudy, straw-colored oil. Filtration through filter paper at room temperature gave a clear oil. On the basis of the total weight of grain extracted the Skellysolve B extract contained 0.5 and the Skellysolve F extract 2.5% of lipid material. As a means of comparison a sample of white corn[4] was also subjected to fractional solvent extraction. The unground corn was extracted with Skellysolve B, then ground and ex-

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[3]Western Blackhull, Fort Hays Expt. Sta., Hays, Kansas.
[4]Obtained through the courtesy of E. G. Heyne, Dept. of Agronomy, from The Iowa Experiment Station, Ames, Iowa.
[5]Mazola, Corn Products Refining Company, Argo, Illinois.