

Review of Literature on Fats, Oils, And Soap for 1940*—Part II

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BIOCHEMICAL AND PHYSIOLOGICAL

RESUMES covering this phase of fat chemistry appeared on the following subjects: acyclic constituents of fats (Smith—*Ann. Rev. Biochem.* 9, 93), the chemistry of sterols (Heibron and Jones—*ibid.* 135), chemistry of lipids (Kirk—*ibid.* 115) and fat metabolism (Channon—*ibid.* 253; Editorial—*J. Am. Med. Assoc.* 114, 2220). The reviews on fat metabolism included new methods of research, present theories, their disputed points and recent progress.

The use of "labeled" fats such as those containing deuterium or elaidinized acids has added considerable to the knowledge of fat metabolism and transport. Stetten and Schoenheimer (*J. Biol. Chem.* 133, 329) reported that interconversions of certain fatty acids were normally and continuously taking place in the animal. This conclusion was based on the presence of deuterium-containing palmitoleic, stearic and short chain acids in the body fats of laboratory animals 8 days after feeding of ethyl ester of deuteropalmitic acid. The same investigators (*ibid.* 347) also concluded that alcohols were normal intermediates in the process of elongation of the carbon skeleton. In this work "labeled" acetates of cetyl and octadecyl alcohols were fed to mice and the deuterium-containing fat products were identified in the body fats. The fact that deuterium was present in both saturated and unsaturated fat acids, but not in the highly unsaturated acids of the body fats of rats fed rations low in fats and water containing heavy water, led to the conclusion that the highly unsaturated acids cannot be synthesized by animals, but must be directly derived from the diet (Bernhard and Shoenheimer—*ibid.* 707, 713). The deuterium content of the liver fats was always considerably higher than that of fats of other organs, indicating a rapid regeneration of fat acids in this organ. The saturated acids acquired a deuterium content of half the concentration of body fluids in which they were formed. This was interpreted to suggest that during synthesis one out of every two stable hydrogen atoms was derived from water. Other evidence indicated that stearic and palmitic acids were regenerated at the same rate and that half the saturated acids of the liver were regenerated in about one day. Lovern (*Biochem.*

J. 34, 704) developed evidence to support the theory that in fish also certain saturated and unsaturated acids are interconvertible.

Sperry, Waelsch and Stoyanoff (*J. Biol. Chem.* 135, 281, 291) also used heavy water in investigations on replacement of fats in the body and determined the deuterium present in the unsaponifiable and fat acid fractions of brain, liver, intestine and carcass of rats after 4 to 7 days on heavy water were recorded. The amounts found in the brain lipids were small.

These lipids were, therefore, replaced at a slow rate; that is, about one-fifth of the fat acids of the brain could be replaced in a week. The deuterium content was highest in the liver. Sinclair (*ibid.* 134, 71, 88, 89) estimated that the rate of turnover of fat acids in the phospholipids of rat kidneys was 60% in three days and 90% in a week. He used elaidin as the "labeled" fat. He also found that the turnover of liver phospholipids was rapid. The rates of turnover of fat acids in lecithins and cephalins were practically the same, thus suggesting that both lecithins and cephalins had metabolic functions. Elaidic acid was not incorporated in the testis

phospholipids; testicular phospholipids must therefore have a non-metabolic function.

Reports during the year have added new evidence which involves the water-soluble vitamins in fat metabolism. Gavin and McHenry (*J. Biol. Chem.* 132, 41) demonstrated that the administration of vitamin B₆ in conjunction with thiamine, riboflavin and choline caused an increase in body fat. Vitamin B₆ nicotinic acid or riboflavin did not prevent a deposition of fat in the liver which resulted when thiamine was administered. The amount of liver fat was normal when choline was given. Longenecker, Gavin and McHenry (*ibid.* 134, 693) showed that with absence of the complex and fat in the diet there was a gradual loss of body fat. With restoration of the water-soluble vitamins a rapid deposition of body fat occurred. The synthesized fat was characterized by an increase in the C₁₆ fat acids. Other publications by McHenry and Gavin. (*ibid.* 683; *ibid.* (*Proceedings* 66); *Sci.* 91, 171) revealed that crude liver fractions caused a large increase in liver fat and cholesterol; these deposits were resistant to the lipotropic action of choline but readily responded

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to "lipocaic" from pancreatic extracts, yeast and other materials. It was suggested that "lipocaic" effected the transport of cholesterol while choline was concerned with fat. Other publications pointed out that liver fat accumulated and blood lipids fell in depancreatized animals (Chaikoff and Connor—*Proc. Soc. Exptl. Biol. & Med.* 43, 638; Rubin and Ralli—*Am. J. Physiol.* 129, 578), and that rations containing liver and pancreatic extracts increased the rate of growth and ultimate size attained by salmon (Norris & Donaldson—*Am. J. Physiol.* 129, 214). Ring (*ibid.* 131, 357) found that the specific dynamic action of fat was not affected by pancreatectomy unless the animals were on a fat diet for at least three days. Richter and Hawkes (*ibid.* 639) were able to increase or decrease the carbohydrate, fat and protein appetite through regulation of the vitamin B components.

Besides lipocaic and vitamin B complex, choline, certain sulfur-containing amino acids and phospholipids have been associated with this line of fat metabolism studies. Hemorrhagic degeneration of the kidneys which occurred in rats on a diet low in fat and in choline increased in severity with additions of cystine, lard or cholesterol (Griffith *et al.*—*J. Biol. Chem.* 132, 627, 639). Chanon *et al.* (*Biochem. J.* 34, 866) showed that the increased liver fat was produced by the addition of cystine to diets low in caseinogen and high in fat; and the fat deposition progressively increased with time up to 21 days and the effect did not occur when caseinogen was replaced by albumin. The fat in the blood was not affected. Tucher *et al.* (*J. Biol. Chem.* 135, 85) also evaluated the effect on liver of cystine and methionine in low protein diets. In the work of Artom and Freeman (*ibid.* 59) feeding large doses of olive oil produced high values for lecithins and low for cephalins in the blood. This was interpreted to suggest that plasma lecithins and not cephalins or sphingomyelins were involved in transport of fat acids; this also agreed with the reports that choline was effective and cholamine ineffective in the cure of fatty livers.

Schantz, Boutwell, Elvehjem and Hart (*J. Dairy Sci.* 23, 1201) improved the nutritive value of vegetable oils by adding phospholipids to them. Sphingomyelin, sphingosine sulfate and ethanolamine had no effect on the nutritive value of corn oil, but choline seemed to improve the nutritive value of the fat for female animals.

The effect of various fats on blood ketones was investigated by several writers. Administration of 25 to 30 g. of oleic acid or olive oil to healthy subjects by a duodenal tube did not increase the ketone content of the blood (Markees—*Z. klin. Med.* 135, 516). The increase of blood ketones after ingestion of butter was prevented if oleic acid in 2:1 ratio was given simultaneously. The feeding of glycerine esters of odd-numbered carbon fat acids higher than propionic to rabbits led to an increase in the ketone bodies in the blood (MacKay *et al.*—*J. Biol. Chem.* 136, 503).

Work on essential fat acids was continued. Burr, Brown, Kass and Lundberg (*Proc. Soc. Exptl. Biol. Med.* 44, 242) and also Hume, Nunn, Smedley-MacLean and Smith (*Biochem. J.* 34, 879) pointed out that linoleic, linolenic and arachidonic acids differed in growth effect and action on skin lesions and should therefore not be treated interchangeably, but as individuals. Other work by Smedley-MacLean and Nunn (*ibid.* 884) indicated that a minimum intake of arachidonic acid was necessary in order that the cells of the fat depots might take up fat. Sinclair (*J. Nutr.* 19, 131)

found that in rats on diets deficient in the essential fat acids better growth was obtained when the diet was high in carbohydrates than when it was high in fat. This was attributed to the synthesis from carbohydrates of some of the fat acids necessary for growth. Schneider, Steenbock and Platz (*J. Biol. Chem.* 132, 539) cured skin lesions of rats from fat acid deficiency by feeding these essential acids or rice bran. This second cure was dependent upon vitamin B₆ and a second "accessory factor." Weil and Russel (*ibid.* 136, 9) showed that the reduced plasma phosphatase activity induced in rats by fasting could be ameliorated by ingestion of several types of unsaturated fat acids. For obtaining highest plasma phosphatase activity, 8% lard was required in the diet, a further amount causing no increase.

Deuel and co-workers (*J. Nutr.* 20,215,227) studying the absorption of fat from the gastrointestinal tract, found no consistent differences between of hydrogenated cottonseed oil, butter fat and coconut oil; the absorption of rapeseed oil was somewhat slower. Triacetin and tributyrin were more readily absorbed than natural or other synthetic fats. As the carbon chain of the saturated fatty acid esters increased they were less readily absorbed. Fats of odd chain acids such as tripropionin, trivalerin and triheptylin were absorbed at half the rate or less than their nearest "even-chain" fats. Menezes and Banerjee (*J. Indian Inst. Sci.* 22A, 203) reported that clarification, neutralization and decolorization reduced the rate of digestion for peanut and cottonseed oils but not for coconut oil.

Two groups of investigators compared the nutritive value of butter with certain other fats. Schantz, Elvehjem and Hart (*J. Dairy Sci.* 23, 181) demonstrated that young rats grew better when the fat constituent of their diet was butter than when it was corn, cottonseed, coconut or soybean oil. The same authors with Boutwell (*ibid.* 1205) separated the volatile acids of butter by steam distillation, and the unsaturated from the saturated by precipitation and after converting them to the glycerides fed them to the rats with corn oil. The saturated fraction with corn oil was found to be superior to butter fat whereas the other two remained approximately equivalent to straight corn oil. Harris and Mosher (*Food Res.* 5, 177) obtained slightly different results; animals on a butterfat diet consumed a little more of the diet but increased in weight much less rapidly than animals on a coconut oil diet. Neither of the fats in special tests at high levels was harmful to rats.

There were a few reports on the effect of adding certain fats to fat-poor diets. Henderson and Irwin (*Poultry Sci.* 29, 389) recorded that the mean weight of chicks fed increasing amounts of soybean oil did not vary significantly until the ration contained 10% oil after which there was regression of weight.

The addition of soybean oil meal in place of beet pulp and the addition of soybean oil to a cattle ration low in fat increased, respectively, the percentage of butterfat and the amount of milk produced (Gibson and Huffman—*Mich. Agr. Expt. Sta. Quart. Bull.* 21, 258).

According to Woodman and Evans (*J. Agr. Sci.* 29, 502) meat meals containing 70% fat gave as good growth, conformation, and carcass quality of bacon-pigs as meat meals whose fat contents had been reduced to 2-3%.

Krewson and Elvehjem (*Oil & Soap* 17, 30) recorded that licanic acid possessed no energy value and might be slightly deleterious to the growth of rats. However, this acid was apparently capable of assisting in the utilization of the lactose of milk as indicated by

its prophylactic action in preventing sugar loss via the urine. Edwards (*Wis. Med. J.* 37, 1004) found low-fat evaporated milk more satisfactory in infant feeding than regular evaporated milk.

Coffey, Mann and Bollman (*Am. J. Digestive Dis. Nutr.* 7, 141, 143, 144), after determining normal values for fecal residue of fat, protein and carbohydrate in the dog, studied the effect of exclusion of bile and the influence of pancreatectomy on utilization of food-stuffs. Either measure produced a marked loss of fat in the feces. Winter (*J. Biol. Chem.* 135, 123) found that injury to the liver of rats with carbon tetrachloride reduced the loss of fat acids from the liver as compared with untreated animals but increased the loss of sterols. Liver damage may thus produce a change in fat metabolism resulting in a decreased oxidation or other conversion of fat acids and an increased destruction or decreased synthesis of sterol.

The effect of tumor producing substances in mice was accelerated by 15% of fat in the diet (Jacobi and Baumann—*Am. J. Cancer* 39, 338). Fat applied locally to the treated areas has had less effect than fat in the diet. Ciaranfi (*Arch. Sci. Biol. Italy* 26, 8) pointed out that *omega*-oxidation of fats takes place in tumors with the same speed as in normal tissues, thus enabling the neoplastic cells to use the fats as a source of energy.

Investigation on the influence of fat in healing rickets were reported in two papers. According to Knudson and Floody (*J. Nutr.* 20, 317) addition of 5% of fat to rachitogenic diet gave much better healing with a given amount of vitamin D than with no fat in the diet; with 10 or 20% fat the healing was less than with 5% fat. In similar work Jones (*ibid.* 367) demonstrated that fat increased calcification on diets containing excessive or moderate amounts of calcium. The effect of fat was less pronounced on diets very low in phosphorus than on diets containing 0.09% phosphorus.

New work on the effect of food fats on body and milk fat of animals was recorded. Hostetler, Halverson and Sherwood (*N. Carolina Agr. Expt. Sta. Tech. Bull.* 61, 44 pp.) designed feeding procedures for producing firm pork from peanut-fed pigs. The characteristic of body fats of steers and swine on feeds containing peanuts, velvet beans and corn were recorded by Edwards and Holley (*Proc. Am. Soc. Animal Production* 32, 376). Similar data showing the effect of various oil feeds on butter were prepared by Herzer *et al.* (*Miss. Agr. Expt. Sta. Tech. Bull.* 25, 62 pp.).

Hilditch and Pedelty (*Biochem. J.* 34, 40) studied the influence of starvation on the composition of pig depot fat; there was no great evidence of selectivity in mobilization of any one fat acid component of the depot fats of starving pigs. The possibility was suggested that simultaneously with mobilization, building up of glycerides took place, either from newly formed fat acids or from fat acid fragments or partly metabolized mixed glycerides.

DETERIORATION

During the year resumes dealing with spoilage of fat products covered its prevention (Singer—*Seifensieder-Ztg.* 66, 829, 840, 849, 859, 869, 879; Pannewitz—*ibid.* 67, 18, 28, 47), the deterioration of stored butter (Cameron—*Can. Dairy & Ice Cream J.* 19, 2), a review of the work of the German Society for fat research (Täufel—*Fette u. Seifen* 47, 398), antioxidants, (Ciusa—*Chimica e industria* 22, 63) and control of soap rancidity (Smith—*Am. Perfumer* 40, #3, 59).

Schramme and Neu (*Fette u. Seifen* 47, 447) demon-

strated that the diphenylcarbazine reagent was not usable for judging spoilage of food fats. The tests were not consistent with other commonly used tests for rancidity. According to Grandel and Newmann (*Z. Untersuch. Lebensm.* 79, 57) there was enough correlation between the vitamin E content of wheat germ oils and spoilage tests, such as acid value, peroxide value, and Fellenberg reaction, to recommend approximating the vitamin E value of the oils by means of the tests for deterioration. Biological and physical-chemical methods were too tedious. Romeo and Catalano (*Riv. Ital. essenze, profumi piante offic.* 20, 71) preferred the use of hydroxylamine value for expressing the rancidity of butter. Nile blue sulfate, methylene blue or *p*-aminodimethylaniline monohydrochloride color changes could not be used as a specific indication of microbial deterioration of fats because the changes were not due to simple reactions (Castell and Bryant—Iowa State Coll. *J. Sci.* 13, 313). Reduction of color may be due to extraction by moisture, reduction, etc.

The action of microorganisms was the subject of two series of papers. Thaler and Geist—(*Biochem. Z.* 302, 121, 368) pointed out that acetone could be formed by *Penicillium glaucum* from all saturated fat acids containing 4 to 14 carbon atoms. Maximum formation of acetone occurred at pH 3. With hydroxy acids, maximum ketone formation occurred at pH 6; β -hydroxy acids may be intermediates for ketone formation from saturated fat acids. Castell and Garrard (*Can. J. Research* 18C, 158) investigated the so-called "opaqueness" surrounding lipolytic colonies on fat-emulsion agar plates. They suggested that the phenomenon was due to formation of fat crystals as well of fat acids.

The relationship of some minor components of butter to rancidity was studied. Fouts (*J. Dairy Sci.* 33, 307) found no relationship between the percentage of volatile free acids and degree of rancidity. Different organisms released different amounts of both volatile and non-volatile acids. Prill and Hammer (*ibid.* 159) found that the changes in amounts of diacetyl and acetylmethylcarbinol in butter were slight even on holding at 70° F., which was the temperature at which chemical deterioration was especially rapid in the butter. Kiermeier (*Molkerei-Ztg.* 53, 851) pointed out that the formation of methyl ketone was directly related to the stability of butter.

Mutton fat could be stored 155 days at -2 to +6° with no effect on quality (Nakoynechni—*Myasnaya Ind. U.S.S.R.* 10, #1, 33). At 18° storage, traces of aldehydes and peroxides could be detected on the 95th day, but storage to 125 to 155 days was possible. At 37° it was impossible to keep mutton fat more than 60 days. Razima and Semenova (*ibid.*) recommended that refractive indices be used as a criterion of fat storage tests. With pork fat they showed that increases in the indices of refraction were related to increase in peroxide value and were also parallel to the acetyl value of the fat.

Simons, Buxton and Colman (*Ind. Eng. Chem.* 32, 706) observed interesting relationships between vitamin A destruction and peroxide value of fish liver oils. In oils of higher unsaturation the percentage of vitamin A oxidized was smaller at various peroxide values than in other oils of similar peroxide values. Within each group of oils the percentage of vitamin A oxidized was related to the peroxide value of the oil. When two samples of oil of the same peroxide value were stored at different temperatures, less vitamin A was oxidized at the lower temperature.

Reports on stability of margarines were made by

several investigators. Kiermeier (*Fette u. Seifen* 47, 400) recorded acid value, "quality value," ketone value and peroxide value of margarines stored at several temperatures between—16.5 and 18.5°. On the basis of the tests the storage life of fresh margarine was 32-38 days at 18.5°, 38-54 days at 8.5°, 96-129 days at 0°, about 340 days at —6.5°, and over 340 days at —16.5°. Schmalfluss (*ibid.* 46, 719, 47, 1) preferred the use of diacetyl to benzoic acid for the protection of margarine from spoilage. It was demonstrated that margarine fat mixtures containing palm kernel or coco fat were more stable than those without these fats. Milk or salt reduced the stability of the mixtures, but milk and salt together were not as deleterious as milk alone. Ravich and Schmidt (*Masloboino Zhir. Delo* 15, #4, 20) obtained encouraging results in storing margarine in combustion gases containing carbon dioxide 85.8, nitrogen 14.1, and oxygen 0.1%.

High moisture in olive kernels favored hydrolysis of the oil contained in them (*Chim. Chronika Greece* 1938, 342). On drying reesterification took place. Sterilization at 105° stopped hydrolysis of the oil without affecting esterification. Ciusa (*Ann. chim. applicata* 30, 141) reported that the antioxidants of olive or cod-liver oils were removed by absorption on carbon or silicon dioxide.

Kedvessy (*Ber. ungar. pharm. Ges.* 16, 114) recorded chemical and organoleptic tests on stored almond, cod-liver, linseed, rape, castor, sesame, sunflower-seed and olive oils. The data of Riemenschneider *et al.* (*Oil & Soap* 17, 145) characterized the stability of distilled fractions of cottonseed oil. The stability of the fractions decreased from fraction 1 to 15. In fractions crystallized from acetone the iodine number and oleic acid content increased from fraction 1 to 7, except that there was a drop in the oleic acid content in the last fraction.

Roasting of coffee tripled the stability of the oil fraction (Elder—*Ind. Eng. Chem.* 32, 798). The oil from green coffee when subjected to the roasting treatment by itself did not acquire increased stability. The stability may be due to pyrroles.

Researches on the stability of vegetable oils, especially soybean oil, were carried out by Bickford, Anderson and Markley (*Oil & Soap* 17, 138, 252) and Bickford and Markley (*ibid.* 232). The spectral transmission curves of 35 soybean oils were produced; the transmission was influenced by processing. Carotenoids and chlorophyll disappeared during refining. The greatest loss of carotenoids occurred during deodorization. In this series of investigations a stability apparatus based on the reduction of methylene blue in a fat-dye system was designed. It was applicable to the determination of the relative induction period of fats and oils; the relative rate at which a fat was capable of consuming its dissolved oxygen and the latent capacity of a fat to consume its residual oxygen.

Mechanical means of protecting oils were devised. Godfrey and Serbell (*U.S.* 2,223,724) prepared highly stable shortening by steaming, subjecting to vacuum to remove oxygen, congealing in nitrogen atmosphere and filling unoccupied spaces in containers with nitrogen. Ralston and Conquest (*U.S.* 2,209,904) produced a refined soybean oil product with improved stability by heating the oil to 250-300° in inert atmosphere before refining. Vitamin oil-containing tablets were more stable toward autoxidation when the oil and granule mixture was precooled before compression.

Many naturally occurring substances were patented as antioxidants. Thurman (*U.S.* 2,201,061-4) claimed the use of phosphatides containing fat acids less un-

saturated than linoleic acid. Crocker (*U.S.* 2,205,620) used components of licorice resins. Grettie (*U.S.* 2,201,692) stabilized lard with 1-10% hardened refined soybean oil. Ellis and Dannerth (*U.S.* 2,204,728) stabilized fats and oils with admixtures derived from unripe peas, cabbage leaves and apples by maceration at below 50°. They eliminated rancidity in partially rancid products by treatment with green coffee bean material. Patents issued to Musher (*U.S.* 2,193,695; 2,198,197-222; 2,199,363; 2,210,112) described the stabilization of fat-containing products with cereal seeds, raw coffee, raw nuts, their extracts, by heating with a phosphatide-sugar mixture or with dried milk. A publication pointed out the efficiency of some of Musher's methods (Garrett—*Milk Plant Monthly* 29, #2, 41).

Several investigators prepared publications on their investigations with natural antioxidants. Diemair, Strohecker and Reuland (*Z. Untersuch. Lebensm.* 79, 23) demonstrated that oat flour yielded a little protection to olive oil. Distinct protection of peanut, corn, olive, sesame, almond, poppy seed, soybean and hardened train oils was obtained by addition of 1-2.25% solvent extracted oat oil. Rancidity was not retarded in linseed, train liver and certain soybean oil samples. Partly rancid oils were not influenced by oat products. Treating the active oat oil with alcohol or ice-cooled acetone yielded a precipitate containing antioxidant material. The dried precipitate was insoluble in most organic solvents it reduced Fehlings solution, and it was soluble in pyridine and alkaline water at pH 12.2. Pepsin digestion destroyed antioxidant capacity. The evidence suggested that the active material was a protein. Macarovic (*Bull. Sec. scientifique acad. roumaine* 22, 496) reported that oat flakes were pro-oxidant in sunflower seed oil although in most other oils he found them active in preventing rancidity. Thaler and Schulte (*Fette u. Seifen* 47, 522) also pointed out the inconsistent nature of germ oil and germ oil concentrates toward protection against rancidity. Basu and Mazumdar (*J. Indian Chem. Soc.* 17, 280) obtained antioxidant concentrates from sesame cake. Fiero (*Pharm. Arch.* 11, 1) recommended sesame oil as a lard preservative. Govindarajan and Banerjee (*Current Sci.* 8, 559) found that "Kamala" dye, a natural dye, was a good preservative for ghee in 0.02% concentrations.

Täufel and Müller (*Biochem. Z.* 304, 137, 275) studied the influence of chlorophyll, xanthophyll and catalase on spoilage of fats. Chlorophyll contained a reactive carbon atom that produced oxidative changes unless decomposed by catalase. The addition of crude chlorophyll solutions seemed to prevent autoxidation whereas purified chlorophyll made the oils more sensitive to autoxidation. The antioxidant effect of catalase was said to be due to its ability to decompose peroxides.

The chemicals patented for their antioxidant properties during the year were betaines, their esters or salts (Shappirio—*U.S.* 2,217,711), reaction products of castor oil and aliphatic acids having at least 2 reactive groups (Guillaudeu—*U.S.* 2,197,269), aminoalkyl esters of carbocyclic acids (Böhm and Sabalitschka—*U.S.* 2,223,244), alcohol esters of tannic acid (*ibid.*—*Belg.* 435,981) reaction products of primary-amino-substituted diarylamine and a chlorocarbonic ester (*U.S.* Rubber Products, Inc.—*Brit.* 508,442), metallic salts of aminophenols (Craig—*U.S.* 2,189,417), *N*-aryl or *N*-alicyclic thiourethanes (Martin—*U.S.* 2,225,124) and mono-aryl substituted biguanides (Sibley—*U.S.* 2,221,333). Journal publications described and recommended the thiourea compounds (Sibley—*Soap* 16, #2, 21) and

aminoalkyl esters of carbocyclic acids (*Fette u. Seifen* 47, 542; *Z. Untersuch. Lebensm.* 77, 256).

Only a small number of investigators worked on the effect of heat on fats. Chertok and Baskovich (*Voprosy Pitaniya* 7, #4-5, 217) reported that in frying with butter at 150-200° hydrolysis and oxidation produced low molecular acids; saponification value increased from 224.44 to 247.50; free acids, peroxides and hydroxy acids also increased, and the iodine values decreased from 40 to 29. Brambilla (*Ann. chim. applicata* 29, 303) heated linoleic acid 3 hours at 320-5 in a nitrogen atmosphere and reported the formation of propionic, butyric, caproic, sebacic and glutaric acids, water, carbon dioxide and an unsaponifiable portion containing ethylenic hydrocarbons and a tarry residue.

Isikawa *et al.* (*Sci. Repts. Tokyo A-3*, 273) subjected castor oil to pyrolysis in the presence of various inorganic catalysts. The major portion of the products consisted of enanthaldehyde and undecylenic acid.

COMPOSITION AND CHARACTERISTICS

Such new data on composition and characteristics of fats and oils as came to our attention during the year and could be conveniently tabulated are appended to this section of the review. Some data of purely local interest and other publications of which only a reference was available are as follows:

Characteristics of oils of Gargano. Sallusto & Centulio.—*Ann. ist. super. agrar. Portici* 8, 69.

Saponification value of 66 oils. Meyer—*Wien. pharm. Wochschr.* 73, 64.

Characteristics of Argentinian edible oils. Ceriotti *et al.*—*Rev. facultad cienc. quim. U. of LaPlata* 14, 17.

Characteristics of oils of the province of Frosinone. Sallusto and Bisleti—*Ann. facolta agrar. Portici univ. Napoli* 10, 186.

Oil from high quality oil flax. Minkevich.—*Maslo-boino Zhir. Delo* 15, #6, 29.

Characteristics of olive oils from Lucca. Lucchetti—*Olivicoltura* 18, 27, 37.

Characteristics of tobacco seed oils. Curelici—*Bul. cultivarii fermentarii Tutunului* 28, 469.

Oil content of the basic grades of soybeans of the Ussuriisk station. Shugin—*Bull. Far East Branch Acad. Sci. U.S.S.R.* 33, #1, 202.

Characteristics of various types of Rumanian corn oils. Slusanschi—*Analele Inst. Cercetari Agron. Romanici* 9, #8, 243.

Other writers have pointed out how the character of oils or oil-bearing material may be effected. Olives gathered at various stages from green immature to completely mature olives showed a progressive increase of oil content but very little difference in the characteristics and composition of the oils (Sallusto—*Ann. ist. super. agrar. Portici* 8, 34). The fat content of cacao beans increased until the 5th day during fermentation (Humphries—*Ann. Rept. Cacao Research* 8, 34). The total increase was approximately 4%. No further increase took place on drying. Grau (*Z. Untersuch. Lebensm.* 80, 338) pointed out that the difference value according to Polenske for judging lard was usually low for the back fats of Rumanian, Hungarian and some German hogs. This was attributed to oil-containing feeds. Dollear, Krauczunas and Markley (*Oil & Soap* 17, 120) examined some high iodine number soybean oils from the standpoint of the relation between iodine number and composition. The iodine numbers varied from 102.9 to 151.4, the percent saturated acids (11.9 to 13.5) varied only insignificantly and the distribution

of the unsaturated acids varied in a specific manner with the iodine number of the oil. The composition of the oils from the lowest to the highest iodine number, respectively, was oleic 60-11.5, linoleic 25.0-63.1 and linolenic 2.9-12.1.

New records of standards for oils were: olive and other oil specifications for Norwegian canning industry (Mathiesen—*Tids. Hermetikind.* 26, 10, 198) standards and suggested standards for corn oils (Chapman and Macbeth—*Australasian J. Pharm.* 20, 1037; Nye and Barned—*ibid.* 188) and standards for tung, perilla, soybean and linseed oil (Am. Oil Chemist Soc. Committee—*Oil & Soap* 17, 151)

Hilditch and co-workers (*J. Soc. Chem. Ind.* 59, 47, 67, 138, 162; *Biochem J.* 34, 971, 1299, 1301) added new information on the glyceride content of fats. They presented fuller data on the glyceride content and structure of fat than is usually reported by other investigators. In addition to giving the true picture of the composition, the data aided in biochemical and physiological interpretations of some of the phenomena of fat metabolism. The procedures used included fractionation from acetone solution, hydrogenation, elaidinization and fractionation by distillation. By elaidinization and fractionation they proved that the linoleic acid of nondrying seed oils was present largely in the form of dioleo-glycerides. In oils containing less than 60% oleic acid a considerable portion of the oil consisted of monooleic-monolinoleo- monosaturated glycerides. When the oleic acid was considerably above 60% the monooleo-glycerides were present in very small proportions. In palm oils the chief components were oleo- and/or linoleo-dipalmitin and palmitodin-olein and/or linolein in amounts which varied according to the proportion of palmitic, oleic and linoleic in the whole fats. Their work on body fats of pigs and butter fat was of physiological significance. The data on butter fat as compared with the body fats of the animal supported the hypothesis that butter fat was the result of transformation in the mammary gland of the pre-formed oleo-glycerides including large proportions of palmito-oleo-glycerides. The fats of the Indian ox were found to be more saturated than those of European or American animals. Work on the ox and pig fat supported the hypothesis that stearo-glycerides in these animals had resulted from the saturation of pre-formed oleo-glycerides. A gradual increase was also noted in the proportions of dipalmito-glycerides as the general degree of saturation became more pronounced.

In addition to Hilditch other investigators utilized crystallization technic in fat investigation. Shinowara and Brown (*J. Biol. Chem.* 134, 331) isolated pure arachidonic acid by crystallization of the methyl esters of adrenal phosphatides. A method for determining the saturated acids in the acids of soybean oil (Earle and Milner—*Oil & Soap* 17, 106) depended on crystallization from acetone. Coffey and Spannuth (*ibid.* 216) used this same principle in their method for the determination of the predominant saturated glycerides in shortenings and margarines. Under the conditions of the method the saturated glycerides of cottonseed oil, coconut oil and partly hydrogenated cottonseed oil (I. No. 667) were not precipitated from the acetone solution at 30°.

Schuette and Vogel (*Oil & Soap* 17, 155) added information to their earlier studies on solidification point curves of binary mixtures. Data on palmetic-stearic, stearic-arachidic, arachidic-behenic and behenic-lignoceric acid mixtures were tabulated. The information was of value as an analytical aid and is of theoretical

interest in that it might lead to information upon the tendencies in compound formation.

A solvent extraction method was used for the separation of hydroxy and non-hydroxy acids (Kurtz and Schaffer—*J. Am. Chem. Soc.* 62, 1304).

The information on distillation procedures in fat analysis included a review on ester distillation methods (Longenecker—*Oil & Soap* 17, 53), a description of a laboratory molecular or short-path still (Detwiler and Markley—*Ind. Eng. Chem.* 12, 348) and an investigation in ethanolsis of sardine oil (Takano *et al.*—*J. Soc. Chem. Ind. Japan* 43B, 132). Ethanolsis activity, in decreasing order of the fat acids combined in the glycerides, was: solid fat acids, liquid fat acids and highly unsaturated fat acids.

Adsorption separation of fat acids is a new technic in the field which showed promise of a great future. Kaufmann and co-workers (*Fette u. Seifen* 47, 294, 460; *Angew. Chem.* 53, 98) were very active in this field. In work on fat acids, their glycerides, cocoa fat and palm-kernel fat the lower molecular weight acids were more strongly adsorbed than the high molecular weight acids in columns containing aluminum oxide, silica gel, or other adsorbents. Monostearin was more highly adsorbed than tristearin; distearin was intermediate. A mixture of mono-, di- and triglycerides of a fat acid was separated into its components. Cassidy (*J. Am. Chem. Soc.* 62, 3073, 3076), recorded data on the adsorption isotherms of several saturated fat acids on two carbons, alumina, magnesium oxide, active clay and silica gel. He concluded that the behavior of the acids was too uncertain as a criterion of their separability by the method. Nakamiya (*Bull. Inst. Chem. Research Tokyo* 18, 787) was successful in separating higher alcohols and hydrocarbons from liver oil by adsorption on alumina. Thornton, Kraybill and Mitchell (*J. Am. Chem. Soc.* 62, 2006) removed sterol glucosides from expressed soybean oil by adsorption on a special aluminum silicate.

Some investigations on fats were directed to specific fractions only. Nobori (*J. Soc. Chem. Ind. Japan* 43B, 59, 110) separated and determined the amounts of lauric, capric and caprylic acids in herring and sardine oils. Murty and Rao (*Current Sci.* 9, 75) found that rancid cottonseed oil deposited pure palmitic acid on standing, thus supporting the theory that very little, if any, stearic acid was present. In work by Tuzimoto (*J. Soc. Chem. Ind. Japan* 43B, 208) the leaves of 6 out of 7 land plants were found to contain linolenic acid. The land plants did not contain as highly unsaturated acids as did algae. Kass, Lundberg and Burr (*Oil & Soap* 17, 50) developed data that indicated the presence of only one form of linoleic acid in seed fats. The work of McCutcheon (*Can. J. Research* 18B, 231) in which the α - and β -linoleic acids of linseed oil were proved identical suggested that there was only one natural linoleic acid. Matuda and Ueno (*J. Chem. Soc. Japan* 60, 49) isolated 3 C₂₂ fat acids from bonito oil. Sūna (*ibid.* 173) isolated a C₂₀ dicarboxylic fat acid from Japan wax. Several higher alcohols were isolated from sukeso liver oil by Nakamiya (*Bull. Inst. Phys. Chem. Research Tokyo* 18, 777).

Podol'skaya (*Masloboino Zhir. Delo* 15, #3, 9) in studies to determine whether gossypol was present as a primary product or as a derivative spectroscopically observed by color changes from pale yellow to red. The rapidity of the changes varied; the gossypol of seeds stored 2 months was in the red form. Royce *et al.* (*Ind. Eng. Chem. Anal. Ed.* 12, 741) modified the pyridine-

aniline method so that it was capable of recovering 98% of the gossypol from a 0.2% solution in oil.

Heddle and Brown (*Can. J. Res.* 18B, 386-7) determined the phosphorus and iodine content of Columbia fish oils. The phosphorus content was too low to exert much antioxidant effect. The iodine content varied widely, but the oils were a good source of iodine. There was some analytical interest in phosphatides. Goldowski and co-workers (*Russ. Central Sci. Fat Research Inst.* 1939, 118) found that the amounts of phosphatides in expeller and extracted cottonseed oil varied, but both were in the same range between 1.48 and 1.82%. Information on the structure of cephalin and sphingomyelin was developed by Gray (*J. Biol. Chem.* 136, 167) and Thannhauser and Reichel (*ibid.* 135, 1). Täufel, Heinisch and Heimann (*Biochem. Z.* 303, 324) found variable quantities of squalene in the unsaponifiable from olive, wheat germ and yeast oils; none was found in coconut, soybean, rape and cottonseed oils.

Two papers contained tabulated reactions and characteristics of fat acid derivatives. One by McCorkle (*Iowa State Coll. J. Sci.* 14, 64) dealt with nitriles and aromatic addition compounds produced by the Friedel-Crafts reaction. Data by Kimura and Turugi (*J. Soc. Chem. Ind. Japan* 42B, 390) were on tolyl- and methyl tolylstearate and the *p*-xenylamide of tolylstearic acid.

Factory control and general industrial analytical procedures were actively investigated. Humphries (*Ann. Rept. Cacao Research* 8, 39) reported that petroleum ether extracted about 1% more fat than trichloroethylene from cacao. Sethne (*Kgl. Norske Videnskab. Selskabs Skrifter* 1939, #3, 150 pp.) recorded results obtained in fat analysis on peanuts, copra and their cakes by several solvents and methods. Kitto (*Analyst* 65, 97) criticized the Grossfeld method because it gave results higher than the soxhlet method. A few other writers (Huber—*Bul. Facultat Stiinte Agr. Chisinau, Comun. Lab. Chim. Agr.* 3, 201; Slusanschi—*Analele Inst. Ceretari Agron. Romanici* 10, 233; Zaichenko and Semenov—*Masloboino Zhir. Delo* 16, #1, 25) stated their preference or suggested slight modifications in the usual methods. Zajcev (*Seifensieder-Ztg.* 67, 469) developed a formula and factors by which the oil content of several seed cakes might be calculated from the readings obtained by a refactometric procedure.

Hankins and Ellis (*Proc. Am. Soc. Animal Prod.* 32, 314) developed equations for calculating the fat content and quality of hog and cattle carcasses from the ether extract of the edible portion of 9-10-11 rib.

The publications on unsaponifiable consisted of the work of Grossfeld (*Chem.-Ztg.* 63, 749; *Z. Untersuch. Lebensm.* 79, 113; 80, 1; 434). The methods were mentioned in the last annual review. They depended on two determinations with different amounts of solvent. From the results the unsaponifiable and the amount of hydrocarbons could be ascertained. The sterol content of egg oil was sufficiently above that of other common fats to be used as a criterion for the determination of egg content of food products. Methods for determining the egg contents of baked goods and alimentary pastes which depended on the unsaponifiable constituents of the fat were developed and compared with existing methods.

New information on physical tests for fats was developed. Herold and Mastny (*Casopis Ceskiho Lekarnictva* 19, 215) pointed out that the iodine content of iodated oils containing large amounts of iodine could be approximated from the specific gravity. Tables showing the relationship were prepared. Schloemer

(*Z. Untersuch. Lebensm.* 79, 138) plotted the relationship between the refractive index of butterfat and the season. During summer the refractive index was high and reached a maximum in either August or September; a minimum occurred in January. Buogo and Gasparro's (*Ann. Chim. Applicata* 30, 79) work indicated that the Hoeffler viscosimeter gave better results than other instruments on both drying and non-drying oils. Kulikov (*Org. Chem. Ind. U.S.S.R.* 7, 176) recommended solubility in alcohol as a criterion for determining the degree of dehydration of castor oil. Coffey and Spanuth (*Oil & Soap* 17, 41) revealed that dilatometric measurements were useful in the study of food fats. The readings were reproducible. The fats having the greatest volume change in decreasing order were saturated fats, isoölein, olein and linolein. Information on the dielectric properties of oils by Winkelmann (*Allgem. Oel- u. Fett-Ztg.* 37, 121) and Tareev and Rabchinskaya (*Vestnik Elektroprom.* 1939, #10) was in support of this physical measurement in judging transformer and switch oils. Thiessen (*Naturwissenschaften* 28, 265) used this characteristic in the study of surface activity of fat acid crystals. Bhide and Bhide (*J. Univ. Bombay* 8, #3, 220) used dielectric measurements for following the changes of α -monoglycerides to the β -form during various temperature treatments. Two methods for determining consistency were reported. In one an apparatus was designed to record the pressure exerted in cutting samples with one or more cutters (Krüger—*Ger.* 686,420 Cl. 41 I; *Fette u. Seifen* 47, 465). The other method was designed on the principle of dropping a ball on the sample under set conditions (Lexow—*ibid.* 334); the diameter of the impression was used as criterion.

In the activities on melting tests Lexow (*Fette u. Seifen* 47, 204) and Erlandsen (*ibid.* 510) discussed flow points, drop points, melting points, flow melting points, clear melting points, melting interval and consistency from the view point of their value in margarine manufacture. The work on the titer test comprised a modified procedure (Loseva and Kolkov—*Masloboino Zhir. Delo* 16, #1, 27), a discussion on the use of the titer test on rosin and fat acid mixture (Pohle—*Soap* 16, #3, 61) and information on the significance of the titer test on textile oils (Burke—*Am. Dyestuff Repr.* 28, 355).

Smoke, flash and fire points were determined on 20 samples of soybean oil and several samples of corn, olive, castor, linseed, perilla, menhaden and fish oils (Detwiler and Markley—*Oil & Soap* 17, 39). Crude expeller soybean oil exhibited lower smoke, flash and fire points than mechanically- or alkali-refined oil. The solvent extracted oil was superior to the expeller oil with respect to these properties. The soybean oil was higher in these characteristics than all the other oils of corresponding type which were examined. D'Ollivier (*Rev. Combustible liquids* 17, 167, 225) fostered the use of soybean oil as a motor fuel in a publication on its heat value and on design of motors to handle this fuel.

Data on interfacial tensions of castor oil and pure water were graphically presented by Trillat and Nardin (*Pub. Sci. Ministère Air, France* #152, 35 pp.). The interfacial tension varied on passing from 10° to 82° from 18.5 to 19.4 dynes per sq. cm. Standing, oxidation and other factors affected the interfacial tension. Efforts to devise a test for detecting refining of oils based on surface tension were unsuccessful (Kaufmann and Kirsch—*Fette u. Seifen* 47, 191, 196). Tests in which finely divided air bubbles were passed through oils

yielded foams on crude oils, and practically no foam on highly refined oils except that the results on coconut and palm-kernel oils were not consistent. The foaming was attributed to lecithin, slimes and saponins. Robinson, Black and Mitchell (*Oil & Soap* 17, 208) tested the foaming tendencies of deep-fat frying fats by heating to 375° F. and dropping water soaked pieces of bread into them. Hydrogenated oils had the greatest resistance to foaming. There was a fair correlation between the increase in the refractive index or the viscosity of a shortening, and the tendency to foam.

Jarrett (*J. Oil Colour Chem. Assoc.* 23, 34) found a 1:2 alcohol:benzine solution suitable as a solvent in the determination of the acidity of fats. Kaufmann (*Fette u. Seifen* 47, 338) discussed corrections for the peroxide content in spoiled fat in a procedure for determining acidity iodometrically. A formula developed by Hawke (*J. S. African Chem. Inst.* 23, 21) for calculating the mean molecular weights of triglycerides contained adjustments for the presence of free fat acids and unsaponifiable.

Publications on evaluating total unsaturation were on comparison of methods, modifications and new methods. It was shown that the reagent ratio influenced the results obtained by the Wijs method with oils containing conjugated double bonds (Forbes and Neville—*Ind. Eng. Chem. Anal. Ed* 12, 72). With pure esters of oleic acids the method gave results close to 98.8% of the theoretical unsaturation (McCutcheon—*ibid.* 465). The Scotti method (*Olii minerali grassi e saponi* 18, 96) which depended on the use of iodine in benzene gave results slightly lower than the Hübl method (Buogo and Meduri—*Ann. chim. applicata* 30, 119). On olive oils the Hanus method agreed excellently with the Hübl. In a new method the fat was treated with bromine in methyl alcohol and the excess halogen was titrated with arsenite (Kaufmann—*Fette u. Seifen* 47, 4, 338). The method gave results substantially the same as those of Hanus and the Kaufmann iodometric methods. In another method fat was dissolved in carbon tetrachloride and treated with potassium bromate, potassium bromide and hydrochloric acid; and the liberated bromine which was not used up was back titrated with arsenite (Ullrich—*Wollen- & Leinen-Ind.* 60, 67). Addition of nitrosyl chloride to fats was found to indicate unsaturation in the same manner as the iodine value (Kaufmann and Röver—*Fette u. Seifen* 47, 103). Rubinskii (*Masloboino Zhir. Delo* 14, #2, 24) prepared curves with which the iodine value of linseed oil could be estimated from refractometric readings. For determination of total unsaturation by absorption of hydrogen Zhabrova (*ibid.* 15, #5, 34) recommended the use of platinum precipitated on barium sulfate.

Using 4 hours as the reaction time in the thiocyanogen value determination, Wheeler and Riemschneider (*J. Biol. Chem.* 132, 687) obtained values closely agreeing with the theoretical on triolein and trilinolein. Sher and Coysh (*Analyst* 64, 814) found that the preferable reaction times of the thiocyanogen reagent for oil were olive 5, teaseed 15, almond 15, and more unsaturated oils 20 to 24 hours. Kass, Lundberg and Burr (*Oil & Soap* 17, 50) reported that the American Oil Chemist's Society thiocyanogen method gave values higher than the theoretical for linoleic acid and Kass, Loeb, Norris and Burr (*Oil & Soap* 17, 118) also reported that this value of ethyl linolenate was considerably lower than it should be theoretically. Hilditch and Murti (*Analyst* 65, 437) also reported this irregularity together with data to show that the results

CHARACTERISTICS REPORTED ON FATS DURING THE YEAR

Oil or Fat Source	% of oil or fat	Density	Refr. Index	Acid No. (% Free Acids*)	Sapon. No.	Iodine No.	R-M No.	Polenske No.	Acetyl No.	% Unsap.	(SCN) No.	m.p.
Apricot kernel (Mongolia) ⁸	13-20	0.9187 ¹⁵	1.4698 ³⁰ 1.4654-1.4662	0.5 0.41-0.87	185.1-197.7	89, 28 70.6-76.4				0.2-0.7	76.8	
Avocado pear (Peru) ¹				2.4	190	53						30-32
Baba kernel				11.8*	192	56						
<i>Mimusops Heckelii</i> ³	52			2.8	211.0	91.3				1.6		
<i>Ouvatea parviflora</i> ⁶	11.4	0.910	1.4603 ³⁰	3.8*	318.6	37.78	31.5	0.6	32.33	0.165		47.6
<i>Banksia variegata</i> tree seed kernel ⁷	16.5	0.9206 ³⁰ 0.9273 ³¹	41.3 (Zeiss-Wollmi)	23.7*	186.12	97.98	8.20	6.17	23.26	15.55		40-52
Butter fat of Turkish buffalo ⁸	5.39	0.9475 ¹⁵	47.53° (Butyro)	6.9	179.6	174						
<i>Callistemon lanceolatum</i> berries ⁹	19.0	0.9319 ³⁵	1.4712 ²⁰ 1.4660 ³⁸	10.5	189.1 178.6	77.5 29.1	2.5 1.21	1.65	37.2	0.67 0.73		
<i>Camphora basilica</i> seeds ¹⁰	27			93.2	200.5	124.2	6.6	12.5		0.38	68.08-69.07	24.2
<i>Carya Cordifolia</i> nuts ¹²	15.8	0.9203 ^{30/4}	1.4789 ²⁵	1.1	260.6	8.7	0.20	0.22				
<i>Cerbera odallam</i> (tree) kernel ¹³	47.2	0.9074	1.4691 ⁴⁰	0.41	177.8	87.11	1.81	0.25	19.05			
<i>Chrysanthemum</i> seed	28-35	0.9197 ^{25/25}	1.4698 ²⁵	0.95	193.0	100.9	0.47	0.20	2.4	0.48		
Coconut kernel (Hainan Island) ¹⁰	12.4-13.9	0.9210-0.9245 ³⁰	1.4712-1.4720 ²⁰	0.71-3.62	197.2-197.5	81.67-84.97			2.28-6.62			
<i>Crambe hispanica</i> seeds ¹⁷	6.7	0.9219 ²⁵	1.4789 ²⁵	2.4	184.6	158.4	0.20	0.22				
<i>Euphorbia lathyris</i> seeds ¹⁸	19.0	0.9156 ^{31,5}	1.4691 ⁴⁰	16.6	189.62	90.73	1.81	0.25	19.05			
Fennugreek seed	28-35	0.9197 ^{25/25}	1.4698 ²⁵	0.95	193.0	100.9	0.47	0.20	2.4			
<i>Triagonella foenum graecum</i> ¹⁰			1.4706-1.4713 ²⁵			129-132					76.2-77.8	
<i>Ferula aliiaca</i> fruit ²⁰	11.5	0.9116 ^{25/25}	1.4710 ²⁵		1.84	120.4	0	0.24	4.18	1.65		
Grapefruit seed ²¹	11.00	0.9188 ^{15,5}	1.4730 ²⁵		190.0	136.4				1.0		
Grape (Muscadine) seed	27.1-31.5	0.9335-0.9399 ^{15/4}	1.4844-1.4852 ²⁰		189.8-195.25	177.5-197						
<i>Muscadina rotundifolia</i> ²²												
Highbush Cranberry seed												
<i>Viburnum opulus</i> ²³												
Kentucky Coffee-bean tree nut ²⁴												
<i>Lallemunia ibérica</i> seeds ²⁶												
Livers, animals ²⁷												
elephant												
dog												
rabbit												
ben												
Macaula nut	65	0.9212 ¹⁵	1.4631 ¹⁵	3.40	239.7	23.6			13.2	1.2	23.6	
<i>Azarcornia totia</i> ²⁹	44	0.9163 ³⁰	1.4665 ³⁰	9.5	197	74.3						
Margosa tree fruit (dried) ³⁰												
Millet (German)												
<i>Sataria italica</i> ³¹	3.55	0.9193	1.4710 ³⁰	0.99	185.7	41.94	0.48	1.4	33.14	2.39		
<i>Oenothera biennis</i> seeds ³³	27.36	0.9291 ²⁰	1.4801 ²⁰			147.68				1.84		
Palm Kernel												
<i>Cocos pulposa</i> ³⁴	59.5	0.9603 ^{15,5}	1.4554 ²⁵ 1.4808 ³⁰	1.7 20.5	260.3 132.6	24.6 149.8	7.1 1.03	24.8 2.00	20.68	0.44 7.0	22.4	17-18
<i>Phascolus vulgaris</i> ³⁵												
Pine seed												
<i>Pinus Pincazo</i> ³⁶	45	0.9181 ^{15/15}	73.2 (Butyro)	1.2	197.3	121.3	1.94	7.67		0.58	77.9	
<i>Pistacia vera</i> ³⁷	48	0.9241 ⁵		0.6*	194.5	92.3				0.35		
<i>Plantago psyllium</i> ³⁸	6.4	0.9276 ^{15/15} 0.9269 ^{20/4}	1.4770 ¹⁰ 1.4792 ²⁰	2.89 2.84	194.2 191.9	139.9 154.9			20.68	0.40 1.65	77.5 94.9	
Poppy seed (Manchoukuo) ³⁹	9.44											
Sapota tree seed												
<i>Rosa canina</i> ⁴¹	20	0.8725 ³¹ 0.9287 ^{15/4}	1.4631 1.4814 ²⁰	8.94* 0.41	205.4 194.3	59.8 164.7	2.8			1.8 0.25		
<i>Acharas sapota</i> ⁴²												
Seal (Antarctic) skin ⁴⁰												
Spiny fern												
<i>Aspidium dilatatum</i> ⁴⁴												
Tobacco seeds ⁴⁵	41.5	0.9144 ²⁰	1.4648 ³⁰ 1.4618 ³⁰ 1.4722 ⁴⁰	0.66 2.89	157.4 188	116.7 129.2	8.32	0.37		14-21		
Turtle (Ocadia stansis) ⁴⁶	6.4	0.9114 ^{30/4}		0.52	202.10	93.27				2.8		
body	19.5	0.9035 ^{30/4}		10.12	203.32	78.98				10.7		
liver	2.5	0.9418 ^{40/4}		7.58	198.88	102.53				6.2		
ovary												
Turtle	18-19	0.9185 ^{15/4}	1.4758 ²⁰	0.51	205.19	49.9	1.07	0.16	3.85	0.91	39.9	29
<i>Chelonia mydas</i> ⁴⁷												
<i>Xanthium strumarium</i> ⁴⁸												
total fruit		0.9236 ¹⁵	1.4758 ²⁰			136.17						

SUPPLEMENT TO CHART ON CHARACTERISTICS

Oil or Fat Source	Hegner No.	Diene No.	Solidification Point
Apricot kernel (Mongolia) ³			—20
Avocado pear (Peru) ⁴			7° to 9°
<i>Bauhinia variegata</i> tree			
Seed kernel ⁷	92.0		
Butter fat of Turkish buffalo ⁸	87		41.3
<i>Callistemon lanceolatum</i> berries ⁹	79.71		37-43
Coconut kernel (Hainan Island) ¹⁰	90.7		
Fenugreek seed			
<i>Trigonella foenum graecum</i> ¹⁹	88.21		
Highbush Cranberry seed			
<i>Viburnum opulus</i> ²³	95.45	5.0	
Kentucky Coffee-bean tree nut ²⁴		1.73	
Macauba nut			
<i>Acrocomia totia</i> ²⁹			18.3
Margosa tree fruit (dried) ³⁰	88.3		
Millet (German)			
<i>Setaria italica</i> ³¹	94.45		
<i>Plantago psyllium</i> ³⁸	94		—17
Poppy seed (Manchoukuo) ³⁹			—18
Sapota tree seed			
<i>Acharas sapota</i> ⁴²		92.6	
Spiny tern			
<i>Aspidium dilatatum</i> ⁴⁴	89.8		
Tobacco seed ⁴⁵			16
Turtle			
<i>Chelonia mydas</i> ⁴⁷			16

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COMPOSITION OF THE FAT ACIDS

Fat Source	Common Saturated Acids			Common Unsaturated Acids			Other Acids Some designated by No. of C and double bonds (= —2H)
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
<i>Algae, Alaria Crassifolia</i> ¹							
thallus	4.64	18.58	8.4	2.3	C16 (—2H) 3.1, C16 (—4H) 9.2
fructation	10.20	40.82	8.4	1.5	C18 (—8H) 14.6 C16 (—2H) 2.5, C16 (—4H) 5.9 C18 (—8H) 2.5
<i>Allanblackia floribunda</i> kernel ²	2.9	57.1	39.4	0.4	Arachidic 0.2
<i>Allanblackia parviflora</i> kernel ²	1.5	2.3	52.0	43.9	Arachidic 0.3
Baku kernel							
<i>Mimusops Heckelii</i> ⁵	4.4	36.0	58.5	0.3	Arachidic 0.5 C16 (—2H) 0.3
<i>Bauhinia variegata</i> tree seed ⁷	1	17	13.4	31.8	35.9	Lignoceric 1
Butter fat of Turkish buffalo ⁸	7.22	25.63	16.18	35.20	1.98	Butyric 4.24, caproic 1.28, caprylic 0.42, capric trace, lauric 2.99, arachidic 3.24
<i>Canarium Commune</i> seed ¹¹	30.5	10.2	39.9	18.7	0.7	
<i>Carya cordifolia</i> nuts ¹²	6.4	5.4	86.0	
Coconut (prepd. from fresh coconut milk) ¹⁵	16.89	7.36	4.01	0.81	Caproic 0.38, caprylic 6.54, capric 8.95, lauric 55.06
Coconut kernel (Hainan Island) ¹⁶	13.06	7.46	2.03	5.46	2.31	Caprylic 8.73, capric 8.05, lauric 51.34, arachidic trace
<i>Euphorbia lathyris</i> seed ¹⁸	6.0-7.4	87-90	3.8-6.0	
Fenugreek seed							
<i>Trigonella foenum graecum</i> ¹⁹	7.3	2.4	21	37	19	Arachidic 0.9, behenic 0.6
Kokum butter seeds							
<i>Garcinia indica</i> ²⁵	1.2	5.3	52.0	41.5	
<i>Litsea cubeba</i> seeds ²⁷	4.5	19.6	Lauric 53.2, capric 22.9
Niger seed							
<i>Guizotia abyssinica</i> ³²	1.7	5	2	38.9	51.6	Arachidic, behenic and lignoceric traces
<i>Oenothera biennis</i> seed ³³	5.6-5.7	26.4-27.6	58.1-64.5	2.3-9.7	
Ox bone marrow ⁴⁹	2.6	32.2	15.1	43.2	2.5	Lauric 0.1, C14 (—2H) 0.7, C16 (—2H) 3.0
Ox depot fats							
of Bombay, India ⁵⁰	5.8	40.8	25.5	22.9	1.1	Lauric 0.1, arachidic 0.7, C14 (—2H) 0.4, C16 (—2H) 2.4, C20-22 0.3
of Calcut, India	5.2	33.4	27.9	29.0	1.5	Lauric 0.5, arachidic 0.5, C14 (—2H) 0.4, C16 (—2H) 1.5, C20-22 0.1
Palm kernel							
<i>Cocos pulposa</i> ³⁴	7.0	1.8	1.3	23.4	2.5	Caproic 1.6, caprylic 10.2, capric 14.2, lauric 36.6, unsapon. 0.44
Sapota tree seed							
<i>Acharas sapota</i> ⁴²	6.2	12.6	12.0	66.2	1.4	Lauric 1.6
<i>Schizandra chinensis</i> ⁴³	3.7	28.5-34.1	54.9-60.8	Resin acids 8.7
Turtle							
<i>Chelonia mydas</i> ⁴⁷	7.2	15.2	6.8	39.4	Capric 3.5, lauric 14.2, C14 (—2H) 2.6, C16 (—2H) 10.9
<i>Xanthium strumarium</i> seed ⁴⁸	8.2	27.1	63.36	

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 50. *Ibid.* 1301.

for linoleic acid were too high when the reaction was carried out for 24 hours as recommended by the standard methods. These investigators recommended that the values determined empirically under prescribed conditions should replace the hitherto accepted theoretical values.

In control of bodying drying oils, Knowles *et al.* (*J. Oil Colour Chem. Assoc.* 23, 4) recommended that the degree of unsaturation of the partially oxidized fat could be determined by the use of potassium permanganate to oxidize the ethylinic linkages; peroxides did not interfere. A procedure for evaluating degree of polymerization of stand oils by McQuillen and Woodward (*ibid.* 8) depended on determining the acetone insoluble contents.

The carbonyl number of fats has been used to give a measure of the amount of ketones present in fats containing ketonic fat acid. During the year Kaufmann and Liu (*Fette u. Seifen* 47, 506) recommended the application of this procedure in investigating fat spoilage. In fats containing abundant active oxygen a correction, peroxide value $X 0.028$, was subtracted from the carbonyl value.

Regilyant (*Farmatsiya* 1940, #5, 9) discovered that by using a 10% solution of phosphoric acid in acetone as a catalyst, acetylation in the determination of acetyl values can be effected in 15 minutes.

Schloemer (*Z. Untersuch. Lebensm.* 79, 463) plotted the relationship between butyric acid and Reichert-Meissel numbers of butter samples. The correlation factor was $+ 0.88$.

Among the publications on adulteration those on olive oil were most numerous. A color reaction for distinguishing refined from virgin olive oil by Romeo (*Il chim. italiano* 2, 33 pp) depended on the pH of 90% alcohol solvent with which the oil was washed. Bromophenol blue was used as the indicator. Fachini and Martinenghi (*Olii minerali grassi e saponi* 19, 86, 136) criticized the above method because refined oil could be washed sufficiently to remove the last traces of soap thus causing an error in the test. After Romeo (*ibid.* 134) reaffirmed the reliability of his test the above two investigators added more evidence which would cast doubt as to the reliability of the method.

Liso (*Boll. soc. ital. biol. sper.* 14, 465) described the fluorescence of various types of olive oils. This fluorescence was lost on treating with carbon. Dorta (*Atti X Cong. inter. chim.* 4, 517) recorded that the presence of extracted oil in virgin oil can be detected by determining the solidification point of the unsaponifiable. This characteristic on the extracted oil was much higher than the figure 20 to 22° usually obtained on natural virgin oil. Marcille (*Ann. chim. anal. chim. appl.* 21 311; *Compt. rend.* 209, 730) recommended the use of the Bellier number for detection of adulteration of olive oil with peanut oil in olive marc and in canned sardines. However, it was pointed out that olive oil from northern Tunis gave abnormally high Bellier numbers when small amounts of alcohol were used in the fractional precipitation of the solid acids. Yalour (*Rev. facultad cienc. quim.* 14, 197) reviewed control methods used on olive and other seed oils. Dickart (*Am. J. Pharm.* 112, 131) reported that palm and olive oils produced a blue color with antimony trichloride. Other oils gave colors ranging from yellow to red. The test was useful for differentiating olive from teaseed oil, hydrogenated fish oil and hydrogenated cottonseed oil, oiticica and tung oil from lumbank, and perilla and linseed oil.

Bauer and Seber (*Kazett* 27, 340) and Fincke (*ibid.* 365) carried on a polemic on the relative merits of color reactions for detecting the presence of extracted cacao-waste fat in cacao fat. Grossfeld (*Z. Untersuch. Lebensm.* 79, 477) pointed out that the amount of husk fat in cacao fats can be estimated from the sterol content. Richard (*Bull. official office intern. cacao chocolat* 9, 267) and Finke (*Z. Untersuch. Lebensm.* 80, 12) reviewed the information on melting points, solidification curves and other characteristics. These were interpreted to show how they could indicate adulteration of cacao butter. A "fat-spot-test" was devised by the latter for detection of adulteration. At 18° a piece of cacao butter placed on unglazed white paper would not form a fat spot; a product containing 5-10% sesame, olive, or other oils gave a spot in the test within 24 hours.

Sutton (*Analyst* 65, 623) thoroughly reviewed methods for detecting the adulteration of lard. Williams (*ibid.* 596) prepared some constructive criticism on the American Chemical Society method for determining beef fat in lard by the modified Bömer procedure.

Livari *et al.* (*Le Lait* 19, 785) investigated the Hoton method for detecting the presence of cocoa fat in butter. The method depended on the refractive index of the insoluble volatile fraction obtained in the Reichert-Polenske distillation. Abnormal values were often due to feed and the method failed on sheep's and goat's milk cheese. A method for detecting adulteration of clarified butter by Muthanna and Mukerji (*Current Sci.* 9, 120) made use of ultraviolet fluorescence technic. Cow and buffalo melted butter gave a deep green fluorescence while other animal and vegetable oils gave various shades of blue by the test. Azadian (*Ann. fals.* 33, 23) recorded data on butters from Egyptian and Sudanese cows in an unsuccessful effort to find a difference which would permit distinguishing butters from these two sources.

Mineral oil could be detected in almond or olive oil by the formation of a turbidity on the addition of 70% alcohol at a temperature above 20° (Anselmi—*Rend. ist. sanita publica* 2, 979).

During the year various committees of societies here and abroad made recommendation and suggested modifications of existing standard methods for the analysis of fats and fat products.

DETERGENTS

Very little was written on the usual fat soap stocks. On rosin, Pohle and Speh (*Oil & Soap* 17, 100, 214) made recommendations to prevent off color in rosin soaps and recorded the properties of soaps containing rosin. The characteristics, *i.e.*, detergency, surface tension, etc., of some of the rosin acid soaps oxidized rosin acid soaps and soaps of mixtures of fat acids and rosin acids were recorded. A method of preparing soap stock from black tall oil comprised crystallization of the rosin acid followed by distillation procedures (Hasselstrom—*U.S.* 2,190,660). Scott and Brown (*U.S.* 2,227,203) saponified the black liquor and then separated the soap from lignin and other impurities.

Among the patents on the use of "builders" in detergents, the majority were on special methods of using alkali phosphates, pyrophosphates and metaphosphates alone, in mixtures and together with silicates and carbonates (Avedikian—*U.S.* 2,187,536; Chem. Fabrik J. A. Benckiser G.m.b.H.—*Ger.* 678,841; Dabsch and Vredenburg—*Ger.* 682,329 *Cl.* 23c; Hall—*U.S.* 2,191,199; Hans H. Hutte G.m.b.H.—*Ger.* 681,370 *Cl.* 22g;

Brodman—*Fr.* 842,473; Lever Bros. and Unilever Ltd.—*Brit.* 509,343; Standard Oil Development Co. and I. G. Farbenind. A.-G.—*Brit.* 509,730; *Fr.* 842,985; Kin *et al.*—*Japan* 128,294). Among the patents on the use of silica compounds in detergents, one was on the preparation of a special silica "builder" from caustic and sodium metasilicate liquor (McDaniel—*U.S.* 2,206,289), one on the use of silica gel in soap (Moreau—*Belg.* 434,326), one on the use of sodium silicate and starch (Curzon—*U.S.* 2,193,329) and another on preparing a cleanser containing a mixture of earths, silica and aluminum silicates (Tainton—*U.S.* 2,213,641). Wood meal (Bergen—*Belg.* 435,506), hydrolyzed wood pulp (Mednikova—*Russ.* 52,312), solubilized casein (Societe savons francais—*Fr.* 844,500), hydrophilic polymerized vinyl compounds (Rowe—*U.S.* 2,226,075), latex (Zartler—*Hung.* 123,521) and a specially prepared silk powder (Lawson—*U.S.* 2,194,858) were other ingredients patented as soap fillers or builders. Pectin, a soap filler that has been used in Italy for at least 15 years, was the subject of a monograph by Wittka (*Seifensieder-Ztg.* 67, 397, 407). Properties, method of use in soap and characteristics imparted to soap were treated in this favorable report.

Various miscellaneous substances were added to soaps for specific purposes. Aliphatic oxy compounds containing alkylolamine, alkylmercapto or alkylsulfonyl radicals were patented as superfatting agents (Henkel & Cie.—*Ger.* 671,711 Cl. 23e). Hubscher (*Seifensieder-Ztg.* 67, 206,216, 226) prepared a review on the information regarding the use of lanolin and sterols as emulsifiers and in soaps. Sulfur compounds were used to remove pro-oxidant metals (Hitchcock and Divine—*U.S.* 2,202,103). Mono aryl substituted biguanides were patented as soap antioxidants (Sibley—*U.S.* 2,221,333). Chromium trioxide and hexamethylene tetramine were added to toilet soaps to prevent perspiration (Erwin—*Brit.* 506,903; *Fr.* 841,802). Hardwood oil of boiling point 180-240°, together with alcohol, was said to yield antiseptic properties in soap (Figg—*U.S.* 2,196,763). Soap containing sulfathiazol was effective in the elimination of impetigo, a skin infection (*Soap* 16, #7, 40). Acid soap washing agents containing a water-soluble organic moth-proofing agent were said to be effective (Stötter and Hermann—*U.S.* 2,184,951). Maple syrup was added to toilet soap to fix perfume (Segal—*Can.* 389,475). Phosphate esters of tributyl, isopropyl and other water-insoluble alcohols were recommended for inhibiting the foam of soap solutions (Brodersen and Quaedvlieg—*U.S.* 2,200,485).

Other special soaps were a solution of partially saponified oil in organic solvent for use as an emulsifier of asphalt, cutting oil, lotions, etc. (Kapp—*U.S.* 2,207,256-7; Sherman—*U.S.* 2,207,229), general metallic soaps of fish oils (Licata—*U.S.* 2,211,139) and tin soaps (Texas Co.—*U.S.* 2,205,994; *U.S.* 2,206,002). Almond meal was recommended as a cleanser for those whose skin could not tolerate soap (Schwarz—*Seifensieder-Ztg.* 67, 416). Another soap for this purpose contained sulfonated neat's-foot oil, petrolatum, gelatin and corn meal (Klauder—*Ind. Med.* 9, 221).

Ono (*J. Agr. Chem. Soc. Japan* 15, 843, 953) studied the saponification velocities of fats in benzene solution. Fish oils were saponified more rapidly than vegetable oils at 30°. The reaction velocity of the fat acid esters decreased reciprocally with the molecular weight. Heilberg (*Ger.* 684,100 Cl. 23e) preferred mixing fat acids with trisodium phosphate and heating to 80° before saponification.

Wigner (*Soap, Perfumery Cosmetics* 12, 751) prepared a discussion on the effect of air in soaps. Apart from floating soaps, air was an undesirable ingredient because it affected texture, viscosity and specific gravity. These variations required new adjustments of cutting wires, caused trouble in pumps and conduits.

McBain *et al.* (*J. Am. Chem. Soc.* 62, 866; *J. Soc. Chem. Ind.* 59, 243; *J. Phys. Chem.* 44, 1013 and Vold *et al.* (*ibid.* 1058; *Soap* 16, #6, 31) presented new information on phase behavior of soaps. The former diagrammed the phases occurring in soap kettles during the manufacture of soap from several animal and vegetable oils. A method was developed for calculating the nigre boundary of a mixed or commercial soap from a knowledge of the composition of the soap and of the phase behavior of the single constituent soaps. Vold *et al.* prepared solubility curves over a large temperature range for anhydrous sodium palmitate in several organic solvents. These data undoubtedly aided in the development of new high quality soaps and of new manufacturing procedures. Datta *et al.* (*Soap, Perfumery Cosmetics* 13, 375) found the detergency of the neat soap and nigre of a soap made from a mixture of fats the same. They suggested that some low molecular weight acids favoring wetting and some high unsaturated acids favoring emulsification passed into the nigre, thereby maintaining its detergency at the level of the original soap mixture and lowering the detergency of the fitted soap to a considerable degree.

Many new improvements for continuous soap making systems were patented (Refining, Inc.—*U.S.* 2,179,001; 2,185,563; 2,190,591-2; 2,193,786, 2,195,377; 2,218,279; 2,225,575; *Metallgesellschaft* A.-G.—*Fr.* 844,687; Lever Bros.—*U.S.* 2,215,539). The developments included design of a multiple stage saponification system, addition of emulsifiers to prevent stratification, use of an inert gas in the system, distillation of glycerine from molten soap while running in a thin layer over a heated surface or by spraying into a vacuum chamber, a device for withdrawing soap from a vacuum chamber and means of controlling water content. Descriptions of the processes covered by patents to Refining, Inc. (Mattikow—*Oil & Soap* 17, 184) and to Procter & Gamble (Anon.—*Soap* 16, #5, 25) were published.

Additional mechanical developments in soap processing were the spray drying of soap in combustible gas (Alexieff—*Gas* 16, #3, 17), an improvement in mineral oil soap by heating with water under pressure (Harder—*Ger.* 684,968 Cl. 23e), a new soap crutcher (Burt—*U.S.* 2,203,980), a machine for working soap to make it homogenous (Pease—*U.S.* 2,048,286), a plodder attachment which deaerated soap before plodding (Strain—*U.S.* 2,213,772), a soap cutting machine (van Buren—*U.S.* 2,216,525), apparatus for the manufacture of tubular soap together with means of collapsing the tubes to form ribbons (Walter—*U.S.* 2,202,972-4) and means of covering soap bars with a soft sheath (Meyer—*U.S.* 2,198,880).

Two methods of producing floating milled soap were described. In one (Hood—*U.S.* 2,210,924) exact amounts of milled soap were placed in containers, evacuated and pressed; in the other (Eagen—*U.S.* 2,195,399) means for producing a hollow core in the soap bars was devised.

Many publications on the manufacture of soaps were reviews of past developments, articles fostering certain ingredients and some of political-economical nature. These are most conveniently incorporated in this review by reference.

Reviews. Ramsey—*Soap* 16, #1, 30. Wigner—*Chem. & Ind.* 59, 335. Vallance—*Soap, Perfumery Cosmetics* 13, 848.

Control of soap—plant operations. Peterson—*Oil & Soap* 17, 66.

Cleansing effect of soap. Watzinger—*Industria y quim.* 3, 1.

Fat acids for soap making. Rayner—*Soap, Perfumery Cosmetics* 12, 898.

The Twitchell process. Wigner—*Soap, Perfumery Cosmetics* 12, 979.

Cold soaps. Vallance—*Soap* 16, #2, 1.

White soaps. Kemp—*Soap* 16, #12, 25.

Toilet soaps. Schmalfuss—*Fette u. Seifen* 47, 526; Tyler—*Soap* 17, #1, 27; Kalish—*Drug Cosmetic Ind.* 46, 280; Kawai—*J. Soc. Chem. Ind. Japan* 43B, 80.

Uses for tall oil soaps. Henk—*Seifensieder-Ztg.* 67, 22; Anon.—*Soap* 16, #4, 61.

Specialized soaps and cleaners. Smith—*Soap* 16, #4, 30; Rayner—*Soap, Perfumery Cosmetics* 13, 437.

Soap making in Jena. Trebitz—*Fette u. Seifen* 47, 530.

Fillers and electrolytes in soaps. Cardew—*Manuf. Perfumer* 4, 336; Nevolin—*Masloboino Zhir. Dclo* 15, #4, 18.

Phosphate builders. Janota and Hull—*Oil & Soap* 17, 96; Cobbs *et al.*—*ibid.* 4; Rudy *et al.*—*Angew. Chem.* 53, 525; Gilmore *et al.*—*Ind. Eng. Chem.* 32, 1233; Vallance—*Soap, Perfumery Cosmetics* 12, 765; Bowman—*Soap* 16, #4, 23.

Clay and bentonite fillers. Schmucker and Radler—*Fette u. Seifen* 47, 213; Anon.—*News Ed. A.C.S.* 18, 990.

Use of silicates in soap. Lehmann—*Allgem. Oel- u. Fett-Ztg.* 37, 122; Foulon—*Seifensieder-Ztg.* 67, 181; Davidsohn—*Soap, Perfumery Cosmetics* 13, 701; Kemp—*Soap* 16, #6, 27; Snell—*ibid.* #11, 35.

Milk and protein soaps. Augustin—*Soap, Perfumery Cosmetics* 12, 586.

Silk in soap. Spirk—*Mydlar a Vonavkar* 17, 6.

Superfating soaps. Davidsohn—*Soap, Perfumery Cosmetics* 13, 186.

Antiseptic soaps. Frydlender — *Arch. drogeuric pharm.* 6, 111, 138, 165, 194.

Dyeing of soap. Richter—*Fette u. Seifen* 47, 61.

Changes in soap due to perfume. Henk—*ibid.* 537.

Soap preservatives. Augustin—*Am. Perfumer* 40, #4, 53.

New uses for soap. Smith—*Seifensieder-Ztg.* 67, 31.

Soaps in the rubber industry. Garner—*Chem. Age* 42, 111.

Chain-conveyor soaps. Warth—*The Crown* 28, #5, 38.

Soaps for creosote disinfectants. Datta *et al.* *Soap, Perfumery Cosmetics* 12, 583.

Hardening semi-axes with soap solutions. Vozlinski and Chirikov—*Novosti Tekhniki* 1940, #9, 20.

Surface active agents in degumming silk hosiery. Morgan and Seyferth—*Am. Dyestuff Repr.* 29P, 616.

Waste in soap manufacture. Wigner—*Soap, Perfumery Cosmetics* 13, 310.

Soap substitutes. Meyer—*Fette u. Seifen* 46, 733; 47, 23.

Laundering with synthetic washing agents. Walter—*Fette u. Seifen* 47, 120.

Enzymes save soap. Zacharn—*Fette u. Seifen* 47, 463.

A list of commercially available detergents, wetting, dispersing and emulsifying agents. Cupples—*U. S. Dept. Agr. Bur. Entomol. Plant Quarantine E* 504, 56

pp.; Sluhan—*Paper Trade J.* 111, #8, 26; *Am. Dyestuff Repr.* 30, 1, 18.

Turkey red oil. Anon.—*Seifensieder-Ztg.* 67, 88.

Sulfonated fatty alcohols. Sisley—*Rev. gen. mat.* 44, 27, 66.

Primary amine detergent, wetting and emulsifying agents. Ralston—*Oil & Soap* 17, 89.

Alkyl amine hydrochloride detergents from mineral oils. Padgett and Degering—*Ind. Eng. Chem.* 32, 486.

Information on detergent action contained data on adsorption upon textiles and data on soap solutions. Data on soap adsorbed by various textiles from solutions of various concentrations and from solutions containing alkaline salts were tabulated by Colt and Snell (*Oil & Soap* 17, 33). Additions of sodium carbonate to fixed concentrations of soap impaired detergency, thus indicating that the effect might have been due, not to the prevention of hydrolysis, but to shifting the soap in the direction of undissociated crystalloid or micelle form. However, fabrics selectively adsorbed alkali in amounts greater than fat acid radicals, thus the detergency was benefited by sodium carbonate in that it prevented development of acid soaps. The carbon dioxide of the air reduced the pH of the foam, but did not affect the washing solution.

In work by Brill and Rieder (*Angew. Chem.* 53, 100) on adsorption of soap by textiles, it was desired to determine whether the soap was adsorbed in molecular or micellar form. Molecules of sodium stearate adsorbed on nitrocellulose were vertical and formed 2-dimensional hexagonal crystals. With higher concentrations, several layers were adsorbed. When fresh, the films washed off easily, but on aging they were much harder to wash off. McBain and O'Connor (*J. Am. Chem. Soc.* 62, 2855) reported that colloidal dispersions of hydrocarbons in soap solutions were thermodynamically stable since the vapor pressure was significantly less than that of the free hydrocarbon until the solution was approximately saturated. They also showed that the solubilities of the hydrocarbons in the soap solutions were greater when alkali silicate was added. Angelescu and co-workers (*Kolloid-Z.* 89, 47; 90, 302) recorded that free fat acids had no appreciable effect on the viscosity of soap solution but in the presence of cresol marked maxima were obtained with various free fat acids; the latter effect was increased by electrolytes. This was interpreted to suggest that cresol tended to change a lyophobic soap-acid complex to a lyophilic complex. Angelescu and Woinarosky (*Bull. sect. sci. acad. roumaine* 22, 251, 261) recorded that cresols increased the degree of dispersion and degree of solvation of soaps in water as indicated by an increase in electrical conductance. Stauff (*Z. physik. Chem.* A185, 45) recorded the activity coefficient of the sodium ion and of sodium palmitate solutions of different concentrations. Hydrolysis curves of the soap showed sharp breaks at a critical concentration which was taken as the characteristic quantity for equilibrium between a colloidal and a molecular dispersed system. The same author (*Kolloid-Z.* 89, 224) reported that the absorption of x-rays indicated the occurrence of large colloidal particles in 0.1 N solutions of sodium tetradecyl sulfate and 0.2-0.25 N solution of sodium laurate. Lamm and Högberg (*ibid.* 91, 10) used refractometric methods for measuring the free diffusion of soaps in water and followed the course by photographic means. The method permitted the study of factors such as temperature, impurities, etc., that affect the formation of micelles.

Some attention was given to evaluation tests for soaps. Halliday *et al.* (*J. Am. Pharm. Assoc.* 29, 367) determined chemical composition, surface tension, ability to form suds, ability to remove soil and pH of several commercial soaps. No correlations were found between ability to form suds and ability to remove soil, or between total alkalinity and pH. Liesegang (*Fette u. Seifen* 47, 458) devised a procedure for determining the soot carrying capacity of washing agents. A "soot number" was a measure of the amount of washing agent in a solution containing soot necessary to prevent a soot stain forming on barite paper on placing one drop of the mixture on it and rinsing with water. Kind (*ibid.* 55) tabulated the effect of 50 washings on various cloths. Walter (*ibid.* 46, 729) tabulated data from a series of 8 tests comparing fat alcohol sulfonates with soaps. The advantages of the former were fat savings, no alkalinity, cloths easily rinsed and washing time reduced. However, they were less effective than soap for removing soil, more corrosive on copper equipment and, since dirt was highly dispersed, they might gray cloths.

Several control procedures for soap factories were developed. Divine (*Oil & Soap* 17, 2) designed a laboratory soap-boiling apparatus of glass. Distillation methods for moisture analyses were shown to be affected by the presence of glycerine (Trusler—*Ind. Eng. Chem. Anal. Ed.* 12, 509). The error was negligible when toluene was the distillation medium.

New procedures for determining the fat acids present in soaps were developed by several investigators (Govan—*Oil & Soap* 17, 262; Semenov and Zaliopo—*Masloboino Zhir. Delo* 16, #2, 22; Metzner—*Fette u. Seifen* 47, 356; Bornhardt—*ibid.* 219 and Hagen—*Seifensieder-Ztg.* 67, 72. One method dealt with the use of bottles similar to those used for butter fat determinations by the Babcock method. Several methods dealt with liberating the fat acids, extracting them with solvent and determining them both gravimetrically and volumetrically. With soaps containing clays, means of preventing emulsions with organic solvents were suggested. In a procedure specifically for castor oil soap stock, it was necessary to precipitate the fat acids as calcium salts and extract the oil (Shuraev and Vasel'eva—*Masloboino Zhir. Delo* 15, #6, 27). Total fat acids in this material could be determined in the usual manner. A potentiometric method for estimating caustic alkali and alkali carbonates in presence of each other in soap was described by Hesse (*Fette u. Seifen* 47, 41). Parsons and Haberstroh (*Oil & Soap* 17, 62) recorded that complex phosphates in soap were not completely precipitated by ammonium molybdate in the American Oil Chemist's method. Hydrolyzing the complex phosphates to the ortho form by boiling for 15 minutes with nitric acid solution was recommended. Other analytical reports dealt with recommendations for the analysis of washing powders (Kubias—*Seifensieder-Ztg.* 67, 445), control procedures for saponifying with sodium carbonate (Bliner and Repin—*Masloboino Zhir. Delo* 15, #6, 27) and there were also reports of various soap analysis committees.

Stock and Francis (*J. Exptl. Med.* 71, 661) reported that soaps rendered epidemic influenza virus non-infectious. The most effective were oleic, linoleic and linolenic acids or soaps. In similar work Burnet and Lush (*Australian J. Exptl. Biol. Med. Sci.* 18, 141) graded the virus-inactivating action of several wetting agents on several pathogenic viruses. Pohle and Stuart (*J. Infectious Diseases* 67, 275) developed evidence to in-

dicate that commercial bar toilet soaps were inactive as germicides for resident bacteria of human skin.

Information on the irritating effects of various soaps on human skin was developed by Edwards (*Soap* 16, #12, 33) and by Emery and Edwards (*Oil & Soap* 17, 64). Generally, soaps of oils containing lower molecular weight acids caused irritation; castor oil soap was most irritant of all soaps studied, and potassium soaps were more irritant than sodium soaps. Damrau (*Med. Record* 152, 187) tested the blandness of castile soaps by patch tests and rabbit-eye tests. The imitation castile soaps were more irritant than the genuine products. In a publication on the dermatitis of hands of housewives (Jordan *et al.*—*J. Am. Med. Assoc.* 115, 1001) the role of soaps and the method of prevention were emphasized. Wagner (*Seifensieder-Ztg.* 67, 421, 432) discussed the hazards in the soap industry. The sources for injury to health were those affecting the blood, irritations and burns or scalds.

General information publications and reviews on glycerine covered synthetic glycerine (Williams *et al.*—*Chem. & Met. Eng.* 47, 834) uses of glycerine in chemical specialties (Leffingwell and Lesser—*Chem. Ind.* 47, 517), glycerine substitutes (Ohl—*Allgem. Oel-u. Fett-Ztg.* 36, 245; Hübscher—*Seifensieder-Ztg.* 66, 345) and significant cosmetic and pharmacological properties of glycerine (Bauschinger—*Fette u. Seifen* 46, 723).

Several publications contained notes on glycerine production. Govan (*Oil & Soap* 17, 108) fostered pH meter control in the operations to reduce corrosion in evaporators. Ueno and Yonese (*J. Soc. Chem. Ind. Japan* 42B, 342) prepared data giving analyses of raw materials and finished products, yields, steam consumption and cost of production of glycerine by apparatus designed by the first investigator. To reduce formation of esters and acrolein in distilled glycerine, Bag (*Masloboino Zhir. Delo* 15, #4, 13) redistilled in the presence of alkalis. For the same purpose Loginov and Kuznetsova (*ibid.* #5, 15) recommended adding iron filings and an excess of lime to the distillation charge. Grover and Nicol (*J. Soc. Chem. Ind.* 59, 175) recorded the vapor pressure of solutions containing 25 to 92% by weight of glycerine.

The patents on production of glycerine by fermentation described a method of aerating the mash to provide for energetic respiration of the yeast (Haehn—*U.S.* 2,189,793); a distillation apparatus (Peterson—*U.S.* 2,215,189) and means of recovery by selective solvents (Mnookin—*U.S.* 2,194,665; Deutsche Gold- u. Silber-Scheideanstalt—*Ger.* 684,014 *Cl. 6b*; Henkel & Cie.—*Ger.* 682,911 *Cl. 6b*). Owen *et al.* (*Intern. Sugar J.* 42, 248) described the production of glycerine from molasses. The presence of sulfites, bisulfites and ammonia were shown to increase yields.

Smith and Matthews (*Oil & Soap* 17, 58) reported that determination of glycerine by the dichromate method was reliable. The average difference between the calculated glycerine and that determined by the method was 0.12%. Fulmer *et al.* (*Ind. Eng. Chem. Anal. Ed.* 12, 729) developed a procedure using ceric sulfate for oxidation in the determination of glycerine in fermentation media. A method by Ka (*Rept. Inst. Sci. Research Manchoukuo* 4, 141) depended on the color developed in glycerine solution in the presence of an oxidizer and codeine.

During the year a considerable number of patents appeared on uses, production and new types of non-soap detergents. The new uses included breaking mineral oil emulsions, flotation agents, cosmetic creams,

lubricant adjuncts, etc. The patents on both the uses and production will be listed as in past reviews of this series. Those that dealt with uses, production and new sulfonated fats, hydrocarbons and esters were:

- Alframine Corp.—U.S. 2,185,817.
 Am. Cyanamid & Chem. Corp.—U.S. 2,176,423, 2,186,132.
 Am. Hyalsol Corp.—U.S. 2,195,418.
 Arkansas Co.—U.S. 2,186,308.
 Böhme Fettchemie G.m.b.H.—Fr. 843,583.
 N. V. Chemische Fabriek Servo—Dutch 48,113.
 Colgate-Palmolive-Peet Co.—U.S. 2,179,174, 2,187,144; 2,195,512; 2,195,581; 2,203,443; 2,204,433; 2,204,969; 2,212,521; 2,216,485.
 Deutsche Houghton Fabrik A.-G.—Fr. 842,621.
 Emulsol Corp.—U.S. 2,185,455; 2,185,541; 2,190,921; 2,221,377.
 Firma Louis Blumer—Ger. 682,590 Cl. 12o.
 Alfred Frame—U.S. 2,205,924.
 J. R. Geigy A.-G.—Brit. 509,096; U.S. 2,199,776; 2,199,789.
 General Aniline & Film Corp.—U.S. 2,218,660.
 General Aniline Works—U.S. 2,188,287.
 B. R. Harris—U.S. 2,193,963; 2,194,522; 2,201,535.
 Harshaw Chem. Co.—U.S. 2,207,989.
 Hercules Powder Co.—U.S. 2,207,890.
 I. G. Farbenind. A.-G.—Ger. 684,431 Cl. 12o; 684,927 Cl. 12o; Fr. 842,184; U.S. 2,182,178; 2,193,944; 2,201,944; 2,203,883; 2,205,021.
 Magnus Chem. Co.—U.S. 2,199,806.
 Monsanto Chem. Co.—U. S. 2,218,472.
 Naamlooze Venootschap, Chem. Fabriek Servo—U.S. 2,224,360.
 Natl. Aniline & Chem. Co., Inc.—U.S. 2,192,721; 2,196,985; 2,205,946-50; 2,221,933.
 Natl. Oil Products Co.—Can. 389,758; U.S. 2,200,299; 2,203,524; 2,203,641.
 Oil Specialties Trustees—U.S. 2,205,924.
 A. J. Van Peski and J. M. Hoeffelman—Can. 388,120; Dutch 47,715; 47,782; 47,897; U.S. 2,204,976.
 Petrolite Corp.—U.S. 2,184,794.
 E. I. du Pont de Nemours & Co.—U.S. 2,174,127; 2,174,131; 2,178,353; 2,187,338; 2,190,733; 2,193,824; 2,199,397-9; 2,199,403; 2,202,741; 2,203,339.
 Potash Co.—U.S. 2,188,931; 2,188,933.
 Procter & Gamble Co.—U.S. 2,187,244; 2,214,254.
 Richards Chem. Works—U.S. 2,181,476; 2,183,929.
 Röhm & Haas Co.—U.S. 2,178,830; 2,184,935; 2,204,323.
 Solvay Process Co.—U.S. 2,195,145-8.
 Sonneborn Sons, Inc.—U.S. 2,201,119.
 Standard Oil Development Co.—U.S. 2,192,713; 2,209,169; 2,209,445; 2,213,588; 2,214,051.
 T. Tanaka—Japan 129,042.
 E. Vogt and K. Smeykal—U.S. 2,216,257.
- Detergents were also prepared by sulfonating nitrogen compounds such as ammonia salts, indoles, proteins, amines, alkylolamines, imides or their derivatives:
- A. W. Baldwin *et al.*—Brit 508,477.
 Böhme Fettchemie G.m.b.H.—Ger. 676,343 Cl. 8o.
 Emulsol Corp.—U.S. 2,178,139; 2,198,806; 2,221,377.

J. R. Geigy A.-G.—Brit. 509,542; Fr. 841,506; U.S. 2,207,021; 2,211,771.

General Aniline Works—U.S. 2,183,856.

I. G. Farbenind. A.-G.—Brit. 508,794; 508,801; 510,308; Fr. 842,743; 842,803; U.S. 2,191,737; 2,199,780; 2,207,603.

W. Kritchevsky—U.S. 2,173,058.

E. I. du Pont de Nemours & Co.—U.S. 2,192,906; 2,201,762; 2,202,791.

Sharples Solvent Corp.—U.S. 2,203,696.

Soc. l'ind. chim. a Bale—U.S. 2,169,515.

Standard Oil Development Co.—U.S. 2,204,326.

E. Waldmann and A. Chwala—Brit. 507,766.

Among nitrogen-containing compounds that had detergent properties without sulfonation were special alkylolamides, amines, amides, quaternary ammonium derivatives, alcohol amines, nitriles, etc.

Alframine Corp.—U.S. 2,186,464.

Armour & Co.—U.S. 2,178,522.

Celanese Corp.—U.S. 2,195,564.

Deutsche Hydrierwerke A.-G.—U.S. 2,186,769.

Emulsol Corp.—U.S. 2,173,448; 2,178,173; 2,189,664; 2,190,133; 2,213,979; 2,217,683.

J. R. Geigy A.-G.—Brit. 508,148; Fr. 842,299; Swiss 206,896-914; U.S. 2,205,728.

General Aniline & Film Corp.—U.S. 2,206,249; 2,215,861-4.

B. R. Harris—U.S. 2,189,397.

Henkel & Cie.—Fr. 841,424.

Hercules Powder Co.—U.S. 2,190,734.

Imp. Chem. Ind. Ltd.—U.S. 2,206,351; Fr. 843,081.

I. G. Farbenind. A.-G.—Brit. 507,207; 509,334; Fr. 841,681; Ger. 676,407 Cl. 12p; 681,523 Cl. 12q; 681,850 Cl. 12q; 685,321 Cl. 12q; U.S. 2,169,976; 2,185,163; 2,187,823; 2,189,648; 2,191,738; 2,206,928.

Nonol, Inc.—U.S. 2,192,664.

Petrolite Corp.—U.S. 2,226,120-6.

E. I. du Pont de Nemours Co.—U.S. 2,181,929; 2,191,753; 2,194,314; 2,212,654.

Röhm & Haas Co.—U.S. 2,170,111; 2,191,922; 2,204,653.

Soc. l'ind. chim. a Bale—U.S. 2,202,328.

Warwick Chem. Co.—U.S. 2,201,041.

A miscellaneous group of detergents contained miscellaneous esters, phosphated compounds, borated compounds and some halogen-containing compounds:

Am. Hyalsol Corp.—U.S. 2,190,769.

Carbide & Carbon Chem. Corp.—U.S. 2,214,152.

Colgate-Palmolive-Peet Co.—U.S. 2,209,634.

B. R. Harris—U.S. 2,177,650; 2,177,983.

Hercules Powder Co.—U.S. 2,202,686.

I. G. Farbenind. A.-G.—Brit. 508,066; 511,036; 511,545; U.S. 2,179,209; 2,183,853.

E. M. Jablonski—Brit. 511,473.

R. Kimbara—Brit. 511,043.

Natl. Aniline & Chem. Co.—U.S. 2,178,571; 2,205,951.

Richards Chem. Works—U.S. 2,172,747.

Röhm & Haas Co.—U.S. 2,176,834; 2,178,831.

Standard Oil Development Co.—U.S. 2,192,689; 2,219,050.

* This review is the report of the American Oil Chemists' Society Committee for Review of Literature on Fats, Oils and Soaps. G. R. Greenbank, Geo. S. Jamieson, H. A. Mattill, R. C. Newton, M. M. Piskur, Chairman.