# REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1938

## PART II

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## BIOCHEMICAL

SUMES of recent literature on metabolism of fats were prepared by F. Verzár (Ann. Rev. Biochem. 7, 163), W. R. Bloor (Oil & Soap 15, 68), R. S. Sinclair (ibid. 70), and A. Horvath (ibid. 75). Verzár discussed the developments during the year 1937. The modern conception of the mechanism of absorption of fats by the intestinal wall, of the role of lecithin, cephalin, sphingomyelin, and cholesterol in fat metabolism, of the metabolic changes in fats in the liver and manner of oxidation of fats in the body were presented by Bloor. Sinclair pointed out three functions of the phospholipids. They are intermediate metabolites in fat metabolism, they serve as an oxidation-reduction system, and they are essential elements in cell structure. The amount of phospholipids present in various skeletal muscles was shown to be a function of the relative extent to which they are used. Horvath drew references from similar literature to point out that soy bean oil has muscular activity-promoting properties.

According to the current hypothesis, fat is broken down, conveyed into the intestinal cell, resynthesised, carried by a detour which avoids the liver, to which it must eventually pass for metabolic use and where it is once more broken down and perhaps re-built into phospholipid. A. Frazer (Analyst 63, 308) discovered evidence that suggests that a certain portion passes straight to the liver in a form suitable for building phospholipids or for desaturation and the remainder, avoiding the liver, passes directly to the fat depots in the form of suitable triglycerides. Since the fat acid is absorbed in aqueous solution owing to the action of bile acids, it is reasonable that it should pass by the same route as other water soluble materials. He concludes that, should this hypothesis prove correct, lipolysis must be regarded not simply as a

mechanism for breaking down fat molecules prior to absorption, but as a factor which determines what proportion of the ingested fat shall pass to the liver for immediate metabolic needs and how much shall be diverted to the storehouse for use in the future.

Two papers dealt on the mechanism of absorption of fats during digestion. Ô. Roemmele (Z. Fleisch- u. Milchhyg. 48, 241) found that the mesenteric lymph nodes of hogs were distended with milk fat 17 hours after ingestion of milk. Water and wheat bran fed hogs did not show this phenomenon of fat resorption. V. Johnson and W. Freeman (Am. J. Physiol. 124, 466) reported that during absorption of digested fat by dogs, a hemolytic agent appeared in lacteal lymph near the intestine and also in the thoracic duct lymph. It was suggested that the absorption of the products of fat digestion into the lymphatics instead of directly into the blood stream probably protects against hemolysis by a toxic agent. Glycerol may be the toxic agent.

Part of the fat injected into the ear veins of normal rabbits was absorbed and destroyed by the lungs (S. Osada — Tolia Endocrinol. Japan. 11, 19). This function of fat absorption and destruction was increased after feeding thyroid powder and diminished after thyroidectomy. The author claimed that fats are absorbed and destroyed to a greater extent in the lungs than in the liver.

H. M. Barret, et al (J. Physiol. 93, 367) studied fat metabolism with fats labeled with deuterium. The results indicated that during fasting, when certain extracts of the anterior pituitary gland and when animals were exposed to carbon tetrachloride vapors depot fat was the source of liver fat. When fat containing deuterium was deposited in the body reserves and the animals were placed on a diet low in protein and rich in carbohydrate, the fat deposited in the liver was not derived from the depots. No transfer from depot to liver takes place with diets rich in proteins. Methods for preparing fatty acids containing deuterium for this type work were described by W. E. V. Heyningen (*J. Biol. Chem. 125, 495*).

Several other investigators provided information relative to the physiology of fat metabolism. P. E. Verkade et al (Z. Physiol. Chem. 250, 47) defended the theory that w oxidation of normal fat acids followed by bilateral  $\beta$ oxidation of the resultant dicarboxylic acids is an important process of metabolism. His experiments determined the amount and character of the dicarboxylic fat acids excreted by dogs after doses of various fat acids. H. Krainick and F. Müller (Klin. Wochschr. 17, 1040) followed the development of ketone bodies after definite fat ingestion. Normal fasting values for ketone bodies in blood averaged 2.04, mg. per cc. of which 1.55 was  $\beta$ -hydroxbutyric acid. E. S. Miller, W. Brown, and G. O. Burr (Oil & Soap 15, 62) applied absorption spectra technic to metabolic studies. Absorption spectra proved to be a good quantitative method for measuring conjugated double bonds. Thus the rat attached only one of the bonds in eleostearic acid at a time, leaving the other two for a sufficient period to be measured spectroscopically. E. S. Barron and C. Lyman (J. Biol. 123, 229) studied the velocity of oxidation of linseed oil by air in the presence of hemin and a series of hemochromogens. Chain reaction inhibitors inhibited the oxidation of linseed oil and oleic acid with hemin as catalyst. This study indicated that the oxidations of these fatty acids is of a chain reaction mechanism.

The action of a dehydrogenase on fat acids was reported by S. Yoshii (*J. Biochem. Japan 26*, 397). The enzyme was not effective against saturated fatty acids

with less than 8 carbons, and of the unsaturated acids only oleic was oxidized. This enzyme is present largely in adipose tissue, less in liver and pancreas. M. Miyazaki (J. Biochem. Japan 26, 1) recorded that neither a high-fat diet nor two weeks fast markedly affected the formation of acetone bodies from butyric acid by dog's liver perfused with defibrinated blood of the same animal. According to G. Hartwell (Biochem. J. 32, 462), coconut oil was digested by pancreatic lipase more rapidly than any other fat; about equally rapidly digested were almond oil, peanut oil, bacon fat, beef fat, beef oleo, beef stearin, cocoa butter, codliver oil, cottenseed oil, mutton fat, lard, olive oil, palm oil, premier jus, soy bean oil, hardened whale oil, and hardened peanut oil.

M. F. Kohl (J. Biol. Chem. 126, 709, 721, 731) obtained much information on fat physiology by using elaidin with rats. The deposition of the acid in various parts of the body was tabulated. When eladin alone was fed, only a small part of the absorbed acid found its way into the depots. When fed with protein and sugar, a large part escaped utilization and was deposited, mostly in the adipose tissue. Over thirty days were required to clear reserves of elaidic acid that had been deposited during a three-day period of feeding elaidin as 40 percent of the caloric intake.

With guinea pigs in contrast to rats, higher melting fats were less readily utilized than oils (C. M. Mc-Cay and H. Paul - J. Nutr. 15, 377). With rats, the rate of absorption of fat was found to decrease as the melting point increased above body temperature; variations in melting point below body temperature had no effect on absorption rate (M. Irwin. J. Weber, H. Steenbock, and T. Godfrey -Am. J. Physiol. 124, 800). The rate of absorption of hydrogenated fat varied inversely with the degree of oxidation produced by blowing with air.

H. J Channon (*Biochem. J. 31*, 2181, 32. 976, 1332) prevented abnormal deposition of fat in livers by addition to the fatty liver producing diet of the base, triethyl- $\beta$ hydroxyethylammonium hydroxide. No evidence was obtained of the presence of the base in the livers of animals receiving it, even though liver fat had been markedly decreased. Proteins were active in preventing the abnormal livers in order of decreasing intensity: "Gromax" (a commercial whale muscle protein), caseinogen, albumin, beef muscle protein, and edestin, fibrin and gliadin, and lastly, gelatin and zein. Pancreatic extracts also prevented deposition of fat in the dietary fatty liver. The average non-choline activity of the extracts was twice as great as the activity due to choline. On the other hand, C. H. Best and Jessie Ridout (Am. J. Physiol. 122, 67) reported that a sample of pancreatic extract gave about the same effect as dietary casein. They do not believe that the pancreas contains any specific factor affecting deposition of liver fat in white rats. Anterior pituitary extracts did effect deposition of fat in livers, and this effect varied in different animals. (C. H. Best & J. Campbell – J. Physiol. 92, 91).

Eunice Flock, et al (J. Biol. Chem. 121, 117) produced very large and fatty livers in geese by forced feeding a carbohydrate diet. In this experiment the liver was more saturated than the depot fat and both fats were more saturated than normal. Apparently the organism has difficulty in keeping up the usual proportion of the more highly unsaturated acids as was shown by the low iodine values of the liquid fat acids.

The experiments by A. E Hansen and W. Brown (J. Nutr. 15, 17) demonstrated that there was a positive correlation between degree of saturation of food fat, depot fat, and blood fat. The blood showed some selective retention of the unsaturated fat acids.

The hardness of pork fat was not affected by allowing pigs free access to alfalfa pastures (E. H. Hughes — Calif. Sta. Bull 616). A control group fed the same basal ration in a dry lot deposited fat of practically the same refractive index. In this study a breed difference in hardness of fat was observed. H. Longenecker and T. P. Hilditch (Biochem. J. 32, 784) reared rats exclusively on milk. Their fat varied only slightly from that of normal rats. Only 1.4 molecular per cent  $C_{10}$  and  $C_{12}$ acids out of a total of 22.8 molecular per cent for C4, C6, C8, C10, and C<sub>12</sub> acids were stored. Capric, lauric, arachidic, and arachidonic acids were present, each in amounts of about one per cent. Various aspects of the problems of quality of lard and butter as

affected by ingested fat, as well as the relation of nutrition to the composition and quality of the body fats of sheep, cattle, and poultry and of the egg fat of poultry, were discussed by N. R. Ellis (*Oil & Soap 15*, 66).

The effect of both diet and temperature on the depot fats of eels were investigated by J. Lovern (*Biochem. J. 32*, 1214). On diet low in fat (1.1%), the ingested fat had no detectable effect on the depot fat. On 20 per cent fat diet, the depot fat was appreciably modified. Lower temperatures lead to more unsaturated fat and higher temperatures to increased saturation.

W. Halden (Fette u. Seifen 45, 211) reviewed the literature on vitamin A. The vitamin A content of ling liver oil slowly decreases from a maximum value of 0.7 per cent during January and February to a minimum value of 0.5 per cent during July and August. These changes were apparently due to spawning (F. Shorland -Biochem. J. 32, 462). Several writers urged the use of red-palm oil on the basis of its vitamin A content (W. Aykroyed and R. Wright-Indian J. Med. Res. 25, 7; N. K. De-ibid. 11, 17). The cost of this oil is about one-third that of codliver oil containing comparable vitamin A activity. The oil as such was unpalatable, but in combination with other oils, it was sufficiently palatable for cooking.

Further studies were made on the unsaturated fat acids essential in nutrition. O. Turpeinen (J. Nutr. 15, 351) proved that erucic, ricinoleic  $\Delta^{12-13}$ -oleic and chaulmoogric were ineffective to cure "fat deficiency" diseases in rats. Methyl linoleate gave maximum growth response at 100 mg. per day; with arachidonic acid methyl ester 33 mg. sufficed to give powerful curative effect and maximum growth response. E. M. Hume et al (Biochem. J. 32, 2162) demonstrated that the ability of unsaturated fat acids to supplement a fatfree diet in promoting weight increase was not necessarily associated with ability to heal skin lesions. The unsaturated compounds of lard were equal in effect to the similar fraction from linseed oil. Raisin oil was more potent than linseed oil. Docosahexaenoic acid methyl ester from cod liver oil was potent as growth promoting substance but did not cure skin lesions. E. Boyd and W. Connell (Canad.

*Med. Assoc. J.* 37, 38) advised the dosing of humans with mixtures of linoleic and linolenic acids from linseed oil for the relief of the common cold.

T. W. Birch (*J. Biol. Chem.* 124, 775) presented evidence that two factors are concerned in the production and cure of the arodynialike dermatitis of rats. One is the water soluble substance vitamin  $B_{6}$ , the other is probably a "fat acid factor." It is suggested that the physiological function of vitamin  $B_{6}$ , is connected with the utilization of the unsaturated acids. The work of J. Dible and W. Gerrard (*J. Path. & Bact.* 64, 77) shows that fatty degeneration of the heart is not due to lack of a so-called "essential fatty acid."

E. C. Maeder (Anat. Record 70, 73) reported that lack of fat in the diet of rats soon impaired the reproductive function. Physiological and histological observations were given in detail.

A new explanation for the counteraction of the anticalcifying action of cereals by fat is that the absorption of calcium from these diets is promoted by the formation of calcium soaps with fat acids, while in the absence of fat, the calcium combines with the phytin to form an insoluble compound which cannot be absorbed. (E. Mc-Dougall — *Biochem. J. 32*, 194).

In recent years there has been much interest in the toxicity of fish oils to herbivora. L. A. Maynard et al (J. Dairy Sci. 21, 143; J. Nutr. 15, 367) demonstrated that the oils do not produce toxic effect on calves when fed in the amount that may be required to supply vitamin D. With cows, the hydrogenated fish oil as compared to the unhydrogenated products do not reduce the per cent of milk fat in the milk produced. Similar work with herring oil and with milk goats was reported wth the like results by W. R. Graham and P. T. Cupps (J. Dairy Sci. 21, 45). T. Tagaya (Sei-i-kai Med. J. 56, No. 10, 1761) recorded experiments which confirm that the toxic factor of medicinal fish oils is found largely in the saponifiable fraction of the oil.

Acute dermatitis caused by exposure to the vapors from hot tung oil was cured by injection of a solution in olive oil of the oily distillate obtained by heating tung oil (M. W. Swaney-Ind. Eng. Chem. 30, 514). The literature on dermatitis caused by tung oil was reviewed. A discussion of allergic

skin reactions on exposure to soaps and oils was written by M. Mayers (*Safety Eng. 76*, No. 5, 9).

## DETERIORATION

A new comprehensive account of the current state of knowledge on the development of rancidity in edible fats and fat-containing foods was prepared by C. H. Lea (*Publ.* by Food Invest. Board No. 46). The scientific aspects of the problem were emphasized.

A theory of the mechanism of rancidification offered by M. R. Coe (*Oil & Soap 15*, 230) is based on the liberation of free H which unites with molecular oxygen to form loosely combined hydrogen peroxide of the structure H-O-O-H. This form of peroxide unites with unsaturated bonds of fats and produces rancid compounds. It is believed that hydrogen is liberated from chlorophyll which acts as a photosensitizer in vegetable oils. Since metals are know to produce hydrogen peroxide, it is believed that they produce active peroxides of the same nature as that pro-duced by light in presence of photosensitizers. Data on oxygen absorption, formation of peroxides and loss of double bonds of oleic linoleic, linolenic, and ricinoleic acids were obtained by W. Franke and D. Jerchel (Ann. 533, 46). These authors support the view that peroxides are first formed and then decompose to  $\propto$ -HO ketone. The individual ethlyenic linkages of highly unsaturated acids were said to autoxidize at different rates and the resultant peroxides have different stabilities. Results of the Lea, Kreis, and Fellenberg tests and test for ketones on storage experiments with fats were given by K. Täufel and F. Kiermeier (Fette u. Seifen 44, 423, 508). Lard samples developed positive ketone reactions regardless of whether the fat had been rendered or exposed to light. Several samples of ether and three of petroleum ether, as well as carbon tetrachlorid and chloroform gave positive ketone reactions. For this reason, the necessity of carefully examining all reagents used in testing for ketone rancidity was emphasized.

E. Lease and co-workers (*J.* Nutr. 16, 571) reported that carotene and vitamin A were destroyed by rancid fats, ozonized fats, and palmitic peroxides. This phase of rancidity is of physiologcal significance. However, these essential food factors were not destroyed in rats that were maintained on a ration containing rancid fats, when the vitamins were introduced into an empty stomach.

Good work was done in investigating deterioration tests on fats. The basis of the various tests for rancidity and their limitations was discussed by K. Täufel (Fette u. Seifen 45, 179). An improvement in the Kreis test method by W. P. Walters et al (J. Soc. Chem. Ind. 57, 53) involved the substitution of a solution of trichloracetic acid in amyl acetate for the concentrated hydrochloric acid. By this modification, the reaction occurs in a single phase. The stamm reaction was investigated by E. Glimm et al (Fette u. Seifen 45, 496). The color reaction produced by the diphenyclarbazide varied considerably with the solvent used. Acetic acid increased the sensitivity. Many compounds which alone gave negative reactions became strongly positive in presence of acetic acid. The intensity of the test on fat samples was influenced by the acidity when no acid was added. E. Glimm (Fette u. Seifen 45, 500) also tested the reaction of acetylsalicylic aldehyde, 3-nitroso salicylic aldehyde, 2-oxy-3, 5-, 6-oxy-2, 5-, 6-oxy-2, 4-, and 6-oxy-3, 4dimethyl benzaldehydes, vanillin, 0-vanillin, and 0-oxybenzaldehyde (salicylic aldehyde) on rancid fats. The latter gives the known Täufel-Thaler reaction. All reactions were weaker than that of salicylic aldehyde, and only those compounds with substitution in the  $\theta$ -position of benzaldehyde aldehyde vielded a rose color in presence of ketones. I. Antener (Mitt. Gebiete Lebersmittelunters. Hyg. 28, 305) discovered that rancid fats give a bright red to violet color in the presence of m-dinitrobenzol and sodium hydroxide.

Another new fat spoilage test involves the use of a 2 per cent solution of 2, 7-diaminofluorene in glacial acetic acid with .01 per cent hemin as a catalyst. A filter paper is saturated with the solution and a test drop of oil is placed upon it. In presence of peroxides, a deep blue spot appears (O. Tréhden — *Mikrochim. Acta 2, 214*). Mikro methods for other well-known tests were also described by the same investigator.

Two papers appeared on stability of shortening for biscuits and crackers and one on stability of fats for use in doughnut manufacture or other deep frying fat (N.

Joyner and J. McIntyre - Oil & Soap 15, 184; O. Crane and T. Hollingshead — *ibid*. 43; C. Lantz and G. Carlin — *ibid.* 38). Crane and Hollingshead described in detail a method of making standard biscuits and incubating them at 145° F. till rancidity develops. According to Joyner and McIntyre, such tests, which are practically modifications of the Schaal's original oven test, give good correlation with the actual stability and may also uncover other faults, such as the fat contributing an off-color, flavor or odor to the product. This test is easily interpreted or explained to the layman. Lantz and Carlin graphically presented the results of commercial doughnut-frying tests using several types of shortening. The broad conclusion to the work was that there was no decided advantage of certain types of shortening for deep-fat frying.

Tests on the back fat of pigs indicated that in three out of four pigs the fat of the inner layer oxidizes more rapidly than the more highly unsaturated fat of the outer layer. (C. H. Lea-*Rept. Food Invest. Board 1937*, 57.) It was suggested that this may be due to actual differences in concentration of the fat-oxidizing enzyme in the two layers or to the existence of conditions in the inner layer more favorable to its operation.

H. Reynolds and E. Hopkins (Oil & Soap 15, 310) grew cultures of fungi and bacteria on media containing oleic acid. From fungi 69 to 98 per cent and from bacterial cultures 59 to 95 per cent of the original oleic acid was recovered.

General information on the influence of associated matter in fats and anti- and pro-oxidants was summarized by F. Kiermeier and K. Täufel (Fette u. Seifen 45, 487) and G. Curli (Ann. chim. applicata 27, 519). Bleaching absorbents reduce the stability of fats by removing some of the stabilizing bodies (J. Hassler & R. Hagberg — Oil & Soap 15, 115). Data on this effect as produced by various bleaching earth and carbon mixtures were graphically represented.

Since the demonstration by Olcott and Emerson that the tocopherols (vitamin E) were good fat stabilizers, active interest was created on these compounds. A. Moss and J. Drummond (*Biochem. J.* 32, 1953) concentrated  $\alpha$ - and  $\beta$ tocopherols from wheat germ oil by absorption on alumina from solution in light petroleum ether. This fraction contained the whole of the vitamin E active ingredient. Separation of the tocopherol from the solution obtained on eluting the alumina was described. The literature on tocopherols, vitamin E, and inhibitols of fats was reviewed for the Germans by H. Fiedler (*Fette u. Seifen* 45, 638).

The use of oat flour in crackers and packaging material to improve keeping quality was fostered by V. L. Koenig (Dairy Industry 3, 20), H. O. Triebold (Food Ind. 10, 71), and F. N. Peters and S. Musher (ibid. 10, 129). E. Takahashi and Y. Masuda (J. Agr. Chem. Soc. Japan 14, 19) reported good stabilization of herring oil by passing smoke from burning oak wood through the oil. A. Banks (J. Soc. Chem. Ind. 57, 124) produced evidence of the presence of an enzyme system in herring that was able to promote rancidity in the presence of salt. He recommended storage of herring at -28° C. F. Kiermeier (Fette u. Seifen 45, 477) reported good results on storage of lard under refrigeration. The fat stored better than the fat tissue. Reviews on rancidity of soap with special emphasis on protective agents were compiled by P. I. Smith (Seifen-sieder — Ztg. 65, 568, 588) and H. Fiedler (Fette u. Seifen 45, 419).

The inventors or assignees, patented for stabilizing oils and fats were:

E. I. du Pont de Nemours & Co., — Brit. 470, 573, — Sugar amines, such as laurylglycamine amylglycamine, methylfructamine, methylglucamine stearate and like compounds; U. S. 2,104,070, 2,104,084, 2,124,749, 2,-131,904, — Phenols having at least one alkoxy group in either o- or pto a phenolic hydroxyl group and at least one carboxyl group or hydroxyaliphatic group or an alkyl radical bonded to a carbon radical of the aromatic ring.

Industrial Patents Corp. — U. S. 2,108,922, — 25 to 50% kapok oil, U. S. 2,113,216, — A mixture of hydrogenated refined soy bean oil and lecithin; Brit. 481,619, — Hydrogenated refined soy bean oil; Brit. 484,-477, — Hydroxy aliphatic monobasic acids.

H. A. Mattill and H. S. Olcott – U. S. 2,098,254, – A concentration of natural antioxidant obtained by collecting the distillate of lipid unsaponifiable matter at 90-220° and at .05 to 0.2 mm. pressure.

F. W. Nitardy, — U. S. 2,115,040, — Hydroquinone on special carriers. A. K. Epstein *et al*, — U. S. 2,140,-793, 2,140,794, — Adding 0.5% aliphatic polyhydroxy substance or 0.1% sugar and heating; U. S. 2,128,952-7 — Adding mono-and/or di-glycerides, phosphoric acid esters of fat derivatives or mixtures of above and heating. H. D. Royce, -U. S. 2,123,863, -Reaction product of hydrolyzed fats with primary amino alcohols.

A. S. Richardson — U. S. 2,104,242 —Phosphoric acid and its acid acting derivatives.

J. Verne & C. Mille. — Fr. 820,124, — Organic pigments of formula  $C_{40}H_{66}$  or their derivatives or isomers which are generally known as carotenoids.

D. J. Maveety, -U. S. 2,124,706, - Residues from distillation of spice oils.

The rates of deterioration of sweet cream, butter, and butter made from pure culture creams of less than .20 per cent acidity were practically identical (G. E. Holm et al – J. Dairy Sci. 21, 385). There was a direct relation between loss of score and oxidation. Acidity promoted fishy flavor. Some high peroxide butters made from low acid cream did not have a fishy flavor while the butters made from acid cream with the same peroxide value had a fishy flavor. Lowering storage temperature from -10 to -17° C. did not lead to proportionate increase in keeping qualities. O. R. Overman et al (Ill. Agr. Expt. Sta. Bull. 446, 47) showed that butter, ripened with starter at 0.44 per cent acidity and churned without neutralization, scored higher and held its score better in storage than did butter from the same cream after it was ripened with starter to 0.61 per cent acidity and churned without neutralization. Butter churned from sweet cream, and salted, scored slightly higher but lost score more rapidly than unsalted butter from the same cream. J. C. Flake and E. H. Parfitt (J. Dairy Sci. 21, 545) reported that commercial butter samples of 89 to 89.5 score keep better at 15.5° C. than butters of either higher or lower score.

Bacteriological data prepared by D. H. Jacobsen (J. Dairy Sci. 21, 187) indicated that unsalted butter deteriorates more rapidly than salted butter from the same cream. Hans and Helene Schmalfuss (Fette u. Seifen 45, 479) found that salt in margarine accelerates peroxide and free aldehyde formation. B. N. Banerjee (Agr. Live-Stock India 8, 153) recommended that nitrogen be bubbled through ghee during preparation to improve stability of its vitamin A.

A keeping quality test for butter comprises holding the sample overnight at 45 to 50° F., scoring, incubating at 60° F. for 14 days, and before scoring again, holding overnight at 45 to 50° F. The difference in score indicates the keeping quality (C. H. Parsons — Nat'l. Butter Cheese J. 29, No. 7, 6).

Reviews of recent literature on keeping qualities of butters were written by H. Langton (Food 7, 315) and W. Davis (Proc. 11th World's Dairy Congr. Berlin 2, 124).

## COMPOSITION AND CHARACTERISTICS

Data from the reports of 1938 on composition and characteristics of fats and oils have been assembled into charts appended to this section of the review. The data supplied by T. P. Hilditch were obtained by systematic crystallization from acetone in two or more fractions, and the components of these determined by ester fractionation. H. P. Kaufmann and coworkers depended principally on characteristics for approximating the composition. A summary of the equations for determining eleostearic, licanic, linolenic, linoleic, oleic, and saturated acids and unsaponifiable from characteristics was prepared (Kaufmann et al ---Ber. 70B, 2545). The American investigators, G. S. Jamieson and R. S. McKinney, have used various technics. By a modification of the Lapworth and Mottram alkaline permanganate oxidation procedure (*Oil & Soap 15, 30*) 0.6 per cent linoleic and 86.3 per cent elaeostearic acid was found in American tung oil. It was also demonstrated that the elaeostearic acid glycerides in tung oil can be calculated by dividing the diene value by 78.4. The method used for the other oils was ester fractionation for the saturated acids and calculation from characteristics for the unsaturated acids. Reviews on the chemistry and applications of fats and oils were prepared by G. S. Jamieson (Annual Rev. Biochem. 7, 77), T. P. Hilditch (Applied Chem. Repts. 22, 444) and J. B. Brown (Oil & Soap 15, 102).

Other data on fats and oils were not in a form suitable for inclusion in the tables. E. Farmer and F. v. d. Heuvel (J. Soc. Chem. Ind. 57, 24T) recommended molecular distillation for separation of unsaturated acids of fish oils without polymerization. It was shown that fish oil acids of  $C_{28}$  or  $C_{28}$  can have 8 double linkages,  $C_{24}$  7,  $C_{22}$  6,  $C_{18}$ 5, and  $C_{18}$  4. A. Bomer and H. Huttig (Z. Untersuch. Lebensm. 75, 1) cathodically distilled babassu fat in vacuum. The pure glycerides obtained, with their solidification roints, were laurodimyristin 36.1, palmitodimyristin 45.7, myristodilaurin 34.9, and stearodipalmitin 35.9. Distillation of Inguandaranie oil yielded principally cetyl and C<sub>18</sub> alcohol esters of oleic acid (M. Tsujimoto and H. Koyanagi, - J. Soc. Chem. Ind. Japan 40, 403B). S. - I. Ueno and M. Iwai (ibid. 41, 256B) pointed out that olive oil contained 7 to 10 per cent  $C_{16}$ , 90 to 93 per cent  $C_{18}$ , and traces of  $C_{20}$  and  $C_{24}$  acids. The data for  $C_{16}$ acids are higher than those in the literature. The lipids of goat and sheep skins were analyzed by R. Koppenhoefer (J. Amer. Leather Chem. Assoc. 23, 79, 203). The subcutaneous, corium and epidermal divisions and wool or hair were extracted separately, the lipid contents examined, and the data tabulated. The epidermal region had a high lipid content composed of waxes, cholesterol and its esters, phospholipids and free fatty acids. Analytical data on aleurites oils were compiled from the literature by E. D. Frahm and D. Koolhaas (Chem. Weekblad. 35, 643).

Whale oil from the whale catches of 1934 to 1937 contained 18 to 23.2 per cent saturated acids and 22 to 27.9 per cent solid acids of 16 to 22.3 iodine value. The data for blubber oil and flesh oil of the blue and fin whales were tabulated. According to F. Shorland and T. P. Hilditch (Biochem. J. 32, 792) groper liver oils are characterized by abnormally high proportions of palmitic and hexadecenoic acids, together with diminished proportions of  $C_{20}$  and  $C_{22}$  unsaturated acids. The spring and winter groper liver oils contained respectively a trace and 2.0 to 18.8 per cent of phosphatide calculated as lecithin. J. A. Lovern's (Dept. Sci. Ind. Res. Rept. Food Invest. Board 1936, 96) curves on the composition of various fishes indicate that the C<sub>18</sub> unsaturated acids were greatest at 25 per cent in marine and approximately 38 per cent in fresh water fish fats. J. Hadacek's (Casopic Ceskoslav. Lekarnictva 17, 268) data on fresh water fish contained per cent fat in source, content of sterol, and average molecular weight of the fat.

Methods of separating linolenic acid from oils by low temperature crystallization and by debromination of the bromide and low temperature crystallization were described by J. B. Brown and coworkers (J. Am. Chem. Soc. 60, 54). The latter method was recommended as a means of quantitative

estimation. T. P. Hilditch and coworkers (Rec. trav. chim. Pays -Bas 57, 503; J. Soc. Chem. Ind. 57, 84) found  $\Delta^{9-10}$ -hexadecenoic acid in many fats. The amounts varied, in water plants 25-30 per cent of the fat, fresh water fish 18-25, salt water fish 10-15, frog 15, chicken 7, rat 7-8, milk 3-4, beef 2.5-3, pork 9, soy bean 2, palm oil 1, olive oil 1, cottonseed oil 1, and tea seed 0.8 per cent. The products of oxidation of the mixed acids of linseed oil by means of alkaline permanganate under Rollets conditions were investigated by L. Nunn and I. Smedley-Maclean (Biochem. J. 22, 1974). The estimation of oleic acid in a mixture of unsaturated acids was most conveniently made as dihydroxy-stearic acid. The yields of tetrahydroxy acids from the linoleic acid present in linseed oil acids were only 28 to 32 per cent; yields of 52 to 54 per cent were obtained when pure linoleic acid was similarly oxidized. By the action of sulfuric acid on olive oil, and analysis of products formed, A. Steger and co-workers (Rec. trav. chim. 57, 25) obtained indications of the presence of oleic acids containing the double bonds in the 8-9, 9-10, and 10-11 positions. The lauric, myristic, palmitic, stearic, and oleic acid derivatives of 18 organic compounds were prepared and their melting points tabulated (G. M. Iowa State Coll. J. Sci. Ford -12, 121).

Work on the rarer fat acids included the identification of a tetra decenoic acid in Tohoku nut oil (S. Komori & S-S. Ueno — Bull. Chem. Soc. Japan 12, 433), designation of the structure CH<sub>3</sub>-CH<sub>2</sub>-(CH:CH)<sub>4</sub>-(CH<sub>2</sub>)<sub>7</sub>-CO<sub>2</sub>H for parinaric acid (H. P. Kaufmann et al - Fette u. Seifen 45, 302) and analysis of two chaulmoogra oils (H. I. Cole and H. Cardoso - J. Am. Chem. Soc. 60, 614, 617). Carpotroche brasiliensis oil fat acids contained chaulmoogric acid 24.4 and gorlic 15.4; for Oncoba echinata these figures were, respectively, 74.9 and 14.7. The mixed fat acids of the former also contained 45 per cent hydnocarpic acid.

The fat acids found in seed glycerides were also found in the phosphatides of the same seeds, although they were present in different proportions (T. P. Hilditch *et al* — *Biochem. J. 31*, 1964). In the phosphatides of soy beans and rape seeds, the amount of linoleic acid was twice, or more than that of any other acid. R. Riemen-

## CHARACTERISTICS REPORTED FOR VARIOUS FATS AND OILS

Oil or Fat Source	% of Oil or Fat	Density	Re- fractive Index	Acid No.	Sapon. No.	Iodine No.	R-M No.	Polen- ske No.	Acetyl No.	% Unsap.	Thiocy- anogen No.	M.p.
Akebi seed <sup>1</sup> Akebia lobata	. 27.7	0.9326 <sup>20</sup> /4	1.4652 <sup>20</sup> /¤	6.6	254.9	78.6	49.3			<b>.</b>		
Akebi seed <sup>1</sup> Akebia quinata	. 19.5	0.935420/4	1.466720/D	2.0	259.5	77.3	44.8			2.6		
Alfalfa seed <sup>49</sup> Medicago sativa	8.63	0.9253 <sup>25</sup> / <sub>25</sub>	1.479720		185.2	167.8	0.6	0.2	16.6	3.15		
Anda assu <sup>2</sup> Johannesia princeps Apple seeds <sup>3</sup>		0.926315	1.474915	23.0 24	178	138.03 104	1.17	0.53			··	<b>.</b>
Ash seed <sup>4</sup> Fraxinus excelsior		0.92318	•••••	4.8	167	131.7	1.04	0.76			•••••	
Babassu nuts <sup>5</sup> Orbignya speciosa	• •	•	B <b>⁴</b> 35.8	12.5	250.4	16.3	5.8	12.1		0.3		25°
Bonito fish <sup>e</sup> Euthynnus pelamys	• •••••	0.9265-	1.4840-	1.5-	182.1-	209.7				1.13-	••••••	<u>`</u>
Butia Palm fruit <sup>7</sup>	<b></b>	0.929515/4	1.487620	25.6 0.5	184.5 237.3	219.9	·····	••••		1.27 0.06	 20 2	••••••
Palma campestris Cape gooseberry seed <sup>9</sup> Physalis peruviana				0.5 39.06	237.3 179.6	48.7 120.5	4.3	8.8	41.58	0.00	38.2	
Chufa seed <sup>fo</sup> Cyperus esculentus				0.7	179.0	88.4	•	·····		0.4	 74.6	••
Cinnamomum japonicum <sup>11</sup> seeds		·····		0.2	273.2	3.3		••••••				32-4
Cleome pentaphylla seed <sup>12</sup> Croton seed <sup>18</sup>		0.926820	1.465325	36.5	194	122.6			33.5	2.08		
Croton megalobotrys Dumpalm nuts <sup>14</sup>		0.9292 <sup>15.5</sup> / <sub>15.5</sub>	1.4756 <sup>20</sup> 1.447 <sup>40</sup>	1.5 45.8	196.5 229	129.2 29.8	4			0.9 	••••••	
Erythrina indica <sup>15</sup> Goat tallow (from Punjab		0.882120	1.4596**	1.24	184.5 sap:	63.3			••••••	••••••	••••••	201
male goat) <sup>16</sup>	• •••••	•••••	1.4564**	2.1	equiv. 282	33.5	••			•••••••	••••	
Grape seed (1937 Ger. production) <sup>17</sup>	- 8.9 10.3			1.2– 12.6		134.7 137	••				73.7– 76.4	<b>-</b>
Horse chestnuts <sup>18</sup> Aesculus hippocastanum.				11.7	188.3	107.8	•			1.3	85.3	
Ikanago fish <sup>19</sup>	4.8 	0.936515/4	1.484920	3.82	194.4	169.1			·	0.83		
Iron wood seed kernels (dried) <sup>20</sup> Mesua ferra	. 77.14	0.9306**			203.5	89.1				1.87		
Jamba seed <sup>21</sup> Eruca sativa		•		0.10-	- 172.1-	104.5-			0.9-	0.81-	81.1-	
Linden seed <sup>22</sup>		<b></b>		0.45	175.9	107.9			2.1	1.48	82.7	
Tilia parifolia & Tilia ulmifolia	13.25– 22.95	••••••		9.34	181.8	125.5	••••••	<b>·</b>	9.88	1.8	77.7	
Macassar or Kusum seed <sup>23</sup> Schleichera trijuga		<u> </u>	1.4637**	44.3	220.1	57.1	<b>.</b>	<b>.</b>				<u>.</u>
Mammee seed <sup>24</sup> Mammea americana		0.909829/15.5	1.4691		183– 184.4	19.3– 20.5	2.5	0.7				•
Molds <sup>25</sup> Aspergillus niger				71.2	169.	95.1	0.99	0.7		12.0		•
Mowrah seed <sup>26</sup> Madhucca latifolia		<b></b>		20.1		63.9	<u> </u>		<b></b>	2.1		
Mowrah seed <sup>21</sup> Madhucca latifolia		0.897-	<b></b>	6.8-	188.8	53.4-	·				<b></b>	24–5
Ouricury Palm Kernel <sup>50</sup> Syagrus coronata	. 69.7	0.898 <sup>100</sup> 0.9221 <sup>25</sup> / <sub>25</sub>	1.4543 <sup>25</sup>	17.0 11.2	194.0 256.9	67.8 14.69	5.93	18.38		0.27	12.78	<b>-</b>
Phulwara seed kernel <sup>28</sup> Madhuca butyracea Piscara setigera seeds <sup>30</sup>		0.9063-	1.4728-	13 11.9–		40.6 120.5–			9.17-	2.1	 	
Po-Yoak nuts <sup>21</sup>	26.4	0.9183 <sup>25</sup>	1.4737 <sup>25</sup>	16.86	185.65	134.1 207–	0.43		41.03	0.58		
Parinarium sherbroense . Quince seed (German) <sup>32</sup>		0.925078/4	1.520918	1.35	192.0	208	0.40					••••••
Cydonia vulgaris Raspberry seed <sup>33</sup>		0.926215	B60.3	21.4	186.3	113.4			••••••	1.64 22.8		 60 5
Rubus idaeus Sambuccus calicarpa pericarp <sup>34</sup>		<b>-</b>	••••••		181 201.2	105 83.11	1.22	 0.98		22.8 0.70	•	60.5
Sambuccus calicarpa seed <sup>34</sup> . Sandalwood tree seed <sup>35</sup>	. 32.15	<b></b>	<b></b>		201.2 198.7	85.11 187.7	1.22	0.98	•	0.61	·	······
Eucarya spicata Sandalwood tree seed <sup>25</sup>		0.9522 <sup>25</sup> / <sub>25</sub>			196.85	108.25	7.19	<b>-</b> -	42.43		52.13	
Santalum album		0.932525/25	·		177.65	141.85	3.2		20.53		71.45	·····•

## CHARACTERISTICS REPORTED FOR VARIOUS FATS AND OILS (cont.)

% of Oil or Fat Source Oil or Fa	t Density	Re- fractive Index	Acid No.	Sapon. No.	Iodine No.	R-M No.	Polen- ske No.	Acetyl No.	% Unsap.	Thiocy- anogen No.	M.p.
Sandalwood tree seed Santalum album (resin free oil)	0.929225/25			184.25	116.4			20.98		36.62	
(Teshi mee on)	0.9292 / 25	••••••	*	104.23	110.4		•••••••	20.90		00.02	
Sardine livers <sup>37</sup> 13.6– 16.3	0.9229 0.9347²º/4	1.4815 1.483820	7.45 14.8	- 177 194.8	185.3– 194.8				3.44 5.35	*******	
Solanum nigrum seeds <sup>39</sup> 2	0.896430	1.4436**	2.4	184.7	111.7		••••••	9.97	1.4 1.6		•••••
Soy bean (an abnormal											
oil) <sup>40</sup> Dunfield variety 20.06 Stillingia tree seed <sup>41</sup> Amer	0.9159 <sup>25</sup> / <sub>25</sub>	1.4700 <sup>25</sup> 1.4830 <sup>25</sup>	1.47 3.1	191.1 211.7	102.9 176.1	0.6	0.6	5.3 8.5	0.84 0.61	78.0 102.7	••••••
Saprum sebiferum Chinese		1.481725	3.7	206.2	169.1	1.64	0.97		0.78	100.7	
Tohaku nuts <sup>42</sup>	0.040420/	1 470120	20.2	026.1	77.7						
Lindera obtusiloba Tsubaki seed <sup>44</sup>	0.9494 <sup>20</sup> /4	1.470120	28.2	236.1	11.1				••		•••••
<i>Camellia japonica</i> Turtles (from Celon) <sup>45</sup>		<b>-</b>	1.05	197.2	78.0	•••••		0		76.1	*
leathery turtle	0.8696100/5	1.465040	1.6	197.5	98.9				3.3		•••••
Dermochelys Coriacea	0.8671 <sup>100</sup> /5	1.4635*	17.1	199.6	103.8				1.8		
Chelonia mydas	0.8644100/5	1.4591**	1.1	207.6	68.2		······ `		0.5	*******	*******
Lepidoehelys olivacea	0.8710100/5	1.4698**	0.4	191.5	148.7			••••••	1.3		
Whale blubber <sup>46</sup>	0.919515/4	1.475515	0.87	187.1	140.1				0.97		
Sei whale	$0.9195 /_4$ $0.9206^{15}/_4$	1.4735	0.87	193.4	138.5				0.97		
Fin whale Humpback whale	0.919715/4	1.474815	0.81	190.1	135.2	*******		·····	0.73		
Humpback whale		1.482429	21.6	177.8	100.2	7.9	1.1	47.7	5.48	********	*******
1.81	0.7544 / 26	1.1047	21.0	177.0	*******		1.1		5.70	*******	••••••
Wheat germ <sup>48</sup>	<b></b>		7.3	179.6	198.7	1.39	2.14				<b>.</b>
Coffee bean (Raw) <sup>51</sup> 14.23	*******	1.479919.5	4.3	175.55	90.5		*******	11.45	6.55	59.76	
(Roasted) 11.45		1.4778	5.6	177.2	93.4			10.16	9.64	62.86	

SUPPLEMENT TO CHART ON CHARACTERISTICS Oil or Fat Source Hehner Diene No. No.

Alfalfa seed <sup>**</sup>		
Medicago sativa	92.8	
Apple seeds <sup>3</sup>	89.70	
Ash seed <sup>4</sup>		
Fraxinus excelsior	94.5	
Cape gooseberry seeds <sup>9</sup>		
Physalis peruviana	93.4	
Cleome pentaphylla seed <sup>12</sup>	91.5	
Jamba seed <sup>21</sup>		
Eruca sativa		6.8-7.0
Sambuccus calicarpa pericarp <sup>34</sup>	93.02	**********
Sambuccus calicarba seed <sup>34</sup>		
Solanum nigrum seeds <sup>30</sup>	93.10	
Wheat flour <sup>47</sup>	87	
Wheat germ <sup>48</sup>		

## COMPOSITION OF FAT ACIDS FROM FATS AND OILS

Fat Source Akebi seed <sup>1</sup>	Common Myristic	Saturated Palmitic	Acids Stearic	Common Oleic		ted Acids Linolenic	Other Acids
Akebia lobata Alfalfa seed <sup>49</sup>		23	2	53	22	•••••	
Medicago sativa *Butia Palm <sup>7</sup>		- 7.11-		1.4	67.5	20	
Palma campestris Butter fat <sup>8</sup>		51.6 25.3	9.2	30.8 29.6	11.6 3.6	••••••	Butyric 3.0, <i>n</i> —Hexanoic 1.4,
Datter fat	- 16.1	23.3	7.2	23.0	5.0		n—Octanoic 1.5, n—Decanoic 2.7, lauric 3.7, 9-10 decenoic 0.3, 9-10 dodecenoic 0.4, 9-10 Tetra- deconic 1.6, 9-10 Hexadecenoic 4.0
Chufa seed <sup>10</sup> Cyperus esculentus	<u>14.68</u> <u>2.1</u>	17.3 9.57 13.69 36.7 25.5 11.6 16	9.53 4.71 28.1	67.6 32.02 53.4 38.34 12.1– 19.7	15.2 38.97  9.9  67.2- 73.2		Arachidic 0.44 Caprylic 1.31, capric 2.74, lauric 31.38 Lauric 3.5, arachidic 2.4
Oncoba echinata	• •••••	7.8		2.2	<b>*</b> ***	•	Gorlic 14.7 Chaulmoogric 74.9

92

(Continued on next page)

Horse chestnuts <sup>18</sup> Aesculus hippocastanum		4.4	3.6	67.2	22.7	2.2	
Jamba seed <sup>21</sup>	********	7.7	5.0	07.2	44.1	£1.24	
Eruca sativa		- 6.7		5.4	28.5	*******	Erucic 58.5
*Molds <sup>25</sup>							
Aspergillus niger		7.1	0.9	21.5	23.9	••••••	Lignoceric 1.8
Mowrah seed <sup>26</sup>							Unsap. 12
Mowran seed Madhuca latifolia		23.7	19.3	43.3	13.7		
*Ouricury Palm Kernel <sup>59</sup>		20.7	17.0	10.0			
Syagrus coronata	8.43	7.15	2.15	12.18	2.04		Caproic 1.66, Caprylic 9.10, Capric 7.64
							Lauric 42.7, Arachidic 0.1
Phulwara seed <sup>28</sup>			24	26.0	2.0		
Madhuca butyracea		56.6	3.6	36.0	3.8		
Pilchard (Produced July 1935) <sup>29</sup> Sardinops caerula	5.09	14.38	3.19				Unsatd. acids: C14-0.07, C18-11.74
Suramops cuerma	5.09	17.50	5.19		17.00		$C_{20}$ —17.88, $C_{22}$ —13.80, $C_{24}$ —15.24
Sapucainha tree seed <sup>36</sup>							020 11100, 022 22000, 220
Carpotroche brasiliensis		6.6		6.3		••••••	hydnocarpic 45.0
							chaulmoogric 24.4
C1 138							gorlic 15.4
Shea seed <sup>38</sup> Butyrospermum Parkii		5.7	41.0	49.0	4.3		
Soy beans (an abnormal oil) <sup>40</sup>		5.7	41.0	42.0	4.5		
Dunfield variety		-12.0 -		60.0	25.0	2.9	
*Stillingia tree seed*		12.0		0010	-0.0		
Sapium sebiferum American		4.6	1.5	8.0	58.5	25.5	Arachidic 0.35
Chinese		6.2	2.8	10.9	51.9	26.4	Arachidic 0.15
Tricosanthes cucumeroides seed <sup>43</sup>		- 8.6 -		20	42.01	·····	Trichosanic 29.3
*Tsubaki seed4		10.4		016	2.1		
Camellia japonica	<b>.</b>	10.6 15.6		82.6 34.6	2.1 46.0	3.8	
*Based on total fat or oil		-15.0 -		34.0	40.0	3.0	

\*Based on total fat or oil **REFERENCES TO TABLES** 1. S. Komori and S.-S. Ueno. Bull. Chem. Soc. Japan. 13, 505. 2. M. Silva. Rev. chim. ind. (Brazil), 6, Soc. Japan. 12, 505.
M. Silva. Rev. chim. ind. (Brazil), 6, 329.
Z. Hokrova. Casopis Ceskoslov. Lekarnict-va 18, 137; C. A. 32, 9533.
F. Rures and K. Bednar. Casopis Ces-koslov. Lekarnictrva. 18, 107; C. A. 32 7758.
A. Bomer and H. Huttig. Z. Untersuch. Lebensm. 75, 1.
S. Matsuoka and S.-S. Ueno. J. Chem. Soc. Japan 59, 289; C.A. 32, 8810.
H. P. Kaufmann and J. Baltes. Fette u. Seifen 45, 176.
T. P. Hilditch and H. E. Longenecker.
Biol. Chem. 122, 497.
M. P. Gupta and J. B. Lal. Proc. Natl. Acad. Sci. India 7, 131; C.A. 32, 6086.
F. Josephs. Fette u. Seifen 45, 292.
T. Kariyone and H. Iwao. J. Pharm. Soc. Japan 58, 238; C.A. 32, 2655.
R. N. Misra and S. Dutt. Proc. Natl. Inst. Sci. India 3, 352 C.A. 32, 2769.
Anon. Bull. Imp. Inst. 36, 151; C.A. 32
T.S8.
I. Ubaldini. Ann. chim. applicata 28. Anon. Bull. Imp. Inst. 50, 121, Carl. 27758.
 I. Ubaldini. Ann. chim. applicata 28, 191; C.Z. 1938, II, 3342.
 P. S. Rao et al. Proc. Indian Acad. Sci. 7A, 179; C.A. 32, 5240.
 D. R. Dhingra and D. N. Sharma. J. Soc. Chem. Ind. 57, 369.
 H. P. Kaufmann. Fette u. Seifen 45, 288.

schneider and co-workers (J. Biol. Chem. 126, 255) reported that there was a difference in the composition of the fat acids of the lecithin and glyceride fractions of egg oil. His data were tabulated. G. Shinowara and J. Brown (Oil & Soap 15, 151) prepared 3 new ester octabromides of the arachidonic acids separated from beef suprarenal phosphatides. F. Earle and R. T. Milner (Oil & Soap 15, 41) tentatively divided the phosphorus compounds in soy beans into 4 groups: phytins, phosphatides, nucleic compounds, and inorganic phosphorus compounds. The separation of the various phosphorus compounds was by selective solvents. The phytins contained most of the phosphorus present in soy

H. P. Kaufmann and J. Baltes. Fette u. Seifen. 45, 175.
 S.-S. Ueno and S. Ishihara. J. Soc. Chem. Ind. Japan 40, 435.
 N. C. Deb. Indian Soap. J. 5, 16; C.A.
 8175.
 H. P. Kaufmann and H. Fiedler. Fette u. Seifen. 45, 149.
 H. P. Kaufmann and H. Fiedler. Fette u. Seifen. 45, 149.
 K. A. N. Rao. J. Annamalai Univ. 6, 198; C. A. 32, 8810.
 K. Bernhauer and G. Posselt. Biochem.
 C. H. P. Klubwan. Seifensieder-Ztg. 65, 285.
 K. Bernhauer and G. Posselt. Biochem.
 C. A. 32, 9537.
 W. J. Bushell and T. P. Hilditch. J. Soc. Chem. Ind. 57, 447.
 M. Brocklesby and K. J. Harding. J. Fisheries Research Board Can. 4, 59.
 H. N. Brocklesby and Can. 4, 59.
 J. D. Smith et al. J. Am. Pharm. Assoc.
 F. G. C.A. 32, 8176.
 J. Pritzker and R. Jungkunz. Z. Unter-such Lebensm. 76, 40.
 H. Marcelet. J. Pharm. chim. 26, 361; C.A. 32.
 K. M. Cook and F. J. Goodrich. J. Am. Pharm. Assoc. 26, 1252 C.A. 32, 2389.
 W. V. Kotasthane and N. Narayana.

beans. The phosphorus compounds extracted from various seeds by several solvents were determined by M. Lishkevich (Masloboino Zhir. Delo 13, No. 6, 9). The lecithin content was usually about one-tenth that of the phosphatides soluble in alcohol and benzene. The phosphatide contents of seeds decreased in the order given: cottonseed, soy bean, sunflower, flax, castor bean, and peanut.

Work on gossypol, a constituent of cottonseeds, was principally for the determination of its structure (R. Adams et al - J. Am. Chem. Soc. 60, 2967, 2970, 2972). The character of new derivatives and the properties of similar synthetic compounds confirmed the previously postulated formula for gossypol. Poona Agr. Coll. Mag. 29, 126; C.A. 32. 36. H. I. Cole and H. T. Cardoza. J. Am. Chem. Soc. 60, 614, 617. 57. Y. Toyama. J. Soc. Chem. Ind. Japan.

Y. Toyama, J. Soc. Chem. Ind. Japan.
 40, 402B.
 38. T. G. Green and T. P. Hilditch. J. Soc.
 Chem. Ind. 57, 49.
 39. G. P. Pendse. J. Indian Chem. Soc. 14, 367; C.A. 32, 377.

40. F. G. Dollear et al. Oil and Soap 15,

263.

263.
41. G. S. Jamieson and R. S. McKinney. Oil and Soap 15, 295.
42. S. Komari and S.-S. Ueno. Bull. Chem. Soc. Japan 12, 433; C.A. 32, 817.
43. H. P. Kaufmann et al. Ber. 70B, 2535;
C.A. 32, 1958.
44. H. P. Kaufmann and J. Baltes. Fette u. Seifen 45, 152.
45. Aon. Bull. Imp. Inst. 35, 316.

Seifen 45, 152. 45. Anon. Bull. Imp. Inst. 35, 316. 46. Y. Toyama and K. Uozaki. J. Soc. Chem. Ind. Japan 40, 398. 47. B. Sullivan and Marjorie Howe. Cereal Chem. 15, 616. 48. E. Bures and Z. Rosenberg. Casopis Ceskoslov. Lekarnictva 17, 244. 49. H. A. Schuette, H. A. Vogel and C. H. Wartinbee. Oil and Soap 15, 35. 50. R. S. McKinney and G. S. Jamieson. Oil and Soap 15, 172. 51. K. H. Bauer and R. Neu. Fette u. Seifen 45, 229.

E. S. Wallis and co-worker (J.Org. Chem. 2, 335) submitted evidence which shows that the chief sterol in cottonseed oil is  $\beta$ - sitosterol. No evidence was obtained for the presence of a second phytosterol,  $\gamma$ -sitosterol and  $\alpha_1$  and  $\propto$  2-sitosterols. P. Mohs' (Fette u. Seifen 45, 152) review on sterols of wool fat emphasized that cholesterol and dihydrocholesterol are the only sterols in the fat that have been established without question. A method of isolating the sterols of wool fat by T. Kuwata and M. Katuno (J. Soc. Ind. Japan 41, 228B) depended on selective extraction with hot methyl alcohol. The same investigators (ibid. 227B) isolated lanooctadecyl alcohol and an alcohol of formula

 $C_{21}H_{40}$  (OH)<sub>2</sub>, which they named lanyl alcohol, from wool fat. The following substances were obtained from the unsaponifiable matter of wheat germ oil: An oily alcohol  $C_{29}H_{50}O_2$  m. 78-79°; an eicosanol,  $C_{20}H_{42}O$ , m. 68°; tritiol, of probable formula  $C_{22}H_{40}O_2$  m. 84-85°;  $\beta$ -amyrin, C<sub>30</sub>H<sub>50</sub>O, m. 195-196°; and a tritisterol m. 178° (A. Ichiba -Sci. papers Inst. Phys. Chem. Res. Tokyo 34, 121). Nonacosane, C29H60; hentriacontane, C31H64; sitosterol C<sub>29</sub> H<sub>50</sub>O, and primary alcohols of the  $C_{22}$  to  $C_{28}$  series were identified in the fat of grape pomace (K. Markley, C. Sando, and S. Hendricks — J. Biol. Chem. 123, 641). B. Bailey (J. Fisheries Res. Board Con. 4, 55) found the following amounts (milligrams) of pigments in 100 grams of pilchard oil: carotene 0.06-0.25, xanthophyll 0.49-0.84, and fucoxanthin 0.16-0.84.

M. Vuk and A. Gömöry (Z. Untersuch Lebensm. 75, 430) recommend hydrolysis of baked goods with hydrochloric acid and hydrogen peroxide followed by extraction for determining the fat content. In a comparison of various methods for determination of oils in extraction residues, the above method was not recommended because of too high results, due to hydrolysis of phosphatides (G. v. d. Kamper – Verslag. Landb. Onderzoek 43E, 313). A new method proposed for determination of oil in seeds comprises weighing, drying, reweighing, extraction, and reweighing the residue (G. Loew — Olii minerali, grassi e saponi 18, 81). A simple method, which is accurate enough for plant breeding experiments, comprises rubbing the seed with sand and sodium sulfate, adding exactly 5 cc. petroleum ether (b.p. 80-90°), and centrifuging, one cc. is transferred to a weighed filter paper which is dried by holding 20 cm. above a hot plate and the residue is weighed (F. Werr — Chem.-Ztg. 62, 367).

The data necessary and the method of calculation of oil content by refractometric method were prepared for corn and aleurites seeds (H. Cleve — Mühlenlab. 7, 159; E. Frahm and D. Koolhaas — Rec. trav. chim. 57, 395). Gravimetric methods gave 0.2-0.4 per cent higher results for total oil in soy beans than refractometric methods (A. Scharrer and H. Laurel — Fette u. Seifen 45, 262). This difference was demonstrated to be due to gravimetric m ethods sand unsaponifiable matter. F. Wittka (*Seifensieder-Ztg. 65, 742, 762*) stated that the refractometric oil analysis methods are convenient aids for process control but are unsuitable for seed analysis.

The need for uniformity in grades of glass and lighting technic so that more consistent results on color determinations of oils could be obtained was emphasized by G. Haupt (*Oil & Soap 15, 282*) and P. Thomson (*ibid.* 4).

Tabulation of viscosity with other characteristics of oils was prepared by several investigators (H. P. Kaufmann et al — Fette u. Seifen 45, 255, 349; G. Ravich -Acta Physichim U. S. S. R. 6, 207; H. Boekenoogen — Chem. Weekblad. 34, 759). Kaufmann showed that the iodine value of two fatty oils was an additive function of the values for the individual oils, while the viscosity was additive logarithmically. Therefore, the log of the viscosity of unsaturated compounds undergoing polymerization should be directly proportional to the simultaneously occurring decrease in iodine value. Data on the effect of structure, e.g., hydroxyl groups, isomers, double bonds, etc., on the viscosity were discussed. All the above mentioned investigators discussed the utility of the data for use in following polymerization or hydrogenation.

Information on latent heat and crystallization of fat acids of tallow, useful for commercial pressing of tallow fat acids to obtain oleic acid, was recorded by H. Abbott and A. P. Lee (*Oil & Soap 15*, 265). The new "consistency line" technic is also associated with crystallization of fats (J. Straub and R. Malotaux — Rec. trav. chim. 57, 789). The term is described as a curve which expresses the relationship between percentage of solid components and temperature. This characteristic is determined colorimetrically and is represented by a curve in which calories per gram taken up by oil during cooling are plotted against temperature. An apparatus for measuring the rigidity of fats comprises means of expelling the fat through a clean steel tube.

Isopropyl alcohol can be substituted for the denatured alcohol now used for free fat acid titration (G. W. Agee — Oil & Soap 15, 189). In the United States, the principal advantage in this substitution would be that the laboratories using it would not be required to have a special denatured alcohol permit or to make bond for the purchase and use of alcohol; the inconvenience of making monthly sworn reports would be avoided. P. Thomson (Oil & Soap 15, 291) found a variation of 0.29 in the free fatty acids of a sample of seeds when groups of ten seeds were analyzed. The mean value was 2.04 per cent. In a modified Bertram method for determination of saturated fat acids by K, Pelikan and J. V. Mikusch (Oil & Soap 15. 149), the petroleum ether extraction of the unsaponifiable matter was omitted.

Several methods for determination of glycerol in fats were compared (A. Nelson *et al* — Oil & Soap 15, 10). The investigators proposed a modified catalytic method whose advantages were a saving of time and manipulation, with no decrease in accuracy.

By the usual methods for determining unsaponifiable matter 100 per cent of added paraffins and about 27 per cent of added cholesterol were recovered (J. Gross-feld and K. Höll — Z. Untersuch. Lebensm. 76, 478). For improving the extraction of cholesterol, the investigators suggested saponifying, adding a fixed amount of petroleum ether and extracting the soap with water. The weight of unsaponifiable matter in an aliquot of the petroleum ether is determined. According to E. Bolton and K. Williams (Analyst 63, 652), the Norwegian method for the determination of unsaponifiable matter in whale oil extracts only 65 per cent of the actual quantity present. This method was approved by the Belgian, Danish, German, British, and American chemists. Extraction from a more dilute soap solution was recommended. A method for continuous extraction of unsaponifiable matter was devised by I. Wood and H. Roschen (Oil & Soap 15, 287). The method and apparatus allow completion of a greater number of determinations per day with less manipulation than the usual methods. Micro-technic for determination of saponification value was developed by M. Furter (Helv. Chim. Acta 21, 601). A method for determining molecular weights for fat acids comprised converting to a neutral salt of zinc, uranium or copper and determining the amount of metal consumed in its formation.

An innovation for the hydroxyl value determination is the use of acetyl chloride as the reactant and pyridine as solvent as described by

H. P. Kaufmann (*Ber. 70B*, 2549). Means of preventing or compensating for anhydride formation during analysis was also worked out. M. Jakes and J. Hökl (*Fette u. Seifen* 45, 306) pointed out the need of avoiding di- or poly- ricinoleic acid formation during separation of the fat acids for determination of hydroxyl groups. Saponification was followed by pouring the soaps into a large excess of hydrochloric acid. Washing the free fat acids with water was recommended.

Formulas for calculating the iodine value of oils and fats from the refractive index were developed by F. Fritz (Ole, Fette, Wachse, Seife Kosmetik 1938, No. 5, 7) and V. Illarionov and M. Forchinskii (Maslobocino Zhir. Delo 13, No. 6, 23). Nomographs for refractive indices at various temperatures were also included. K. Yokota and M. Tachimori (J. Soc. Chem. Ind. Japan 40, 426B) pointed out that there is a constant relation between densities and iodine values. Exceptions to this rule were oils having hydroxyl fat acids, low molecular weight fat acids, and oils containing low density hydrocarbons or fat acid esters of monohydric alcohols.

J. v. Mikusch (Oil & Soap 15, 186) pointed out that the present iodine value method does not give the true value for tung oil. This oil has two partial iodine values, corresponding to one and two of the three double bonds of eleostearic acid. A modified Wijs method for iodine value determination on tung oil was described. Suggestions for improving this method were made by E. Bolton and K. Williams (Oil & Soap 15, 315). A bromometric method for iodine value determination was described by L. Szebelledy and I. Tanay (Pharm. Zentralhalle 79, 425).

For many highly unsaturated oils and oils which contain hydroxy or ketonic acids, determination of hydrogenation value is the most satisfactory method of measuring unsaturation (W. Stitson — Paint Manuf. 8, 119; H. P. Kaufmann et al — Ber. 70B, 2537). Detailed description of a method and apparatus for determining hydrogenation values of oils with data on several fat acids and paint oils was prepared by H. P. Kaufmann et al. Slight modification of the polybromide determination was proposed by Vizern and Gullot (Ann. fals. 30, 329).

Work on the thiocyanogen number of fats included descriptions of semimicro methods (H. P. Kaufmann et al — Fette u. Seifen 45, 356), tabulation of the thiocyanogen value of various sardine and herring oil samples (S-S. Ueno — J. Soc. Chem. Ind. Japan 41, 200B), and a demonstration of the use of this characteristic with iodine value in following the course of hydrogenation during hardening of sardine oil (*ibid.* 201 B).

Tests on pure organic compounds and various oils demonstrated that neither the Ellis nor the Kaufmann diene value measures the true extent of conjugation in oils of low diene value (W. Bickford, F. Dollear, and K. Markley - Oil & Soap 15, 256; J. Am. Chem. Soc. 59, 2744). Pure hydroxylated compounds having appreciable initial diene value were found to have little or no diene value after acetylation. However, soy bean, perilla, and linseed oils, which have low initial diene values, were found to have larger values following acetylation. E. Frahm and D. Koolhaas (Rec. trav. Chem. 57, 79) reported that the diene values of fresh wood oils are related to the refractive index by the equation D.N.=1400  $(n^{25}/P_{-1.4681})$ . A micro method for determining diene value was described by H. P. Kaufmann and L. Hartweg (*Ber. 70B*, 2554). Meinel's method for detecting conjugation was recommended for detecting the presence of tung oil in admixture with linseed oil (O. Preise -- Farbe u. Lack 1938, 161, 173).

A measure of the ketonic fat acids in oils can be obtained from the extent of the reaction of hydroxylamine with the oils (W. Leithe — Fette u. Seifen 45, 615; H. P. Kaufmann et al — ibid. 616). The results of the reaction are calculated to give what has been named the "carbonyl value." Together with other characteristics, one can determine the percentage composition of a mixture containing, licanic, eleostearic, linolenic. linoleic, oleic, and saturated acids.

H. Heller and C. Clever (Seifensieder — Ztg. 65, 820, 839) fostered the dielectric constant measurements for the oil and fat industries. The tabulation or plotting of dielectric constants of mixtures of soy bean oil and poppy seed oil, rosin acids in tall oil, soy bean oil —benzene mixtures, water in emulsions, water in oils, and linseed oils subjected to various heat treatments were some of the evidence produced to emphasize the utility of dielectric measurement apparatus.

W. Nagel and R. v. Have (Wiss. Veröffentl. Siemens-Werken 17, No. 1, 48) recommended measurement of the speed and the amount of oxygen uptake of oils under accelerated catalytic conditions for evaluating the drying qualities of the oils.

In addition to the above reports on analysis of fats and oils, there were many publications by active committees on testing and improving current methods. Throughout the year reports on analytical methods for oils were prepared by G. S. Jamieson and R. S. McKinney for the Official Agricultural Chemists. Reports of the international committee for Study of Fats were prepared by H. P. Kaufmann for many journals. Kaufmann also prepared the reports of the German fat research committee for the journal "Fette und Seifen." Reports of the analytical committees of the American Oil Chemists' Society by several committee chairmen appeared in "Oil & Soap." Next year the fat analysis committees of the American Oil Chemists' Society will cooperate with the international committee for Study of Fats.

Search for methods that differentiate the various types of olive oils has continued; none has been agreed upon as giving specific in-formation. W. Ciuso (Olii min-erali grassi e saponi, — 18, 33) defended the Wood's fluorescence test for differentiation of pressed and refined oils. Decolorization with 5 per cent active charcoal removes interfering substances. The addition of chlorophyll to refined oils veils the fluorescence but this can be detected with the use of active charcoal. S. Fachini and G. Martinenghi (*ibid. 17*, 54) pointed out that first, second, and third give different fluor-They maintained that pressings escence. Wood's light cannot be used to distinguish expressed from refined olive oil. F. Torrisi (ibid. 17, No. 3, 32) reported that the Bellier reaction and index of refraction gave the most useful data for distinguishing between expressed and solvent extracted oils. For the same purpose, G. Dorta (ibid. 18, 67) preferred determination of cloud and pour points. It was pointed out that 5 per cent of solvent extracted oil in normal olive oil causes a turbidity at 20° and a clouding of the unsaponifiable at

29-28°. An "emulsion value" for characterizing olive oils is obtained by measuring the number of drops of water, plus the same number of drops of dilute sodium hydroxide simultaneously added, that will be emulsified by a 1 per cent solution of the oil in benzene (M. Francois *et al* — Ann. fals. 31, 211).

Treatment of cottonseed oil with a saturated solution of potassium hydroxide in *n*-butyl alcohol was suitable for micro-chemical (microscopic) differentiation between the crude and refined oils (L. W. Greene — Cotton and Cotton Oil Press 39, No. 14, 3). Refined oil gave characteristic crystals, while crude oil produced an amorphous soap.

Outlines of systematic methods for investigating butter for adulteration and margarine for the fats used in its preparation were organized by L. Erlandsen (Fette u. Seifen 45, 215; Allgem. Oel-u. Fett-Ztg. 35, 237) and J. Grossfeld (Z. Untersuch Lebensm. 76, 340). They discussed luminescence test, Kolle reaction, butyric acid value, A and B values, thiocyanogen value, Tortelli-Jaffe reaction, amount of iso-oleic acid present and methods of interpreting the results both quantitatively and qual-The characteristics of itatively. 245 butter fat samples from various parts of the world were tabulated by J. Grossfeld (Z. Untersuch. Lebensm. 76, 123). Fat extracted from baked goods by hydrolysis of the sample followed by solvent extraction gave a sample from which the amount of butter fat could be calculated by the usual formulas The variation in the ratio of insoluble to soluble volatile acids in the milk of two goats during a complete lactation period were 22.8 to 35.5 and 24.3 to 41.4 (A. Chollet and A. Camus -Ann. fals. 31, 224). One should be aware of these variations when attempting to test for adulteration. V. Athavale and S. Jatkar (J. Indian Inst. Sci. A21, 15) recommended determining the refractive dispersion of buffalo butter fat, 'ghee," for detecting adulteration with vegetable oils. Data on several oils and fats were tabulated as an aid in the test.

Chromatographic analyses of butter by dissolving in benzene and pouring through a tube containing aluminum oxide or an active earth gave characteristic chromatograms. Artificial fat and butter colors gave chromatograms which were greatly different from those obtained from pure butter (H. Thaler — Z. Untersuch. Lebensm. 75, 130).

Hydrogenated fats may be detected by a method of separating iso-acids (E. Ol'shevskaya *et al* — Masloboino Zhir. Delo 13, No. 6, 27). These acids can be obtained by precipitating saturated acids in methyl alcohol with mercuric acetate and decomposing the mercury salts of the iso-acids in the filtrate with hydrochloric acid.

Communications on detecting adulteration of cacao butter were principally lists of characteristics and tests most commonly in use. Some writers expressed doubt as to whether solvent extracted products c o u 1 d be distinguished from pressed products (B. Paschke — Z. Untersuch. Lebensm. 75, 316, 318; K. H. Bauer et al — Fette u. Seifen 45, 342; A. Burger — Riechstoff Ind. Kosmetik 13, 126).

The original Bömer method for detecting tallow in lard, which depends on the melting point differences of the insoluble glycerides, was claimed to be sufficiently satisfactory without the various new modifications (A. Bömer *et al* — *Fette u. Seifen 45*, 473).

A method for detection of horse fat in pork, beef, or mutton fat depends on the linoleic acid content. The hexabromides of the fats are horse 41.2, pork 2.8, beef 3.0 and mutton 3.3 milligrams per gram. The addition of 30 or more per cent horse fat was detectable (B. Paschke — Z. Untersuch. Lebensm. 76, 476).

The presence of erucic acid in fat mixtures, and hence adulteration with fats containing it, can be detected by oxidation with alkaline potassium permanganate to dioxylbehenic acid, separating this acid and identifying it by melting point determination (H. P. Kaufmann *et al* — *Fette u. Seifen 45*, 465).

Rough estimation of fish oil in linseed oil can be made by dissolving 3 drops of sample in 5 cc. acetone, adding 05 gram lithium carbonate and 10 cc. of water, filtering in a 100 cc. volumetric flash, filling to mark and noting the transparency. If the solution is clear enough so that common printed matter can be read through it, the oil contains less than 20 per cent fish oil. The clupanodonic acid in fish oil forms an insoluble suspension with lithium ions.

A method for detecting fuel oil in whale oil comprises filtering 20 grams of the oil in 80 cc. of petroleum ether through a column of aluminum oxide, washing the oxide with petroleum ether, extracting the first inch of aluminum oxide with ether and evaporating the ether. The final residue is dark brown if more than .005 per cent of fuel oil was present (E. Bolton and K. Williams — Analyst 63, 84).

### DETERGENTS

Inventors of soap manufacturing equipment are striving to develope and improve continuous and semi-continuous processes. The Procter & Gamble Company developments (U. S. 2,126,099; 2,133,-666; Can. 373,547; Brit. 482,535) include apparatus and processes in which fats are hydrolyzed by passing through a heating zone counter-currently with water: the split fat is continually reacted with alkali; the water content is adjusted and the molten soap is sprayed in moist atmosphere of low pressure to cause volatilization of water and glycerol or the moisture of the molten soap may be adjusted and the spray drying controlled to yield a product of definite moisture content. The patents assigned to Refining Inc. (U. S. 2,123,647, U. S. Reissue 20,772; Brit. 471,172; 487,399; 487,470) deal with passing mixtures of reactants through a heating zone, then into a vacuum chamber where vapors are removed, and the soap is mechanically extruded from the chamber without loss of vacuum. A similar patent was issued to Lorenz Patent Corp. (Fr. 828,022). Continuous reacting of fat acids with sodium carbonate and simultaneously adding water and fillers was patented by a Welter (Brit. 473,220; 478,-536; Ger. 664,289 Cl. 23a). In the apparatus of L. and J. Rouget (Fr. 818,348), the fat acids and saponifying agent meet in the form of jets in a reaction vessel. The V. Kokatnur method (U. S. 2,102,-849) comprises dropping the molten soap into organic cooling liquids to effect rapid cooling and case hardening of the beads formed.

The usual soap making method can be hastened by emulsifying the fatty material with an oxidizing substance, e.g., sodium peroxide, adding water and concentrated lye (R. Gerber — Fr. 820,999; 821,-000). A process of drying kettle soap to the plastic stage, adding perfume and filler, and granulating, was patented (Lever Bros.

Ltd. — Brit. 486,819). Finished soap powder may be prepared in a mixer from fats at 50-80° and concentrated lye solutions. Saponification is rapid and the soap is powdered by the movement of mixing blades (G. Posniak — Fr. 815,-478). L. and J. Rouget (Fr. 48,-182) patented the making of soap for sea water from fats containing low molecular weight acids and certain amounts of castor oil fat acids.

S e v e r a l mechanical improvements in soap equipment were suggested. L. Lascaray (Seifensieder — Ztg. 65, 899) recommended the use of the equation a (kettle coefficient)

## $= \frac{\text{height x total outer surface}}{\text{kettle capacity}}$

in designing soap kettles. Dimensions which yield a low a are pref-Controlled heating for erable. continuous apparatus was designed by B. Clayton et al (U. S. 2,137,-213). Milling and plodding was combined in one operation by special communicating equipment (Procter & Gamble Co. - U. S. 2,135,325). Centrifuges were rec-ommended for recovering oils from soap stock (Akt. Separator — Brit. 469,204). H. Gräbler (Seifensieder-Ztg. 65, 144, 175) recommended improving plodders by designing gratings with special shaped small openings in the center with gradual increase in opening size toward the periphery of the grating disk and also stream-lined cone to allow movement of soap without turbulence. The use of small rotating disk rather than jets in spray drying of soap was fos-tered by B. Thomas (Seifensieder-Ztg. 65, 146, 176). A means of stripping soaps from drum drier rolls was invented (H. Hershey ---U. S. 2.117.958).

New soap forms include soaps covered with a soft sheath (C. Meyer — U. S. 2,132,746; 2,138,-873) and soap tablets which were bored and the bores being filled with other wetting agents, disinfectants, or insecticides (G. Kereszty — Fr. 47,931; 814,035).

J. W. McBain *et al* (J. Am. Chem. Soc. 60, 1866, 1870) demonstrated that the phase rule is applicable for describing the behavior of a soap system. References are drawn from literature to explain nigre lye, neat soap, middle soap, crystalline phase, and curd fibres in a multiphase equilibria of a soap system. Data were presented on the system sodium laurate-sodium chloride-water. The data on sodium palmitate-sodium chloride-water in both tabular and graphical form was prepared by R. Vold and R. H. Ferguson (J. Am. Chem. Soc. 60, 2066). It was shown that the curd phase and neat soap are two phases and that no stoichiometric hydrates occur in the system at 90°. The curd phase varied continuously in water content.

Soaps made from wool fat, sperm oil, oxidation products of mineral oils, or other fats which contain appreciable unsaponifiable must be subjected to treatment to remove these impurities. This removal of unsaponifiable can be accomplished by distillation (Metallges. A. G. - Ger. 656, 556 Cl. 23d.) or extraction with solvents (H. Smith and S. Campbell -Brit. 470,715; Henkel & Cie G. m. b. H. - Fr. 824,756) or by a preliminary distillation followed by solvent extraction (I. G. Farbenind. A. G. — *Brit.* 474,476). The by-products of these processes can be used for the manufacture of other wetting agents.

Patents have been issued on the use of high molecular weight aromatic-aliphatic ketones (Henkel & Cie G. m. b. H. — Ger. 653,217 Cl. 23e.), and cetyl alcohol, choles-terol, and like compounds (F. Schmocker — Swiss 193,628) as super-fatting agents. Other superfatting agents, e. g., alkyl esters of glycol, glycerol, or polyglycerol were also recommended for inhibiting separation of certain substances from liquid potassium soap (Henkel & Cie G. m. b. H. -U. S. 2,105,366). A neutral bleached soap is produced by adding boric acid and polybasic hydroxy aliphatic acids (citric, tartaric, etc.) to the liquid or solid soap (C. Rost and H. Wortman - Brit. 481,-481).

Proteins are now being used as raw products for soap manufacture. The proteins are usually hydrolyzed and condensed with fat acids (Chemische Fabrik Grunau Landoff & Meyer A. G. — Ger. 654,166; 666,006 Cl. 23e; U. S. 2,-119,872; Th. Goldschmidt A-G. -U. S. 2,121,305, Procter & Gamble Co. — U. S. 2,113,819). C. Gillet (Ger. 662,810 Cl. 23e) adds glue and sodium carbonate to resin soaps to improve the solubility of the soap. Other developments on resin soaps include recovering rosin waste, saponifying, and removing impurities (N. Marinkin -Russ. 44,291), treating wood containing resins with alkalies to produce a soap (W. Lehman — Ger. 662,512 Cl. 23e) and spray drying rosin soap in an atmosphere of carbon dioxide (F. Solodkij — J. Applied Chem. U. S. S. R. 11, 85).

The filler for a milled soap was prepared by kneading starch with a solution of water glass containing sucrose (C. Stiepel – Ger. 654,460 Cl. 23e). Dried and sifted sea ooze was added to soap by R. Weissbach (Ger. 662,141 Cl. 23e). Waste curd soap may be processed with alkali metasilicate and mixed with water glass as a means of recovering the waste (I. G. Farbenind. A.-G — Ger. 664,331 Cl. 23e). A method of calcination of soaps with inorganic salts was also patented (*ibid.* — Brit. 469,334). A degreasing composition comprised soap, alkali, alkali phenolates and liquid hydrocrabons (A. Curran -U. S. 2,107,288). Saponins from soap root were recommended as raw materials for preparation of washing agents. A symposium which includes information on extraction methods, composition, sources and properties of saponins and methods of preparing saponin washing agents was edited by A. Lomanovich et al (Vsesoy. Nauch-Issledovatel Inst. Zhir. 1936).

A therapeutic soap contained lecithin and cyclohexanol or its esters (Ges. Fett-und Oel-Raffination - Ger. 666,208 Cl. 23e). Addition of vitamin F to toilet soap was fostered to prevent the suds from irritating the skin (J. Augustin — Seifensieder-Ztg. 65, 325,-345). The bactericidal value of soap and auxiliary germicides and compounds, such as sodium hypochlorite, sodium metaphosphate, etc., was studied by G. Hall and C. Schwartz (Ind. & Eng. Chem. 30, 23). The necessity for using an auxiliary germicide with detergents was shown to be questionable.

M. Kelso (Soap 14, No. 10, 31) attributed the splintering, slivering, checking, and decay of wood floors to the sodium of sodium soaps replacing the combined potassium of the wood, thus causing the breakdown of the inner structure of the Cleaning and scrubbing wood. with potash base soap to prevent this undesirable feature was suggested by the author's experience and by the records that piles driven in beds of lakes whose water contained potash salts in excess of sodium salts outlasted those of lakes in which sodium salts predominated.

Investigations on soap defects were by H. Zilske (Seifensieder-Ztg. 65, 17, 38, 56), P. Das Gupta (Indian Soap J. 4, 251) and H. Alber and C. Rodden (Ind. & Eng. Chem. Anal. Ed. 10, 47). Zilske pointed out that the charring of soap in powder and milled flakes occurs during compressing, during storage of finely divided soap, and during heating. Neutral or acid soaps were most susceptible to charring. Das Gupta pointed out that soap having low iodine value in its fat acids does not always exhibit the least sweating. The moisture absorption and sweating of several soaps were illustrated in a table. By microchemical methods, Alber and Rodden demonstrated that specks in soaps may be due to dehydrated inorganic salts or tin soaps.

General information. which included formulas, reviews, and discussions, were as follows:

Cold process soaps: J. and A. Davidsohn — Soap, Perfumery & Cosmetics 11, 601.

Consumer investigations: J. Schaal — Seifensieder-Ztg. 65, 646; G. Klaass — Soap, Perfumery & Cosmetics 11, 542.

General formulas, equipment, and methods: A. Foulon — Seifensieder-Ztg. 65, 505; Hermada — ibid. 679; J. Schaal — ibid. 143; O. Wurster — Chem. & Met. Eng. 45, 16; W. Gangloff — Oil & Soap 15, 14. L. Hall — Amer. Dyestuff Reporter 27, 612; P. Boone — Soap 14, No. 7, 21; J. Glenn — ibid. 28; A. Raynor — Soap, Perfumery & Cosmetics 11, 1086; W. Fisher — ibid. 11, 520; J. and A. Davidsohn — ibid. 11, 794; A. Vasnyi and G. Lozner — Masloboino Zhir. Delo 14, No. 2, 12; R. Brauchmeyer — Fette u. Seifen 45, 125; M. Münch — ibid. 137.

Fillers (Inorganic compounds): A. Debecq — Verre silicates ind. 9, 65; L. Labaune — Rev. Marques parfums France 16, 10; H-J. Henk — Seifensieder-Ztg. 65, 317; Hermada — ibid. 527; W. Schulze — Fette u. Seifen 45, 630; H. Steinfeld — ibid. 633; A. Kling ibid. 634; H. Katz — ibid. 641; F. Ohl — Allgem. Oel- u. Fett — Ztg. 34, 464; J. Wilson — Sand, Clays & Minerals 3, 149; B. Hirschmann and P. Bechtner —Soap 14, 24.

Fillers (Wood-Cellulose byproducts): K. Otto — Seifensieder-Ztg. 65, 91; Hermada — *ibid.* 94; W. Schulze — *ibid.* 111; J. Augustin — *ibid.* 225; H. Meier — *ibid.* 275; K. Braun and H. Plauson — U. S. 2,100,-047.

Medicinal soaps: A. Foulon — Seifensieder-Ztg. 65, 92; R. K. — ibid. 608.

Preventing defects in soaps: H. Zilske — Allgem. Oel.- u. Fett Ztg. 35, 198. F. Kurskii — Masloboino Zhir. Delo. 14, No. 2, 14; B. Tyutyunnikov — ibid. 15; J. C. — Seifensieder-Ztg. 65, 486, 506; J. Vallance — Soap 14, No. 2, 26; Hermada — Seifensieder-Ztg. 65, 527.

Soap manufactured from mineral oils, coal byproducts, hydrogenated phenols, paraffin, etc.: A. Foulon — Seifensieder-Ztg. 65, 606; S. Deryabin and A. Yasnyi — Masloboino Zhir. Delo. 13, No. 5, 24; Burstenbinder — Klepzigs Textile-Z. 41, 425; J. Vallance — Soap, Perfumery & Cosmetics 11, 998; C. Bauschinger — Fette u. Seifen 45, 629; W. Meyer — Süddeut. Apoth.-Ztg. 78, 47; A. v. Selasinsky — Rundschau deut. Tech. 18, No. 1, 9.

Soap perfumes: H. Henk — Seifensieder-Ztg. 65, 8; F. Rottenberger — ibid. 23; Oculus ibid. 99; R. Fornet — Seifensieder-Ztg. 65, 381, 400; C. Vaillancourt. — Fr. 825,502.

Soaps containing organic solvents: A. Davidsohn — Öle, Fette, Wachse, Seife, Kosmetik 1938, No. 2, 1; Mat. grasses 30, 58, 86, 114.

Soft soaps: Hermada — Seif en sieder-Ztg. 65, 128; R. Krings — ibid. 335, 356; J. and A. Davidsohn — Soap, Perfumery and Cosmetics 11, 437.

Shampoo soaps: B. Pöll — Riechstoff-Ind. u. Kosmetik 12, 242; J. Kalish — Drug Cosmetic Ind. 42, 320.

Shaving soaps: K. Pfaff — Soaps, Perfumery & Cosmetics 11, 700; J. Augustin — Seifensieder-Ztg. 65, 661.

Sulfonated and sulfated products: C. Mullin — Soap 14, No. 2, 32, No. 3, 30, No. 4, 32; A. Hecking — Fette u. Seifen 45, 626; S. Puntambeker — Ind. & News Ed. J. Ind. Chem. Soc. 1 No. 1-2, 19; H. Friedrich — Monatschr. Textil-Ind. 53, 29; T. Ruemele — Seifensieder-Ztg. 65, 614.

This year, patents on non-soap detergent wetting agents and like material will be listed with the inventor or assignee as has been done in the past reviews of this series. The patents on sulfate deriva-

tives of fats were as follows: American Hyalsol Corp.

Can. 372,884; U. S. 2,114,042.

Böhme Fettchemie G. m. b. H. — Ger. 652,433 Cl. 12<sub>0</sub>; 659,-277 Cl. 8<sub>0</sub>; 659,528 Cl. 8<sub>0</sub>; 664,-387 Cl. 12<sub>0</sub>.

Chemische Fabrik. R. Baumheier — U. S. 2,125,072.

Chemische Fabrik Stockhausen & Cie. — Ger. 656,000 Cl. 12<sub>0</sub>; 660,736 Cl. 12<sub>0</sub>; U. S. 2,-127,641.

Chemische Fabrik vorm. Sandoz – Swiss. 192,832 Cl. 24a.

Colgate-Palmolive-Peet Co. — Belg. 420,994; Fr. 827,544; Ü. S. 2,127,567; 2,130,361; 2,130,-362.

Compagnie nationale de matieres colorantes — U. S. 2,107,-197.

Deutsche Hydrierwerke A.-G. – Brit. 475,809; Ger. 656,600 Cl. 12<sub>0</sub>; 662,092 Cl. 12s; U. S. 2,113,807.

E. I. du Pont de Nemours & Co. — U. S. 2,104,782.

Flesh-Werke A. G. – *Ger.* 662,052 *Cl.* 12<sub>0</sub>.

Friedrich Steinfels A.-G. — Brit. 486,850.

B. R. Harris — U. S. reissue 20,636.

Henkel & Cie G. m. b. H. — Ger. 657,704 Cl. 12<sub>0</sub>; 661,883 Cl. 12<sub>0</sub>.

Imperial Chemical Industries ---U. S. 2,100,297.

I. G. Farbenind. A.-G. — Fr. 48,173; Ger. 652,410 Cl. 12<sub>0</sub>; 657,116 Cl. 8i; 657,357 Cl 12<sub>0</sub>; 657,404 Cl. 12<sub>0</sub>; U. S. 2,103,879; 2,108,755; 2,118,995; 2,130,668.

H. Lederer — Brit. 483,301.

F. Lindstaedt — U. S. 2,110,-398.

J. Linhart — Austrian 153,-057.

National Aniline & Chem. Co. - U. S. 2,136,379.

N. V. Chemische Fabriek "Servo" — Brit. 473,760; 474,-229; Dutch 41,743; U. S. 2,140,-882.

Oranienburger Chemische Fabrik A. G. — Ger. 649,323 Cl. 12<sub>0</sub>; 658,650 Cl. 12<sub>0</sub>; 659,181 Cl. 8<sub>0</sub>; 662,182 Cl. 12<sub>0</sub>.

Petroleum Rectifying Co. — U. S. 2,110,899.

Procter & Gamble Co. — Brit. 479,482; U. S. 2,098,114; 2,135,358. R. Reuter — U. S. 2,113,807. Rohm & Haas Co. — U. S. 2,106,716; 2,127,135.

Soc. pour l'ind. chim. a Bále
 — Brit. 481,346; Swiss 194,186.
 Unichem. Chemikalien Handels A.-G. — U. S. 2.125,656.

dels A.-G. — Ü. S. 2,125,656. R. Vidal — Fr. 815,422.

The patents on sulfate derivatives of non-fat material, e. g., mineral hydrocarbons, organic esters, etc., were as follows:

- Böhme Fettchemie. G. m. b. H. Ger. 650,758 Cl.  $12_0$ .
- Friedrich Steinfels A.-G. Fr. 813,128.

G. & A. Laboratories — U. S. 2,121,032; 2,121,033.

I. G. Farbenind. A.-G. — U. S. 2,108,901; 2,130,668; Fr. 820,514; Brit. 479,122; 479,897; Ger. 651,794.

J. R. Geigy A.-G. — Brit. 477,196; Fr. 816,959; Ger. 660,-

579; U. S. 2,122,958. Newport Industries, Inc. —

U. S. 2,117,851.

N. V. de Bataafsche Petroleum Maatschappij — Brit. 479,-137.

A. Ofner - Brit. 468,956.

Procter & Gamble Co. — U. S. 2,108,756.

Röhm & Haas Co. — U. S. 2,-115,192.

Standard Oil Development Co. — Brit. 475,075; Fr. 827,-468; U. S. 2,103,255; 2,111,911; 2,115,807; 2,115,847.

The patents on sulfate derivatives of organic compounds containing nitrogen, e. g., amides, amines, etc., were as follows:

Colgate-Palmolive-Peet Co. — Fr. 812,793.

Deutsche Hydrierwerke A.-G. - U. S. 2,114,256.

Henkel & Cie G. m. b. H. — Brit. 484,910.

Imperial Chemical Industries Ltd. — U. S. 2,097,640. I. G. Farbenindustrie A.-G. —

I. G. Farbenindustrie A.-G. — Brit. 479,835; 481,557; Fr. 814,-166; 816,667; Fr. reissue 47,851; Ger. 651,794 Cl. 8k; 661,429 Cl. 8<sub>0</sub>; U. S. 2,108,725; 2,108,886; 2,108,887; 2,120,557.

J. R. Geigy A.-G. — Fr. 821,-844; Swiss 191,011 Cl. 36q; 192,756 Cl. 36q; 193,223.

S. Perlmuteer — *Fr.* 826,299. Röhm & Haas Co. — *U. S.* 2,112,434.

Soc. pour l'ind. chim. a Bale — Fr. 818,919. Swiss 192,157 Cl. 36p; 193,222 Cl. 36p; 194,-343 Cl. 36p; 194,943-5 Cl. 36p; 195,948 Cl. 36<sub>0</sub>. The patents on nitrogen containing compounds, e. g., amines, quaternary ammonium compounds, etc., as wetting agents were as follows:

Alba Pharmaceutical Co. — U. S. 2,113,606.

Böhme Fettchemie G. m. b. H. – U. S. 2,104,728.

Chemische Fabrik vorm Sandoz — Fr. 822,637; 828,015; Swiss 191,827 Cl. 24a; 194,167 Cl. 24a; 195,845-7 Cl. 36q.

Deutsche Hydrierwerke A.-G. — Brit. 483,324; U. S. 2,127,-841.

E. I. du Pont de Nemours & Co. — U. S. 2,129,264.

General Aniline Works — U. S. 2,097,864; 2,098,551.

Henkel & Cie G. m. b. H. — Ger. 557,055 Cl. 12<sub>0</sub>; U. S. 2,-120,512.

Imperial Chemical Industries Ltd. — *Brit.* 470,346; 475,119; 475,170.

I. G. Farbenind. A.-G. — Brit. 474,671; 475,867; 478,308;
481,357; 484,683; 486,973; Ger.
656,933 Cl. 12<sub>0</sub>; U. S. 2,103,872.
J. Geigy A.-G. — Brit. 478,-843; Fr. 815,634.

J. Leimdörfer — Hung. 117,-137.

Röhm & Haas Co. — Fr. 822,-326; Brit. 470,636; U. S. 2,114,-122; 2,115,250; 2,127,103.

Soc. pour l'ind. chim. á Bále - Swiss 193,075.

A group of patented wetting agents comprise certain ketones, phenolates, high molecular esters, and other miscellaneous compounds:

A. Butignot — U. S. 2,107,-197.

A. Curran — U. S. 2,107,287. E. I. du Pont de Nemours & Co. — U. S. 2,096,036.

Henkel & Cie G. m. b. H. — Brit. 485,633; Fr. 820,496; 823,-154.

I. G. Farbenindustrie A.-G. — Brit. 480,117; 482,367; Ger. 657,208; U. S. 2,128,946.

N. V. Chemische Fabriek Servo. – Fr. 821,731.

Röhm & Haas Co. — U. S. 2,097,441.

Soc. pour l'ind. chim. á Bále - Fr. 811,478.

Several new laboratory technics for determining the composition and properties of soaps have been developed. Three methods for determining fat acids in soaps were recorded. Innovations in these were the use of a modified Roese-Gottlieb apparatus for extraction,

a new specially designed separatory funnel which was attachable to a hot water bath and a modified procedure for the determination (resp., O. Szakacs — Kiserletügyi Közlemenyek 40, 203; V. Smirnov and A. Kashnitskaya — Masloboino Zhir. Delo. 14, No. 2, 24; M. Shpak — Org. chem. Ind. U.S.-S.R. 3, 365). The use of a bomb calorimeter and calculation by comparison with 100 per cent sodium oleate was also suggested for certain soaps as an approximate means of determining fat content (B. Ravich — Zavodskaya Lab. 6, 822). A means of determining oleic acid in soap solutions was based on the reaction of barium nitrate with the soap. Titration with a standard barium nitrate solution was carried out until foaming was stopped (V. Gruzdev and B. Zal'tsman - Org. Chem. Ind. U.S.S.R. 4, No. 13, 18). A comparison of the methods for determining rosin in soaps demonstrated that the McNicoll method was most rapid, easiest to run; it produced reliable results and was not appreciably influenced by the grade or type of rosin contained in the soap (E. Randa and E. Boley - Oil & Soap 15, 313).

The use of sulfite lyes in soap necessitates a method for the detection of this type of product. A qualitative method comprises removing the fat acids and testing the neutralized water solution with tryptoflavin, acridin yellow or  $\beta$ naphthylamine. The reagents, which were placed in the descending order of their activity, form a precipitate with lignin sulfate (A. Noll — Seifensieder-Ztg. 65, 35). The apparatus and method for determination of combined carbon dioxide in soap, by L. Hitchcock and R. Divine (Oil & Soap 15, 8) was based on liberating the carbon dioxide with acid, absorbing in barium chloride and titrating. E. Randa (Oil & Soap 15, 6) pointed out that the higher results obtained with ethyl ether extraction of unsaponified matter in soaps as compared to petroleum ether extraction was due to the higher solubility of mono- and di-glycerides in the former.

P. Ekwall (Kolloid-Z. 84, 284) pointed out certain characteristics of soaps which were measurable by electrometric titrations. Sodium laurate was titratable to a 0.015 molar solution. Six inflection points occurred during the titration. Following the inflection due

Reilly-Whiteman-Walton  $\cdot$  Co. - U. S. 2,129,896.

to acid soap precipitation, there appears another due to precipitation of free fat acid and another at complete neutralization.

Proposals for determining the solubility rate and the lathering properties of soaps deal with standardizing a comparison technic (R. Gobhel and N. Chatterji — *Indian Soap J. 4*, 105; A. Klyuchevich — *Masloboino Zhir. Delo. 13*, No. 6, 23; N. Godbole *et al* — *Indian Soap J. 4*, 179). S. Bertram (*Chem. Weekblad. 34*, 707) and P. Das Gusta (*Indian Soap J. 4*, 197) listed and discussed the various methods for evaluating the washing action of soaps. Washing tests were considered impractical for general application by Bertram.

General methods for systematic analysis of soaps were compiled by G. Rosenberger (*Seifensieder-Ztg.* 65, 118), K. Burgdorf (*Fette u. Seifen 45*, 379) and R. Strauss (*Seifensieder-Ztg. 65*, 429). Organized and systematic investigations of analytical procedures on detergents were also reported by committees in Oil & Soap, Fette und Seifen, Analyst, Proceedings of the American Society for Testing Materials, and American Dyestuffs Reporter.

The theories of the structure of soap solutions were reviewed by H. Flammer (*Fette u. Seifen 45*, 133). New physical data, e. g., cataphoretic measurements of particles in soap solutions, specific volume of dilute soap solutions, influence of hydrogen ion concentration of interfacial tension, hydrolysis, and surface tension and vapor pressure of commercial soaps were recorded (resp., A. Buzagh et al — Kolloid-Z. 84, 16; M. Ulmann — Z. physik. Chem. A-182, 18; J. Powney et al — Trans. Faraday Soc. 34, 356, 363, 372; R. Ferguson and R. Vold — Oil & Soap 15, 181). The effect of manufacturing technic, soda ash, and other constituents on soaps was illustrated by several photomicrographs by B. Thomas (Seifensieder-Ztg. 65, 647, 680, 700).

The general communications on glycerin comprise a review on production methods (B. Wolff — *Przeglad Chem. 2, 367*), a description of a continuous distillation process (O. Wurster — Oil & *Soap 15, 292*), an analysis of cost of production (A. Lee — Soap 15, No. 11, 21), a list of new applications (G. Leffingwell and M. Lesser — Chem. Industries 42, 395), and a review of glycerin substitutes (H. Janistyn — Seifensieder-Ztg. 65, 162).

M. Iwai and S.-S. Ueno (J. Soc. Chem. Ind. Japan 40, 430B) compiled data on efficiency of glycerin distillation equipment. In commercial operation 400 to 700 B. T. U. per pound of distilled glycerin were required. Glycerin distillation patents issued to Colgate-Palmolive-Peet Co. (Brit. 486,311: 486,313; 486,415) deal with increasing efficiency of a still by utilization of the heat of condensation for generating steam and preheating glycerin. The removal of odor-forming constituents from glycerin was accomplished by treatment with activated carbon in presence of acids (G. Brant — U. S. 2,120,227).

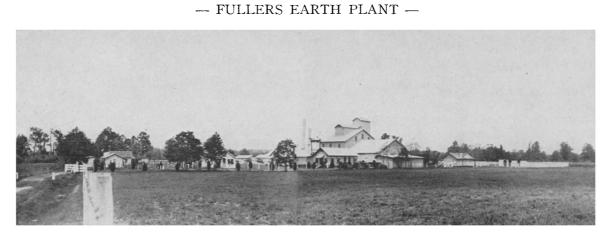
A yield of 25 per cent fermentation glycerin, based on amount of sugar used, was obtained from a solution containing 200 grams sugar, 50 grams salt, 20 grams sodium bicarbonate, and 1 gram each of ammonium and magnesium sulfates per liter by treatment with 10 grams of yeast at 37° (Nord deutsche Hefeindustrie A.-G. — *Ger.* 664,575, *Cl.* 6b). Glycerin is recovered from fermented masses by drying and extraction with selective solvents (Henkel & Cie — *Ger.* 649,101; 664,576 *Cl.* 6b).

The new methods proposed for analytical determination were a ceric sulfate oxidation method (R. Cuthill and C. Atkins — J. Soc. Chem. Ind. 57, 89), several modified dichromate methods (G. Martinenghi-Ölü, minerali grassi e saponi, 18, 21; Procter & Gamble Co. — Oil & Soap 15, 36), a bromine method (O. Jublin — Z. Anal. Chem. 113, 339) and a means of estimating it in the presence of other hydroxylated compounds by precipitation with cupric chloride (S. Bertram and R. Rutgers — Rec. trav. chim. 57, 681).

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