

Annual Review of Literature on Fats, Oils, and Soaps. Part II

Report of the Literature Review Committee*

M. M. PISKUR, Swift and Company, Chicago, Illinois

Deterioration

REVIEWS. One of the most comprehensive reviews on deterioration of food fats that have appeared in recent years was compiled by Lundberg (*Hormel Inst. of Univ. Minn. Publ. No. 20*, 45 pp.). This pamphlet contains information on types of deterioration, flavor reversion, methods of testing, natural and commercial inhibitors, and stability of fats in such foods as meats, fish, dairy products, bakery goods, and cereal foods. In a briefer review of the same nature, Riemenschneider (*Trans. Am. Assoc. Cereal Chemists* 5, 50) dealt principally with cereal products and emphasized the careful application of principles of good processing technology. Such principles were also emphasized in a review on stabilization of olive oil (Salomone—*Olearia* 1947, 31). Brief general reviews on rancidity and its control were also published by McConnell (*Am. Perfumer Essent. Oil Rev.* 50, 241), Paquot (*Inds. corps gras* 3, 111, 140; *Oleagineux* 2, 15), Tollenaar (*T.N.O. Nieuws* 2, 211), and Daubert & Longenecker (*Food Tech.* 1, 7).

METHODS FOR TESTING. Most investigation on methods for testing dealt with the determination of peroxides. Volz & Gortner (*J. Am. Oil Chemists' Soc.* 24, 417) investigated the optimum conditions for determination of peroxides in fats by the Kokatnur & Jelling (*J. Am. Chem. Soc.* 63, 1432) procedure. Their results indicated that reaction time at 80° should be five and at 70° should be seven minutes. In a comparison of a number of rancidity tests on 88 samples of olive oils, Kaloyereas (*Olii minerali, grassi, e saponi, colori e vernici* 24, 8; *J. Am. Oil Chemists' Soc.* 24, 39) found that the Wheeler method gave values which agreed most closely with organoleptic tests. Hills & Wilkinson (*J. Council Sci. & Ind. Research* 19, 430) observed that in some dairy fats, milk phosphatides, at a concentration of 0.05%, interfered with the determination of peroxides by ferric thiocyanate when benzene-methanol was used as the solvent. Acetone, however, did not dissolve sufficient phosphatide to cause interference. Lundberg & Chipault (*Hormel Inst. Ann. Rept.* 1945-6, 12) found that some of these more common methods for peroxide determination did not give reproducible or quantitative results. They adapted the iodometric method to give accurate determinations by careful exclusion of oxygen. This procedure along with spectrophotometric absorption analyses was used in the compilation of some preliminary data in an investigation of the course and mechanism of autoxidation of pure methyl linoleate at temperatures from 40 to 100°.

Heretofore the determination of peroxides in animal tissue fats was complicated by losses during comminuting and solvent extraction. A newly proposed procedure of stirring cubed samples of tissue in a Waring blender with chloroform followed by filtering and determining peroxides on an aliquoted portion allowed more accurate determinations (Rockwood *et al.*—*Anal. Chem.* 19, 851). Variations in the mixing time (20 to 240 secs.) in the blender made no significant differences in the results, and the

process did not affect the free fatty acids and peroxide values.

Schönberg's neutral-red test for the rancidity of animal tissue fats showed that development of a yellow color on bacon or other fatty tissue indicated an unobjectionable product, and a red color indicated rancidity, but intermediate color reactions were inconclusive (Pante—*Z. Fleisch- u. Milchhyg.* 54, 71; Gebauer—*Ibid.* 196; Westphal—*Ibid.* 201; Schönberg—*Ibid.* 221). The test was recommended as a preliminary or a control procedure to recognize the definitely good or bad samples; those of intermediate color reactions must be judged by more tedious but more conclusive procedures.

A new ultra-sensitive reaction for rancid fats depended on the development of a bluish-violet color by reaction of the peroxides with tetramethyl-*p*-phenylene diamine (Kul'berg—*J. Anal. Chem. (U.S. S.R.)* 1, 263; *Priroda* 36, No. 7, 62).

FACTORS INFLUENCING AUTOXIDATION. The stability of hydrogenated vegetable oils was correlated with the fatty acid composition (Fisher *et al.*—*J. Am. Oil Chemists' Soc.* 24, 379). During hydrogenation the change in the keeping quality was inversely proportional to the change in linolein content up to the point of disappearance of the linolein. After all the linoleic acid had disappeared, the keeping qual-

TABLE OF CONTENTS

A. INTRODUCTION.

Statistics, outlook, fostering individual sources, and literature.

B. PRODUCTION.

Animal fats, vegetable fats, tall oil, medicinal oil, hydrogenation, transesterification, refining, fatty acids.

C. PRODUCTS (except detergents).

Table and cookery fats, emulsifiers, protective coating products, resins, fat derived esters, alcohols, ketones, chlorides, etc., fat derivatives containing nitrogen, soaps of polyvalent metals, lubricants, miscellaneous products containing fat or fat derivatives.

D. DETERIORATION.

Reviews, methods of testing, factors influencing autoxidation, flavor reversion.

E. BIOCHEMISTRY AND PHYSIOLOGY.

Desirability in the diet, relative dietary value, absorption, intermediate metabolism, lipids in diseases, fat soluble vitamins.

F. CHARACTERISTICS AND COMPOSITION.

Analysis of fat sources, physical characteristics, chemical characteristics, composition.

G. DETERGENTS.

Manufacture, evaluation, properties, patents on nonsoap types.

* Literature Review Committee

E. W. BLANK

W. H. GOSS

J. B. BROWN

M. M. PISKUR, Chairman

ity was dependent upon the olein content. Holman & Elmer (*Ibid.* 127) compared the rates of oxidation of various fatty acids and their esters by measuring oxygen absorption. An increase in the number of double bonds in a fatty acid by one increased the rate of oxidation of the acid by at least a factor of two. The acids oxidized more rapidly than did their esters.

In work on the effect of ultrasonic waves on oils, a decrease in the acid values of the oils was observed (Kaloyereas—*Ibid.* 283). It was postulated that ultrasonic radiation promoted oxidation of fat, and that decomposition products of this oxidation reacted with the free fatty acids present in the oil. Storage tests were made on packaged corn and cottonseed oils (McConnell & Esselen—*Ibid.* 6). The data illustrated the effect of light, antioxidants, refining, air, and storage time. The authors recommended that the bottle-packed products be in amber glass. Several groups investigated the effect of various dietary constituents upon the stability of animal body fats. Lundberg *et al.* (*J. Biol. Chem.* 168, 379) used an oxidative stability test to compare the quantities of synthetic tocopherols deposited in the abdominal fats of rats. The γ -tocopherol was deposited in much smaller amounts than either the α - or β -forms. The biopotencies (vitamin E) of the tocopherols fed were not directly related to the autoxidative characteristics of the rendered fats in which they were deposited. The stability of poultry carcass fat under frozen storage was decreased as a result of feeding the birds supplements of fish oil or alfalfa leaf (Schreiber *et al.*—*Poultry Sci.* 26, 14). Fasting poultry before slaughter had no influence on the stability of the carcass fat against oxidation, although a greater development of the free fatty acids occurred in the carcasses from the fasted birds (Wagoner *et al.*—*Poultry Sci.* 26, 167, 170, 173). The stability of the body fat was decreased by delayed evisceration or when it was frozen and thawed before evisceration. When the exposed surface of poultry in frozen storage was reduced, the stability of its fat was increased. The fat of beef hermetically sealed in cans and stored frozen for 40 years was almost inedible due to rancid flavors, although the lean had a satisfactory flavor (Ramsbottom *et al.*—*Refrigerating Eng.* 54, 544). There was very little hydrolysis in the fatty tissue near the surface and even less in the deep tissue. The peroxide value of the fat of 40-year old beef was 13-20 as compared to 0.75-1.22 for fresh beef. In tests on frozen sausage meat (Atkinson *et al.*—*Food Inds.* 19, 1198, 1366), smoking, sage, black pepper, avenex, and low-fat-content trimmings were found to retard rancidification; lecithin was ineffective; salt and curing stimulated rancidity.

Some work on rancidity in dairy products was reported. According to Csiszár (*Tejgazdaság* 5, 9) butter with moisture contents below 14% stored better than others; reduction of fat-free dry matter also improved keeping qualities. Vas (*Mezőgazdasági Kutatasok* 17, 1), in a check on various methods of evaluating deterioration of butter, found the test for aldehydes with rosaniline reagent was the most sensitive. The peroxide, acid, Reichert, and Polenske values were recorded on cow and buffalo butterfat during a four-year storage period in cork bottles (Achaya—*Nature* 159, 274). The flavor changes appeared to be due to oxidation rather than lipolysis.

Hills & Conochie (*J. Council Sci. Ind. Res.* 20, 414) continued their work on the effect of salt in accelerating oxidation of butter and have suggested that hydrogen and chlorine ions activate oxidation.

A pork muscle enzyme-extract and hemoglobin solution obtained from hog blood accelerated the oxidation of lard (Watts—*J. Biol. Chem.* 170, 441). The catalytic effect of both products was destroyed by heat, decreased by dilution, and unaffected by cyanides at pH 5.3. The control of ketonic rancidity of butter with boric acid and sodium benzoate seemed to depend on control of bacteria and the enzymes that may be produced (Kieferle & Feichtner—*Fette u. Seifen* 51, 427). A discussion on enzyme oxidation of fatty acids (Jezeski—*Trans. Am. Assoc. Cereal Chemists* 5, 37) was particularly designed for application in the protection of foods. A new procedure for determination of lipoxidase activity depended on decolorization of the carotenoid bixin (Sumner & Smith—*Arch. Biochem.* 14, 87).

Preservation of fat soluble vitamins in oil solutions was considered in some work to be a problem of controlling autoxidation. Bolomey (*J. Biol. Chem.* 169, 323, 331) increased the stability of the vitamin A of fish liver oils by the addition of tocopherol as an antioxidant or by removal of dissolved oxygen. He correlated the oxidative changes in the vitamin with changes in the shape of the spectrum. Euler & Euler (*Arkiv Kemi, Mineral Geol. B* 18, No. 12, 8 pp.) reported that β -carotene was more stable in vegetable oils than in animal fats and that the stability was greatest in the more unsaturated oils. They believed that the unsaturated oils consumed the active oxygen, thus protecting the carotene. Bose (*Current Sci. (India)* 16, 119) recommended the use of isobutyl gallate and citric acid as antioxidants for vitamin A. Sanford *et al.* (*Com. Fisheries Rev.* 9, No. 2, 11; No. 4, 5; No. 5, 7) recorded the losses of vitamin A in gray fish liver and liver oils under various storage temperatures. Under similar conditions the stability of the vitamin A in the two materials was essentially equal. Buxton (*Ind. Eng. Chem.* 39, 225, 1171) suggested the use of antioxidant concentrates from wheat germ, corn germ, and soybean oils for protection of vitamin A in liver oils. His work on the effectiveness of tocopherols indicated that γ -tocopherol was better than the β -form, lecithin enhanced their effectiveness, and α -tocopherol was inactive.

Mattil & Black (*J. Am. Oil Chemists' Soc.* 24, 325) developed a laboratory method for evaluating the ability of antioxidants to stabilize fat in baked goods. They observed that the effectiveness of stabilizers in this case was a function of their relative solubility in fat and water. The carry-over of the antioxidant was related to its partition between equal amounts of fat and hot water. Morris *et al.* (*Ibid.* 309) recorded that alkyl (C_8 to C_{18}) esters of gallic acid were of similar activity in oils, but in baked pie crust the higher gallates were superior to gallic acid and propyl gallates. This may be explained on the basis of the preceding reference. Lips *et al.* (*Can. J. Res.* 25F, 51) found hydrogenated vegetable shortening more suitable than those containing animal fats for preparation of stable ration biscuits. Shortening with Swift stabilities greater than 40 hours at 110° did not yield products of increased keeping quality. Addition of soybean flour to the formulas of frozen

pastry increased the stability of the fat in the products (Overman—*Food Res.* 12, 365). Proportions of 5 to 20% were of about equal effectiveness.

The antioxidant, hydroquinone, was studied in linseed oil to give an insight to its protective mechanism in rubber (Bolland & ten Have—*Trans. Faraday Soc.* 43, 201). It was suggested that hydroquinone removes the peroxides from the system and is converted to benzoquinone.

Several investigators compared the protective capacity of various antioxidants among the quinones. The effectiveness for whale oil in decreasing order was hydroquinone, quinhydrone, naphthoquinone, chrysenquinone, benzoquinone, anthraquinone, and phenanthraquinone (Täufel and Arens—*Fette u. Seifen* 51, 307). The nitrobenzenes also had slight antioxidant properties. Diemar's *et al.* (*Ibid* 50, 349) classification of antioxidants for their effectiveness in the stabilization of fats and methyl linoleate was: Strong—vitamin D, lecithin, vitamin C; Weak—xanthophyll; Inactive—vitamin E, cholesterol, alanine; Pro-oxidants—vitamin B, phytosterol; Strong pro-oxidant— β -carotene, chlorophyll, choline. The development of rancidity in the fat of frozen fish was retarded with ascorbic acid, ethyl, *n*-propyl, *n*-butyl, or hexyl gallates and cysteine hydrochloride (Tarr—*J. Fish. Res. Bd. Can.* 7, 137). In the same investigation ethanol ammonium gallate, dodecyl thiodipropionate, thiourea, citric, and tartaric acids were ineffective. Lundberg *et al.* (*J. Am. Oil Chemists' Soc.* 24, 89) graphically recorded the effectiveness of four phenolic antioxidants in a study of the kinetics of their destruction. The reactions were said to be complicated by the synergists and other products resulting from the oxidation of the fat and possibly from the antioxidant itself. The deterioration curve of gallic acid was quite different from that of the other phenols. This was interpreted to be the result of the synergistic action of gallic acid on itself. In connection with the same work Lundberg (*Hormel Inst. Ann. Rept.* 1945-6, 3) found that rancidity may develop in fats containing any of the antioxidants before the antioxidant has been completely destroyed. Vas's (*Műgyetemi Közlemények* 1947, No. 1, 79) work on stabilization of bone grease resulted in the classification of some antioxidants in descending order of effectiveness as follows: pyrogallol, hydroquinone, sodium pyrophosphate, adrenaline, and phosphoric acid. Salomone (*Olearia* 1, 31) recorded data on hydroquinone and natural extracts of vegetable material in a demonstration of antioxidant protection of olive oil. Likewise, Ono & Toyama (*J. Chem. Soc. Japan* 65, 513) demonstrated the antioxidant effects of several phenolic and aromatic amine compounds on sardine oil.

In the field of antioxidant synergists, the report of Clausen *et al.* (*J. Am. Oil Chemists' Soc.* 24, 403) was rather extensive. They classified the effectiveness of about 70 amino acids and other natural substances as synergists for α -tocopherol, hydroquinone, and nordihydroquaiaretic acid (NDGA) in the protection of lard. Ascorbic acid, methionine, and some milk protein hydrolysates were consistently among the best. A newly proposed mechanism explaining synergistic action was based on certain adsorption and exchange reactions (Caulkins—*J. Am. Chem. Soc.* 69, 384).

Several reports on NDGA described its extraction from the creosote bush (Gisvold—*U. S.* 2,421,118),

purification (Adams—*U. S.* 2,421,109), synthesis (Lieberman *et al.*—*J. Am. Chem. Soc.* 69, 1540), pharmacology (Cranston *et al.*—*Federation Proc.* 6, 318), and its use for prevention of oxidized flavor in stored frozen cream. Norconidendrin, a new antioxidant similar to NDGA, was obtained by extraction of the sulfite waste liquors which are by-products in the manufacture of pulp from the western hemlock (G. S. Fisher—*J. Am. Oil Chemists' Soc.* 24, 340; *Soap, Sanit. Chemicals* 23, No. 6, 49). The most active antioxidant fraction of carrot oil distilled at about 190° in the molecular still (Heftmann—*J. Am. Oil Chemists' Soc.* 24, 404). Täufel & Rothe (*Fette u. Seifen* 51, 100) suggested that the antioxidant from oats was a native protein and that coagulation by heat destroyed its protective activity. Flavones and flavone derivatives were found to be effective antioxidants for butter and lard (Richardson *et al.*—*J. Dairy Sci.* 30, 397). Fumaric acid, contrary to American reports, was inactive according to Glimm & Rozdilskyj (*Ibid.* 389).

In recently patented methods of stabilizing fats and oils the following treatments were used: addition of a reaction product of γ , γ -dialkyl substituted allylic alcohol, having a double bond in the β , γ -position to the -OH group, with aromatic compounds containing an θ -hydroxy group (Smith & Ungnade—*U. S.* 2,421,811); a mixture of monobenzyl ether of hydroquinone and a crude source of vitamin B complex (Gyorgy—*U. S.* 2,420,238); a combination of a nicotinic acid nucleus compound and an unsaponifiable fraction of vegetable oil (Taub & Simone—*U. S.* 2,432,698); an ethylene chloride extract of refining "foots" (Buxton—*U. S.* 2,433,593); phosphatides in combination with other synergists (National Oil Products Co.—*Brit.* 589,273); or decomposition product of trichlorosilane with water (Chem. Fabrik Heyden A. G.—*Belg.* 449,077); and heating the oils with relatively small amounts of ammonium hydroxide with or without other antioxidants (National Oil Products Co.—*Brit.* 589,688; *U. S.* 2,426,485-6), with phosphatides (Scharf—*U. S.* 2,431,347), or with selenium (N. V. Ned. Research Centrale—*Dutch* 55,811).

FLAVOR REVERSION. Golumbic and Daubert (*Food Inds.* 19, 1075) prepared a review on the mechanism and control of flavor reversion in soybean oil. The effect of light, heat, oxygen, antioxidants, metals, bean quality and variety, and injudicious treatment were discussed. Dutton *et al.* (*J. Am. Oil Chemists' Soc.* 24, 261) recommended German processing procedures to combat the flavor instability of soybean oil. Accordingly, oils are subjected to thorough degumming and deodorization, a small amount of citric acid being added during the deodorization.

The role that nonsaponifiable fraction of soybean oil plays in flavor reversion was investigated by Mattil (*J. Am. Oil Chemists' Soc.* 24, 243). The unsaponifiable extract of hydrogenated soybean oil, when added to non-reverting oils, caused the typical reverted soybean flavor to appear; similar tests with unhydrogenated linseed oil did not give analogous results. Selective adsorbent treatments of soybean oils gave some improvement, being much more effective with hydrogenated than with unhydrogenated oils. Uyeno & Matsuda's (*J. Chem. Soc. Japan* 63, 1093) work on fish oils also suggested that the reversion to fishiness was due to constituents in the unsaponifiable fraction. Hietaranta (*Suomen Kem-*

istilehti 19B, 125) attributed development of fishy taste in butter to release of trimethyl amine by microbiological action; buffering the pH to between 6 to 7 was said to almost eliminate the defect.

Lemon (*Can. J. Res.* 25F, 34) continued to support the theory that the reversion of hydrogenated linseed oil was related to isolinoleic acid. The evidence was summarized as follows: (a) Partially hydrogenated perilla oil developed the same odor as the hydrogenated linseed oil products, (b) a concentrate of isolinoleic acid developed a similar odor when heated, (c) when fractionated fatty acids that were crystallized from hydrogenated linseed oil were reesterified with glycerol, most odor development occurred in the fraction containing most isolinoleic acid. Lips *et al.* (*Ibid.* 44), in continuing this work, were unsuccessful in eliminating flavor reversion by removal of impurities from the oil, by selective hydrogenation, or by the use of solvent-segregated material from a commercial polymerization process.

Biochemistry and Physiology

DESIRABILITY OF FAT IN THE DIET. The most exhaustive investigations on the desirability and on the optimum level of fat in the diet have been in progress at the University of Southern California, School of Medicine (Deuel *et al.*—*J. Nutr.* 33, 569; Scheer *et al.*—*Ibid.* 583, 641; 34, 581; *Am. J. Physiol.* 149, 194). Feeding increasing amounts of fats to rats resulted in better growth, reproduction, lactation, and greater physical capacity. As a criterion for physical capacity, the rats were loaded with constant weights and allowed to swim to exhaustion. Here the physical capacity increased with increase of zero to 40% in the fat content of the diet, optimum growth was observed on diets containing 20 to 40% fat, and rats receiving diets with 20% fat fed *ad libitum* had the highest content of body fat. In restricted feeding tests growth, fertility, lactation, and physical capacity were maintained better on the fat-containing diets than on similar diets lacking fat. Likewise, recovery of the above characteristics after severely restricted feeding was best supported by diets with liberal amounts of fat. In another work, an inverse relationship between lactation performance and fat content of purified diets varying in fat from zero to 48% was attributed to missing factors for lactation (Nelson & Evans—*Arch. Biochem.* 12, 229). Supplement prepared from a liver eluate powder induced normal lactation. Also, in other experimental work, female rats on low-fat purified diets produced young with visible hemorrhages (Brown *et al.*—*J. Nutr.* 34, 141). It was suggested that some substance which maintains capillary strength was not synthesized in the body when the diet was low in fat and deficient in vitamin K.

Desirability of fat in the diet was also reflected in work on the so-called "essential fatty acids." Barki *et al.* (*Proc. Soc. Exper. Biol. & Med.* 66, 474) produced symptoms attributed to deficiency of unsaturated fatty acids most rapidly in rats by severe depletion of fat reserves followed by *ad libitum* feeding of fat-free diet. In this work, depleted rats maintained on a fat-free diet for sufficiently long periods recovered from the essential fatty acid deficiency symptoms, thus suggesting that there was some synthesis of essential fatty acid. Loeb & Burr (*J. Nutr.* 33, 541) observed that male rats were more sensitive to a

deficiency in essential fatty acids than females when both derived the bulk of their calories from saturated fats. Mothers deficient in unsaturated fatty acids did not share or transmit the essential fatty acid from their body fats to their offspring when maintained on a fat-free diet (Bernard & Bodur—*Helv. Chim. Acta* 29, 1782). The relation of human eczema to essential fatty acids was studied in patients of various ages (Hansen *et al.*—*Am. J. Diseases Children* 73, 1). In general, the iodine value of the serum fat of patients with eczema was much lower than that of normal subjects, and clinical response to feeding unsaturated fats induced a definite benefit in the majority of cases, especially in infants and young children. Consequently, the authors advised that such treatment should not completely substitute, but must be an adjunct to local therapy.

Two review papers discussed generally the place of fats in the diet (Bernhard—*Mitt. Lebensm. Hyg.* 35, 371; Schmalfuss—*Z. Fleisch- u. Milchhyg.* 54, 155). The same concepts were involved in a discussion on the effect of removal of lipids by solvent extraction on the feeding value of cottonseed and soybean livestock meals (Reiser—*Texas Agr. Exper. Sta. Misc. Publ.* 10, 7 pp.). In some cases, rations made with fat-free meals may require the addition of other sources of fat.

Oleic acid or fats containing this acid was found to be required in culture media for the growth of several lactic acid bacteria (Williams *et al.*—*J. Biol. Chem.* 170, 619; *Research in Agr. (Iowa)* 1945-6, 7; Hutchings & Boggiano—*J. Biol. Chem.* 169, 229). This growth-promoting activity of oleic acid was considerably greater than that of vaccenic acid for *Saccharomyces cerevisiae*, *Lactobacillus arabinosus*, and *Lactobacillus casei*; and elaidic acid was slightly active for the first two species but it exceeded oleic acid in promoting growth of the latter (Axelrod *et al.*—*J. Biol. Chem.* 169, 761). Oleic acid could prevent the growth of certain bacteria, but this property was counteracted by the presence of proteins which bind the acid and permit initiation of growth (Davis & Dubois—*J. Exptl. Med.* 86, 215).

RELATIVE DIETARY VALUES OF FATS. According to Crockett & Deuel (*J. Nutr.* 33, 187), various fats of melting points from 34 to 48° were digested to the extent of 94.3 to 97.0%, and the rates at which these were absorbed during three- and six-hour digestion experiments were not significantly different. Hydrogenated fats of melting points greater than 48° were absorbed at a slower rate, and the total absorption was less than that of the lower melting fats. Similar data recorded by Nhavi & Patwardhan (*Indian J. Res.* 34, 49) and Basu and Nath (*Indian J. Med. Res.* 34, 13, 19, 27, 33) included information from tests with liquid fats. The per cent absorptions were 90 to 99%, but the rates of absorption for the liquid fats and butterfat during the two- and four-hour digestions were greater; and at six hours the absorption rates were approximately that of the other fats. In the same series of investigations, butterfat or mustard, sesame, or peanut oil allowed good retention of dietary calcium and phosphorus while coconut oil increased excretion of calcium. Of the above listed oils and fats, butterfat induced the best growth in rats. Ahmad & Bahl (*J. Sci. & Ind. Res. (India)* 5B, 1) rated the digestibility of fats by *in vitro* hydrolysis tests with pancreatic lipase. Cow milk fat

was digested more rapidly than buffalo milk fat; and the vegetable fats were classified in the following descending order of digestibility: peanut, coconut, sesame, cottonseed, olive, linseed, kadoo, almond, mahuwa, castor, and mustard oils. In a review on the synthetic fats from coal for human consumption, Thomas & Weitzel (*Deut. med. Wachschr.* 71, 18) considered them suitable when free of branched chain and dicarboxylic acids. The importance of using a biologically unobjectionable glycerol was also stressed, for some synthetic glycerol products were found to contain impurities harmful to the liver.

Euler *et al.* (*Arkiv. Kemi, Mineral Geol.* 22A, No. 8, 12 pp.) in a continuation of studies on comparison of margarine and butterfat, recorded that the former was superior for rats in regard to mortality of females, number of litters born, number of offspring, and mortality of offspring during the first month. Vitamin E was suggested as an important factor in these tests. Individual weights of the offspring were higher on the butter diet.

Vaccenic acid, a growth factor recently reported in summer butter by Boer *et al.*, has attracted the interest of several groups of investigators. Boer *et al.* (*J. Nutr.* 33, 339, 359; *Voeding* 7, Suppl. No. 1, 45) and Groot *et al.* (*Rec. trav. Chim.* 66, 633) have isolated the acid from butter and partially hydrogenated tung oil and confirmed its growth-promoting properties. The method of isolation involved distillation of methyl esters of the fatty acids and fractionation, first as lead salts then as mercuric salts. Jack & Hinshaw (*J. Nutr.* 34, 715) also concentrated the growth factor from milk fat. This concentrate was a -53° filtrate milk-fat fraction obtained by fractional crystallization from organic solvents. When pentane (Skelly-solve A) was used as the solvent the growth promoting value of the fraction was lower, possibly because of a deleterious impurity in this solvent. In similar work, Geyer *et al.* (*J. Biol. Chem.* 169, 227; *J. Dairy Sci.* 30, 299) used acetone as the solvent. This solvent had no deleterious effect on the nutritive value of the vaccenic acid fractions. Investigations on other fats by this group indicated that the highest amounts of vaccenic acid occur in fats obtained from ruminants. This confirms several earlier publications, one of the most recent of which also suggested the use of the determination of vaccenic acid to distinguish beef fat from pork fat (Bauer—*Z. Lebensm. -Untersuch. u. -Forsch.* 86, 223). Brouwer & Jonker-Scheffener (*Rec. trav. chim.* 65, 408) recorded that butterfat from cows on grass contained 3.9-4.9% and on winter ration 1.3-1.7% vaccenic acid. In this work there was a positive correlation between the vaccenic acid content and the iodine number of the butterfats. Taking the research on vaccenic acid as a whole, it becomes obvious that the acid is common to animal fats. The fat of ruminants contains the highest concentration, and it is practically absent from natural vegetable oils but it is developed in vegetable oils during hydrogenation.

ABSORPTION OF FATS. Several reviews on the mechanism of absorption of fats from the intestines were prepared by Frazer (*Chemistry & Industry* 1947, 379; *Schweiz. Med. Wochenschr.* 76, 903; *Brit. Med. J.* 2, 641). The information here supports the partition theory in preference to the belief of complete hydrolysis during digestion. He discussed the functions of phosphorylation and choline, the routes of fats after

absorption, and classification of fat absorption defects on an etiological basis with regard to the partition theory. Another review paper also contained a classification of the factors associated with defective absorption of fats (Kirschen & Weinberg—*Am. J. Digestive Dis.* 14, 30).

Some observations on the course of digestion of fat should aid future investigators in planning studies on absorption of fats. Annegers & Ivy (*Gastroenterology* 8, 711; *Am. J. Physiol.* 150, 461) devised a procedure for measuring emptying time of the stomach and, when they applied it to the study of the effect of the fat content of meals, showed that the increased time was a consistent characteristic for given individuals. No significant digestive differences were found between lard and hydrogenated vegetable oil cooking fats. Veghelyi (*Ann. Paediat.* 168, 93) reports that lipase was always present in the stomach and was not dependent on the composition of the food as was pepsin. In cases of arterial hypotension, there occurs a lower rate of fat splitting accompanied by disturbances of evacuation. Crude lecithin added to fat increased the digestibility and rate of absorption of the fat and lowered susceptibility to diarrhea caused by large doses of fats (Augur *et al.*—*J. Nutr.* 33, 177). With supplementary lecithin, larger portions of the lipids were excreted as soaps rather than as neutral fat plus fatty acids. Excretion of soaps in place of neutral fat plus fatty acids also was observed in comparing, respectively, stools of bottle-fed and breast-fed infants (Nielson—*Acta Paediat.* 31, 226). According to Wikoff *et al.* (*Am. J. Digestive Dis.* 13, 228; 14, 58) dogs were constipated with diets containing 5% or more tristearin or tripalmitin; and conversely, small amounts of saturated acids of less than 12 carbon atoms or their glycerides, or olein in over 10% concentration, were laxative. Wollaeger *et al.*'s (*Gastroenterology* 9, 272) plotting of fecal fat losses against fat intake showed enough quantitative relationship to suggest that unabsorbed dietary fat probably accounts for a larger proportion of fecal fat than was commonly supposed.

Some experiments involved the effect of fat on digestion of other constituents of the diet and *vice versa*. The addition of moderate or large amounts of fat to lean beef did not retard evacuation from the stomach of either the protein or the fat of the meal (Killian & Knapp—*J. Am. Oil Chem. Soc.* 24, 71). *In vitro* experiments with pepsin and trypsin digestion indicated the digestibility of food heated in fat was inferior to that of food boiled in water (Yenson—*Bull. faculte med. Istanbul* 9, 166). The presence of acetic acid (vinegar) as in a salad dressing did not affect *in vivo* digestibility of fats (Boekenoogen—*Voeding* 6, 218).

When lactose was the dietary carbohydrate in a 70% sugar and 30% fat diet, survival was longer on rations containing margarinefat or butterfat than on diets containing corn or cottonseed oil (Ershoff & Deuel—*Am. J. Physiol.* 148, 45). With sucrose as the carbohydrate no significant differences in length of survival were observed. Digestibility of galactose by rats was inversely related to the percentage of fat in the diet (Nieft & Deuel—*J. Biol. Chem.* 167, 521).

INTERMEDIATE METABOLISM OF FATS. New facts were observed in work on deposition and synthesis of fats in the body. These were interpreted with regard to their relationship to various theories or hypothesis

on the subjects. For instance, the observation that rats synthesized C_{16} from C_{14} acids and C_{14} , C_{16} , and C_{18} from C_{12} acids was interpreted as evidence for reversibility of β -oxidation (Klein—*Fette u. Seifen* 51, 184). A failure to prevent the decrease in lower fatty acids in milk in fasting cows being nourished intravenously was said to render the theory of a blood carbohydrate origin of the lower fatty acids extremely unlikely (Mann & Shaw—*J. Dairy Sci.* 30, 183). The influence of various feed fats on the fatty acid composition of buffalo milk fat was recorded (*Arch. Biochem.* 13, 389). Melting points of human depot fat were related to their location, *i.e.* visceral fat melted at 30-35°, fat from peripheral organs melted lower, and that of feet often melted between 0 and 10° (Schmidt-Nielson—*Acta Physiol. Scand.* 12, 123). The synthesis of lipids in fetal rats was at a much higher rate than that in adult animals (Goldwater & Stetten—*J. Biol. Chem.* 169, 723). According to feeding tests with deuterium oxide on animals in the last days of pregnancy, half the fetal fatty acids were found to develop in 1.5 days and half of the fetal cholesterol was synthesized in about 2.5 days.

The commercial use of lipogenics was investigated. Fat deposition was stimulated in poultry by oral administration of dienestrol diacetate and dianisylhexane (*Poultry Sci.* 26, 419). By controlled administration it was possible to stimulate the fat deposition below the point where lipemia developed in the birds. The milk and butterfat production of cows was increased by feeding dairy cows iodinated casein (Booth *et al.*—*J. Dairy Sci.* 30, 443). The cows lost weight, and decreases of 30-63% vitamin C and 20-40% urea nitrogen in the skim milk nitrogen were also observed in this work.

The cholesterol and fatty acid content of blood serum of men appeared to be independent of the fat intake except when abnormally large amounts of fat were consumed (Nhavi & Patwardhan—*Indian J. Med. Res.* 34, 257). However, in mobilization of fat reserves by fasting there appeared to be a slight lipemia in the early fasting days followed by a decrease on the fifth day (Hodge *et al.*—*J. Biol. Chem.* 169, 707). The concentration of blood phospholipids appeared to follow the same course. Another observation during fasting suggested that the less saturated of the unsaturated fatty acids of guinea-pig muscles were preferentially mobilized (Capraro & Pasargiklian—*Boll. soc. ital. biol. sper.* 22, 186). In this work the iodine value of the unsaturated acid fractions increased from 33% above that of oleic acid to 81% higher after fasting. Another study on mobilization of fat indicated that in fasting rats the white body-fat was used up much faster than the brown interscapular-fat (Clement—*Compt. rend. soc. biol.* 141, 255). The same phenomenon occurred when mobilization of depot fat was accelerated with administration of extracts of adrenals, or anterior or posterior hypophysis. Weil & Stetten's (*J. Biol. Chem.* 168, 129) observation that pituitary glands contained a fat-mobilizing hormone confirmed similar work by Best & Campbell who had named this hormone, adipokinin. However, this new work produced evidence that during fasting or in diabetes a fat-mobilizing substance was excreted in the urine.

Buchanan *et al.* (*J. Biol. Chem.* 169, 411), in a study of the mechanism of fatty acid oxidation with isotopic acetoacetate, developed evidence that the

appearance of an isotope in the carbonyl carbon of acetoacetate during metabolism of carboxyl isotopic octanoate in liver slices does not result, as formerly suggested, from a preliminary formation of carboxyl-isotopic acetoacetate and a secondary splitting of this material into two-carbon fragments which recondense randomly to form acetoacetate labeled in both the carbonyl and carboxyl position. Their belief was that the two-carbon fragments were split off from fatty acids and, failing to be oxidized, were condensed into acetoacetate. Another study on this phase of fat metabolism by Wilson (*Science* 105, 637) produced evidence which supported a theory that, after the metabolic oxidation of fats and carbohydrates to two-carbon units, the material from both substances enters the same recombination processes.

Buu-Hoi *et al.* (*Helv. chim. acta* 29, 1334) added radio-active bromine to test acids in a comparison of the metabolism of normal fatty acid with branched-chain acids. A lower radio-activity in animal organs after injection of the latter as compared to that for normal fatty acids was interpreted as evidence that addition of side chains to fatty acids retards their metabolism.

The communications on fat metabolism in the liver dealt principally with agents that affected the fat content of the liver and, in some cases, the relation of liver fat to metabolism and mobilization. Some of the newly recorded lipotropic agents were estrone (György—*Arch. Biochem.* 12, 125), caffeine, theobromine, and theophylline (*Ibid.* 15, 439). The obtaining of a lipotropic effect with the ethyl homolog of choline and proof of its *in vivo* incorporation in liver phospholipids were suggested as evidence that the lipotropic effect of choline is associated with the intact molecule rather than its methyl groups (McArthur *et al.*—*Biochem. J.* 41, 612). Montgomery *et al.* (*Am. J. Physiol.* 148, 239) recorded that pancreatic juice was highly active in preventing fatty livers of depancreatized dogs. In similar tests purified casein was inactive, but hydrolyzed casein prevented the fatty infiltration (Chaikoff *et al.*—*J. Biol. Chem.* 168, 177). The failure of purified casein was attributed to the inability of depancreatized dogs to release effective amounts of methionine from this casein. None of the methyl derivatives of pyridine influenced the liver fat of fatty livers (Coulson & Brazda—*Proc. Soc. Exptl. Biol. & Med.* 65, 1). The lipotropic constituent of pancreas extracts was considered to be a compound other than inositol, for the latter had a weaker effect with similar dosage (Eilert & Dragstedt—*Am. J. Physiol.* 147, 346). The extracts of various organs having both lipotropic and hyperglycoside properties in regard to composition of the liver did not run parallel in the potencies of these reactions (Natanzon—*Byull. Eksptl. Biol. Med.* 11, 446). Frada & Cali (*Boll. soc. ital. biol. sper.* 22, 906), working on the lipotropic substance from pancreas, showed that intramuscular injections cause an increase in blood ketone bodies. The animals killed six to eight hours after injection had a 50% reduction in hepatic glycogen and lesser decreases in heart and skeletal muscle.

Replacing dextrin and sucrose with lactose in a diet producing fatty liver caused a decrease in fatty infiltration of the liver (Artom & Fishman—*J. Biol. Chem.* 170, 587). Lactose also improved the effectiveness of choline for reducing liver fat. The inability

of casein to reduce the excess fat in livers caused from alcohol administration suggested that this type of fatty liver was unrelated to lipotropic factors (Ashworth—*Proc. Soc. Exptl. Biol. & Med.* 66, 382). Also a lowering of liver fat resulting from partial nephrectomy was not influenced by lipotropic substances (Ludewig & Chanutin—*J. Biol. Chem.* 167, 35). This operation also caused hyperlipemia (Heymann—*Proc. Soc. Exptl. Biol. & Med.* 66, 82).

Baccari & Fidanza (*Boll. soc. ital. biol. sper.* 22, 772), in investigations on methods of determining lipotropic substances, proposed that pancreatic extracts be evaluated on the basis of their protective action against phosphorus intoxication produced in rats by feeding them phosphorated oils. According to Rose *et al.* (*Proc. Soc. Exptl. Biol. Med.* 64, 352) fatty livers, produced by experimental diets in which mixtures of essential amino acids replaced protein, were not prevented with methionine. In other experimental diets containing casein, deficiencies of labile methyl were aggravated by addition of sulfur-containing amino acids or fat (Salmon—*J. Nutr.* 33, 155).

Some interest was displayed in abnormal pathology related to lipotropic factors, but other than that which occurs in the liver. Clarkson & Best (*Science* 105, 622) reported that addition of fat and choline to stock diets of dogs did not cause the macrocytic anemia as recorded earlier by Davis. Acute choline deficiency to the point of death and choline deficiency during five months did not affect the blood pressure of rats (Sobin & Landis—*Am. J. Physiol.* 148, 557). Thus, it was reported that the renal lesions of acute choline deficiency do not belong to that group which frequently produce hypertension. Hartroft & Best (*Science* 105, 315) recorded several observations in connection with the relationship of choline deficiency to kidney lesions. A formation of fatty droplets occurred before the onset of congestion, necrosis, hemorrhage, or cast formation. Lipase was diminished or absent in affected kidneys, and a reduction of the ratio of phospholipids to total lipids also resulted.

The biochemistry and physiology of cholesterol were studied in relation to various aspects. Sinclair & Chipman (*J. Biol. Chem.* 167, 773) reported that fatty acid composition of rat liver cholesterol esters was governed more by the food fats than were the fatty acids of the liver glycerides. Cholesterol feeding was unusually detrimental to splenectomized guinea pigs (Kennedy & Okey—*Am. J. Physiol.* 149, 1). It reduced the weights of animals and caused rapid breakdown of red blood cells. This was taken to indicate that hyperplasia of the spleen observed in guinea pigs made anemic by cholesterol feeding was not directly responsible for the anemia. Atherosclerosis and arteriosclerosis, similar to those seen in humans, were said to be induced in dogs by ingestion of cholesterol and thiouracil (Steiner & Kendall—*Arch. Path.* 42, 433). One treatment for peptic ulcer comprised elevation of the blood cholesterol level by ingestion of food containing relatively large amounts of cholesterol (Hyman—*Am. J. Digestive Dis.* 14, 235). A decholesterolization of old hens by administration of methionine was observed by Herrmann (*Proc. Soc. Exptl. Biol. & Med.* 64, 204).

The work on sphingomyelin dealt principally with its occurrence and isolation from other lipids which are found in animal tissues (Thannhauser *et al.*—*J.*

Biol. Chem. 166, 505, 669, 677; Carter *et al.*—*Ibid.* 169, 77).

THE LIPIDS IN DISEASE. In a general discussion on atherosclerosis by Moroton (*Science* 106, 190), the disease was associated with people who eat high fat diets. Sims and co-workers (*J. Gerontology* 2, 205) associated deposition of fat in atherosclerosis with an unbalanced relationship of "lipfanogens" and "antilipfanogens" in blood. These biological factors of the blood were said to normally combine in a manner which interferes with formation of fat granules.

High-fat diets (70%) were said to decrease diuresis and eliminate glucose excretion in rats made diabetic with alloxan (Lazaris & Brzezinskaya—*Byull. Eksptl. Biol. & Med.* 22, No. 6, 36). Diets high in fats and restricted in carbohydrates increased postabsorptive (fasting) blood sugar level (Somogyi & Cook—*Proc. Soc. Exptl. Biol. & Med.* 65, 336). This occurred in both healthy and diabetic individuals, but was more accentuated in the latter.

According to Cirio & Rosso (*Pathologica* 39, 79) the course of tuberculosis was more serious on an abundance of lipids as compared to small amounts of lipids in the diet. Negre *et al.* (*Ann. inst. Pasteur* 71, 406) recorded that ethyl esters of stearic and palmitic acids retarded evolution of tuberculosis lesions.

Harris (*Cancer Res.* 7, 26) submitted results of a test to disprove the belief that wheat-germ oil was carcinogenic. The kidney damage observed in hamsters following chronic administration of diethylstilbestrol and sesame oil was said to be in the direction of malignant tumors in the male and of glomerulonephritis in the females (Matthews *et al.*—*Proc. Soc. Biol. Med.* 66, 195). In experimental carcinogenic production in mice with injections of 3,4-benzopyrene, the incidence of tumors was accelerated by cholesterol and inhibited by phospholipids. The incidence of tumors was greater when the carcinogenic material was administered in hydrogenated oil as compared to using a nonhydrogenated oil as the solvent.

After a hemorrhage resulting from a duodenal ulcer, in a patient using aluminum hydroxide as an antacid, small concretions were found which were composed of fatty acid salts of aluminum with small amounts of neutral fat and traces of cholesterol and proteins (Hall & Auerbach—*Am. J. Digestive Dis.* 14, 63).

FAT SOLUBLE VITAMINS. The physiology and biochemistry of fat-soluble vitamins are not included in the scope of this review. For a review of these, readers are referred to Embree (*Ann. Rev. Biochem.* 16, 323.)

Most interest in the analysis of oils for vitamin A dealt with spectral procedures. Jones *et al.* (*Anal. Chem.* 19, 142) described an adaptation of the Beckman quartz spectrophotometer for measurement of vitamin A by the Carr-Price reaction. Jones (*Com. Fisheries Rev.* 9, No. 8, 22) also demonstrated that tungsten light sources could be adapted to give a reliable vitamin A determination in spectrophotometric methods. Sobel & Werbin (*Anal. Chem.* 19, 107) preferred determining vitamin A in fish liver oils with activated dichlorohydrin because it was simpler and the results agree with those obtained spectrophotometrically and with antimony trichloride methods. Bucher *et al.* (*Com. Fisheries Rev.* 9, No. 7, 15) investigated vitamin A analytical methods. They

showed poor agreement between ultraviolet absorption and antimony trichloride methods. Bolomey (*J. Biol. Chem.* 169, 323, 331) recorded absorption data on vitamin A and its decomposition products. During molecular distillation, some constituents of shark-liver oils were converted to vitamin A, for distillates were more potent in this factor than the original oil (Chéchan *et al.*—*Bull. soc. chim. biol.* 28, 577). Several works on analysis of vitamin A dealt with the chromatographic spectrometric procedures and their standardization (Johnson & Baumann—*J. Biol. Chem.* 169, 83; Awapara *et al.*—*Science* 104, 602; Glover *et al.*—*Biochem. J.* 41, 94; Muller & Reinert—*Nature* 157, 876; Wilkie *et al.*—*J. Assoc. Official Agr. Chem.* 30, 382). Morton & Stubbs (*Biochem. J.* 41, 525) also suggested corrections for spectrophotometric methods to bring them in closer agreement with the biological potencies of the samples. In assays of vitamin A, a concentrate fed to chicks as a water emulsion had a greater activity than the same sample administered in oil (Halpern *et al.*—*Science* 106, 40).

The new analytical data on vitamin A in butters dealt with: seasonal variations (Ellenberger *et al.*—*J. Nutr.* 33, 39), vitamin A potency of butters produced in Mississippi (*Miss. Agr. Exper. Sta. Bull.* 434), and in Wyoming (Willard—*Wyoming Agr. Exper. Sta. Bull.* 279), and vitamin A and carotene in buffalo butterfat (De *et al.*—*Indian J. Med. Res.* 34, 3; Ahmad—*Ibid.* 75). Analytical results were also recorded for vitamin A in Indian shark-liver oils (Gajjar—*J. Sci. Ind. Res. (India)* 5, No. 1B, 18), carp-liver oil (Raffy—*Compt. rend. soc. biol.* 139, 537), long-jay flounder-liver (Swain & Barraclough—*Fisheries Res. Board Can. Prog. Repts. Pacific Coast Sta.* 72, 41), brill livers (*Ibid.* 71, 12), fish of the Gulf of Biscay (Demange & Moco-roa—*Anales fís y quím. (Madrid)* 42, 685), liver oil of *Scoliodon Walbeehmi* (Hata & Kunisaki—*J. Chem. Soc. Japan* 63, 1585), and a comparison of the liver oil of sharks, trout, whales, cod, and others (Higashi—*J. Agr. Chem. Soc. Japan* 17, 801).

In determination of vitamin D by chick assay, the British Standard and the Association of Official Agricultural Chemists' methods were about equal in precision, but by comparison with radiographic technique the latter was more satisfactory (Campbell & Emslie—*Poultry Sci.* 26, 255).

The activities on the determination of tocopherols were two modifications of the Emmerie-Engel procedure (Stern & Baxter—*Anal. Chem.* 19, 902; Lundborg—*Arkiv. Kemi. Mineral Geol. A21*, No. 2, 1). Chipault & Lundberg (*Arch. Biochem.* 12, 317) recorded that α -tocopherol may occur in fats of hogs. This tocopherol was isolated from soybean oil by Stern *et al.* (*J. Am. Chem. Soc.* 69, 869) and its properties were recorded. Mason and Filer (*J. Am. Oil Chemists' Soc.* 24, 240), in a review of the inter-relationship of dietary fat and tocopherols, suggested that the tocopherols function as antioxidants to protect fat in diet before digestion, in the digestive tract, and especially during mobilization, metabolic turnover, and storage within tissue cells.

Characteristics and Composition

ANALYSIS OF FAT SOURCES. Several slight modifications were recommended for the American Oil Chemists' Society's standard procedures for analysis of seeds and meals (Hopper *et al.*—*J. Am. Oil Chem-*

ists' Soc. 24, 303). As examples: for moisture determination, a five-gram sample is dried two hours at 130°; the official method for oil in cottonseed was recommended for acceptance as a tentative procedure for soybean; ash should be determined by ashing two grams for two hours at 600°; and similar details were concerned with nitrogen and crude fiber determinations. The accuracy and reproducibility of results obtained by procedures set up by the American Oil Chemists' Society for oil and nitrogen were evaluated in the collaborative work done through the Smalley Foundation (Rettger—*Ibid.* 42). Similarly, the accuracy of performances of approved chemists handling Commodity Credit Corporation processors' soybean analysis work was determined and published (Doughtie—*Ibid.* 265).

With regard to official methods of sampling cottonseed, soybeans, and peanuts, Doughtie (*J. Am. Oil Chemists Soc.* 24, 335) discussed the problems encountered and suggested that recommendations be adopted as to: (a) sampling tools; (b) removal of foreign material by screening; (c) specifications for riffles for reducing sample; (d) specification of a definite, minimum sample drawn per ton of peanuts; (e) size of sample sent chemist; and (f) elimination of all sampling by hand. Stansbury & Guthrie's (*J. Agr. Res.* 75, 49) analyses of cottonseed and peanuts resulted in a recommendation that, for storage, the analytical samples should be dried to a moisture content of 8.3% and stored in sealed containers at 1° or less.

The new studies on determination of fat in various products reflected a desire to gain either accuracy or rapidity. Reisser (*J. Am. Oil Chemists' Soc.* 24, 199) recorded that the use of ether was more efficient in extracting fatty acids than the alcohol-ether method. The latter, however, was more efficient in extracting phospholipids. Fellenberg (*Mitt. Lebensm. Hyg.* 35, 389) preferred ether extraction in contrast to the alcohol-ether methods for most foods. But, for some vegetable matter where fat was occluded in cells, he proposed an ether extraction, followed by treatment with hydrochloric acid and re-extraction by the alcohol-ether method. Taylor (*J. Assoc. Official Agr. Chem.* 30, 597) suggested that where non-protein nitrogen was present in the sample petroleum ether was a more suitable solvent than ethyl ether for determining fat. Stansby (*Ibid.* 595) recorded that binary azeotropic mixtures of benzene and methanol solvent gave higher fat content values for fish than did acetone and some other solvents; however, the procedures with binary solvents were considered too cumbersome for routine analyses. Bohn (*Z. Lebensm.-Untersuch. u. -Forschung.* 86, 64) designed apparatus for the analytical extraction of fat from foods in a closed space, the purpose being to reduce oxidation of the fat by air. A rapid oil determination method comprised allowing one gram of sample to stand over night in 50 cc. of petroleum ether in a 50-cc. volumetric glass-stoppered flask and determining the fat in a 25-cc. aliquot (Cerqueira—*Chimie & industrie* 56, 299). A method for tung kernels was similar except that hexane was used as the solvent and the samples were dispersed in hexane by means of a Waring Blendor before placing in the volumetric flask (Hamilton & Gilbert—*Anal. Chem.* 19, 453). The refractometric method for determining oil in oil pressing residues was modified and equations for

calculating oil content were recorded (Hajdu—*Magyar. Kém Lapja* 2, 256). In the dairy industry it was reported that, for testing homogenized milk, the Mojonnier fat test was most accurate; the Babcock method was modified to assure accuracy; and the Pennsylvania and Minnesota methods were considered unsuitable for this milk product (Trout & Lucas—*J. Dairy Sci.* 30, 145). Also in this regard, Harland & Davis (*Ibid.* 29, 845) tabulated the results obtained by the Babcock *vs.* Mojonnier tests on milks homogenized at 1500- to 4000-lb. pressures. The results by the latter method as compared to the former were higher to an increasing extent as the pressure of homogenization was increased. A preliminary report was made on collaborative work on the method of determination of fat in cheese (Horwitz—*J. Assoc. Official Agr. Chem.* 30, 421).

Some fat analysis developments were designed for use by biochemists and physiologists. Mickelson *et al.* (*J. Am. Dietetic Assoc.* 23, 952) suggested that 0.5% of the emulsifier, "Duponol C," be added to rat diets in nutrition experiments in which the diets are analyzed for fat content. The emulsifier brings about a better dispersion of fat throughout the ration, thus leading to more accurate and more reproducible results in the fat determination. For determination of neutral fat and free fatty acids in feces, Asenjo & Caballero (*Rev. asoc. technol. med. y microscop. Puerto Rico* 5, 37), recommend mixing about 60 grams of sample with enough water in a Waring Blendor to obtain a semi-liquid mass; 2.5-3.5 grams of this were extracted with acetone; the acetone-soluble residue was re-extracted with petroleum ether; free fatty acids were then determined by titration, and the neutral fat was determined from the amount of alkali required for its saponification. A colorimetric procedure for the determination of fatty acids was based on the measurement of color change produced by the reducing action of fatty acids on a sulfuric acid-dichromate mixture (Bloor—*J. Biol. Chem.* 170, 671). Boyer's *et al.* (*Ibid.* 167, 407) measurements by ultra-filtration and dialysis methods of the amount of fatty acids that combine with serum albumins showed that the two procedures agree satisfactorily. The extents to which several fatty acids combine with serum albumin were recorded.

PHYSICAL CHARACTERISTICS OF FATS. The German standard methods for physical tests on fats were published by Lottermoser (*Fette u. Seifen* 51, 391) and Wefelscheid (*Ibid.* 398).

In regard to color, a pamphlet was issued on the use of the Lovibond system for determination of color (*Tintometer Ltd., Colour Lab., England, 1947, 24 pp.*). Thompson (*J. Am. Oil Chemists' Soc.* 24, 387) recommended that color readings on oil be made spectrophotometrically. The red readings would not exactly correlate with the Lovibond readings which are standard, but he claimed that disagreement was due to erroneous values obtained by the standard method on oils containing green. Whyte (*Ibid.* 24, 137) applied a photoelectric photometer with three filters for determination of color of oils. His purpose was to eliminate the personal factor in the visual method. Hinko (*Fette u. Seifen* 51, 149) recommended that the intensity of the yellow color be considered one of the criteria for evaluating the quality of tallow for margarine manufacture. This color in tallow was attributed to vitamin A precursors.

Schmidt-Nielsen (*Acta Physiol. Scand.* 12, 110) made a plea for standardization of the melting point determination for biochemical work. His recommendation was to cool rapidly to an extremely low temperature (-70°) whereby a microcrystalline mass was produced which made possible relatively exact observations of the clear point. Charbonnet & Singleton (*J. Am. Oil Chemists' Soc.* 24, 140) recorded the heat capacity, heats of fusion and transition, and entropy of trilaurin, trimyristin, tripalmitin, and tristearin. This information is of both fundamental and applied interest for understanding the properties of solid fats and for designing processing methods. Ferguson & Lutton (*J. Am. Chem. Soc.* 69, 1445) recorded x-ray diffraction on triolein to characterize more fully the three polymorphic forms observed several years ago by Wheeler *et al.* The types of structure occurring in triolein were comparable with similar types occurring in trisaturated glycerides, but, with triolein, there occurred a translucent state brought about by rapid chilling to -70° which did not occur among the saturated triglycerides. X-ray diffraction data were recorded also on mixed saturated triglycerides (Sidhu & Daubert—*Ibid.* 1451); the mono-, di-, and triglycerides of erucic, brassidic, oleic, and elaidic acids (Carter & Malkin—*J. Chem. Soc.* 1947, 554); diolein (Daubert & Lutton—*J. Am. Chem. Soc.* 69, 1449); and branched chain fatty acids of wool fat (Valick—*Ibid.*, 2317). With the saturated triglycerides all workers confirmed the presence of three forms. Both investigators who worked on diolein obtained only one form, and the data on both the saturated and unsaturated α -monoglycerides showed that two polymorphic forms existed. The data on the branched fatty acids were discussed in terms of a spiral chain configuration. A review of the applications of x-rays to the study of fats was prepared by Trillat (*Oléagineux* 2, 68).

Other physical measurements on fats were made for various reasons. Althouse *et al.* (*J. Am. Oil Chemists' Soc.* 24, 257) recorded the refractive indexes of methyl, propyl, and isopropyl esters of the C_6 to C_{15} saturated fatty acids at temperatures from 20 to 45° at five-degree intervals. Such data find application in fat analysis. The foaming properties of triglycerides, glycol esters, and monohydric alcohol esters of various fatty acids were determined by Wada (*J. Chem. Soc. Japan* 65, 440). The latter esters had no foaming tendency, while the glycol esters foamed considerably. The same author (*Ibid.* 510) also recorded surface tensions of various fatty acids and their esters. Macy & Gehauf (*Science* 106, 274) determined the solubility of chloroform and of methyl nitrite in olive oil as preliminary work in a study of the toxicity of the compounds. A study of the dipole moments of stearic and palmitic acids and their triglycerides in various solvents showed that only acid monomers occurred in dioxane, and any dimers occurring in cyclohexane and benzene have zero moments (Stepanenko *et al.*—*Acta Physicochim. U.S.S.R.* 20, 923). About 80-85% of the acids were associated in pairs in cyclohexane, while the triglycerides showed no noticeable association. Various fatty acids, their mono-, di-, and triglycerides, amines, amides, and other derivatives were evaluated according to their capacity to form close-packed orientated

films on platinum surfaces (Bigelow *et al.*—*J. Colloid Sci.* 1, 513). The data gave an approximate indication of the capacity of the compounds for preventing water from penetrating the metal surface. The test for this characteristic was suggested in connection with the problems of electron diffraction analysis, lubrication, rust inhibition, spreading of oils, and paint adhesion. A procedure for determining the effect of water on dried oil and varnish films comprised definite details of preparing painted stainless steel test panels, soaking them in distilled water, and weighing the amount of water absorbed. Moser *et al.* (*J. Am. Oil Chemists' Soc.* 24, 291) evaluated the ability of eight persons to detect reproducibly various oil samples by odor and flavor and to evaluate them. In demonstrating the application of this subjective test it was shown that addition of citric acid and water washing inhibit flavor reversion of soybean oil. Details for microscopic testing of the water dispersion in butter were designed especially for the study of butter prepared by continuous centrifugal processes (Mohr & Eysank—*Fette u. Seifen* 51, 267).

CHEMICAL CHARACTERISTICS OF FATS. The Kaufmann-Funke method for determining the iodine value of fats was modified so that excess bromine was bound by uncolored excess solution of arsenious acid, and the excess of the latter was back-titrated with potassium bromate (*Kottász-Magyar. Kém. Lapja* 2, 208). The above report and another by Kácl & Fink (*Chem. Obzor* 21, No. 1/2, 3) also described methods of determining iodine value by the use of chloramine reagents. In investigating the thiocyanogen value of fatty acids, Desnuelle *et al.* (*Bull. soc. chim. France* 1947, 325) observed that thiocyanogen absorption by linoleic acid and by methyl linoleate exceeded one mole in 24 hours and continued further after that period. This confirmed older reports by Riemen-schneider & Wheeler and Matthews *et al.* but was contrary to the findings of Kaufmann. Freire [*Bol. ministerio agr. (Brazil)* 34, No. 6, 13] fostered the use of oxidation value, as described about nine years ago by Alexander, for characterizing fats and she recorded this value and the iodine value of several fats and mixtures of fats. As an example of the usefulness of oxidation value, the detection of adulteration of lard with hydrogenated oils of about the same iodine value as lard was illustrated. Kass *et al.* (*Anal. Chem.* 19, 21) in investigation of the hexabromide determination of fats observed that the accuracy of the method was affected by isomerization, sample size, and the method of washing the hexabromide precipitate. They modified the procedures to give more consistent results.

Helrich & Rieman (*Anal. Chem.* 19, 691) simplified the Roberts & Schuette procedure for determining acetyl value by changes in weights of the acetic anhydride used, reduction of sample size, substitution of sodium hydroxide for potassium hydroxide, and other small changes in technic. Two other communications on acetyl value dealt principally with simplifying calculations with the Andre-Cook formulas (Lutz—*Rev. brasil quim. (São Paulo)* 23, 89; Patton—*J. Am. Oil Chemists' Soc.* 24, 158). For determination of monoglycerides in fats, Handschumaker and Linteris (*Ibid.* 143) improved the Pohle *et al.* periodic acid method with regard to accuracy and ease by carrying out the oxidation in a 2:1 acetic acid:chloroform solution.

André *et al.* (*Bull. soc. chim. France* 1947, 215; *Oléagineux* 1, 12) observed that the rapidity of saponification for the saponification value determination was increased as the solvent alcohol used was changed from the C₁ to the C₄ compound. Butyl alcohol as the solvent was not recommended because of discoloration and poor miscibility during back-titration. Propyl alcohol was particularly favored and its superiority was especially evident for the analysis of waxes and nonglyceride oils. In an investigation on the effect of variations from 0.5N to 0.1N of the standard solutions in the saponification determination of solid fats and waxes, low values were obtained when the normality of the titrating reagents was below 0.2 (Toyama—*J. Chem. Soc. Japan* 64, 38).

A newly developed criterium of characterizing bodied oils was named the aluminum value (Eigenberger—*Reichsamt Wirtschafts-ausbau, Chem. Ber.* 1942, 93, 409). It was defined as the number of parts of aluminum by weight combining with 100 parts of sample in treatment of the sample with a solution of aluminum isobutylate in benzene.

Loew (*Industria y quim* 8, 250; 9, 9) reviewed the various physical and chemical tests applicable to detection of adulteration of olive oil. Poggio *et al.* [*Anales fis. y quim (Madrid)* 42, 231] recommended ultra-violet absorption technic for this purpose and recorded absorption data for use as a basis for the investigations. Desai (*Current Sci.* 16, 92) favored the use of the Bellier value together with the index of refraction as a rapid criterion for adulteration of oils. The adulteration of fats with hydrocarbon oil and its detection were discussed by Issoglio (*Olearia* 1, 103).

Reports on results of committee work in modifying and testing standard analytical procedures for fats and oils and discussions on changes in standard methods were published for American Oil Chemists' Society methods (Mehlenbacher *et al.*—*J. Am. Oil Chemists' Soc.* 24, 76; Vollertson—*Ibid.* 334); the German standard methods (Kaufmann & Heinz—*Fette u. Seifen* 51, 258); and the methods of the International Commission for the Study of Fats (Balestrini—*Olii Minerali grassi e saponi, colori e vernici* 24, 6, 18, 30, 42, 52, 65, 75, 89, 100; Burton & Robertshaw—*J. Intern. Soc. Leather Trades' Chemists* 31, 304). Bolley (*J. Am. Oil Chemists' Soc.* 24, 146) classified and made references to analytical methods of the most usefulness for evaluating drying oils. Collaborative evaluations and improvements on the A.S.T.M. chemical and general laboratory tests for greases were also made (Anon.—*A.S.T.M. Bull.* 148, 73). The specifications for the oil used in the Norwegian sardine canning industry were issued (Ronold & Taarland—*Tids. Hermetikind.* 32, 75).

COMPOSITION OF FATS AND OILS. Analytical data on many fats, hitherto accepted, may require revision on the basis of results determined with more accurate new procedures. For example, on applying "amplified distillation" to cottonseed oil the distribution of acids was found to be C₁₂ 0.9, C₁₄ 1.4, C₁₆ 25.9, C₁₈ 69.1, and C₂₀ 0.5 mole per cent (Weitkamp—*J. Am. Oil Chemists' Soc.* 24, 236). "Amplified distillation" in this case, comprised the distillation of the methyl esters of the acids with certain hydrocarbon mixtures; it did not alter the efficiency of the still but allowed full efficiency of the still to be developed with respect to separation of each component, such as adjacent

members of a homologous series or structural isomers. Hilditch *et al.* (*J. Soc. Chem. Ind.* 66, 19, *Analyst* 72, 527), in applying systematic crystallization from acetone, and in spectrographic analysis of alkali isomerized fraction to the analysis of rape and niger seed oils, found a little more linolenic acid than had hitherto been reported. Rapson *et al.* (*J. Am. Chem. Soc.* 24, 84) issued tables and computation schemes which they use in determining the component acids of marine animal oils by the ester-fractionation method. De la Mare & Shorland (*New Zealand J. Sci. Technol.* 27B, 465) in applying latest methods of fractionation to pig back-fat observed evidence of the presence of several C₂₀ polyunsaturated acids in the fat. Ono & Toyama (*J. Chem. Soc. Japan* 64, 1327) converted the fat acids of fish oils into lithium soaps and fractionally crystallized them from acetone-water mixtures. Separation of unsaturated acid from saturated acids and of oleic from linoleic and linolenic acids was quite complete, but separation of linoleic of high purity from the mixtures with linolenic acid was not possible. André & Pradain (*Compt. rend.* 224, 1445) recommended selective-solvent technic for separation of components of fats and illustrated the technic with a description of its application on karité fat. In a study of fat with flowing chromatography, Claesson (*Rev. trav. chim.* 65, 571) observed that special silicas adsorbed branched acids less than unbranched and unsaturated acids more than saturated and that activated carbon adsorbents could separate fat acids according to chain length. Tous & Pizarro [*Anales fis. y quim (Madrid)* 42, 109] advised that alumina should not be used in chromatographic analysis of fatty acids because it reacted chemically with the acids.

A method for analysis of unsaturated fatty acids in blood serum comprised special extraction procedures, saponification, conversion to lead salts, oxidation with potassium permanganate, and analysis of the residue (*Allegria—Boll. soc. ital. biol. sper.* 22, 684). Separation and analysis of dihydroxystearic acid derived from oleic, sativic acid derived from linoleic, and linolic acid derived from linolenic acid were the basis for calculation of the composition. Fisher *et al.* (*J. Am. Oil Chemists' Soc.* 24, 382) compared the analytical results obtained by application of chemical characteristics and a modified Bertram oxidation method to hydrogenated and unhydrogenated oils. There was good agreement with peanut oils. The results with cottonseed oil were in good accord, but the values for linoleic acid by a spectrophotometric method were too high in slightly- or unhydrogenated cottonseed oils. A production of isolinoleic acid in soybean oil was attributed to hydrogenation of linolenic acid. The isolinoleic acid absorbed two moles of cyanogen per mole of acid. McKinney *et al.* (*Ibid.* 212) set up equations for calculating the amount of α - and β -isomers of eleostearic acid in tung oil from the spectroscopic data. Application of the method could be made only where the instrument was sensitive enough to isolate narrow spectrum bands. An investigation on α - and β -linoleic acid indicated that the methyl ester of the α -isomer was chromatographically homogenous in character, while methyl β -linoleate was not (Kummerow & Green—*Ibid.* 196). Part of the differences in the characteristics of the α - and β -isomer was due to the latter retaining some bromine-containing substances as a result of treatments used

in its separation from natural oils. In a review on the application of Raman spectrum to fatty matter, Yvernault (*Oléagineux* 1, 189) indicated that isomers of the linoleic and oleic acids may be distinguished. Baudart (*Peintures, pigments, vernis* 22, 375) synthesized linoleic acid. Such syntheses are of interest in fat analytical work because, when a pure compound can be prepared and its characteristics determined, the latter can yield the basic knowledge required for analytical work.

In connection with work on recording the change in characteristics and composition of tung, Po-Yoak, and oiticica oils, Steger *et al.* (*Fette u. Seifen* 51, 49) isolated derivatives of licanic and γ -ketostearic acids and recorded their properties. Weitkamp's *et al.* (*J. Am. Chem. Soc.* 69, 1936) analysis of human hair fat showed presence of saturated and unsaturated fatty acids ranging in chain length from seven to 22 carbon atoms. This report is of interest with regard to constituents of hair lipids which are responsible for immunity of the adult scalp to ring worm, and also of interest because it is the first time that odd carbon fatty acids were obtained from a natural source. The properties of wool wax acids were reviewed (Lower—*Ind. Chemist* 23, 149).

Breusch & Ulusoy (*Arch. Biochem.* 11, 489) suggested that fatty acids could be fractionated, isolated, and identified as derivatives of bis-(*p*-dimethylamino-phenol)-urea. They have recorded the melting points and solubilities in ethanol, acetone, and ethyl acetate of such derivatives of many fatty acids. Similarly, Kyame *et al.* (*J. Am. Oil Chemists' Soc.* 24, 332) suggested isolation and identification of fatty acids as their hydrazides. These authors also recorded data useful for analysis. Inouye & Yukawa (*J. Agr. Chem. Soc. Japan* 17, 411) demonstrated that mixtures of oleic and elaidic acids could be separated for analysis or identification by crystallization as the hydroxamic acid derivatives. By hydroxylating oleic and elaidic acids, Wittcoff & Miller (*J. Am. Chem. Soc.* 69, 3138) obtained two isomers of 9,10-dihydroxystearic acid, and they discussed these and their properties with regard to their relationship to the oleic acid isomers.

Japanese investigators prepared several reports on detecting fatty acids of more than 18 carbon atoms or of unusual unsaturation in fish oils and in the leg oils of fowl (Toyama & Tsuchiya—*J. Chem. Soc. Japan* 63, 650, 911, 1085, 1160, 1660, 1727, 1731; 64, 299, 489, 738, 1114; Uyeno & Tokunaga—*Ibid.* 63, 1088).

Much information on characteristics and analyses of fats and oils has been entered in tables appended to this section of the review.

Some reports on the composition of fats dealt with glyceride structure. Hilditch & Meara's (*J. Am. Oil Chemists' Soc.* 24, 321) analyses of soybean oils indicated that the distribution of the fatty acids among the glycerides suggested an "even" distribution. Mattil & Norris (*Science* 105, 257; *J. Am. Oil Chemists' Soc.* 24, 274) on analyzing composition data of many oils came to the conclusion that fats do not adhere strictly to either the "even" or "random" theory of structure of glycerides, although animal fats most nearly approach random distribution while seed fats most nearly approach even distribution. Meara (*J. Chem. Soc.* 1947, 773) isolated monooleo- and dioleo-glycerides from piqui-a fruit fat, and recorded their properties. The monooleodipalmitin

consisted wholly of a symmetrical isomer while the dioleomonopalmitin was found in both symmetrical and unsymmetrical forms. A review of recent work on configuration of single glycerides isolated from natural sources was prepared by Daubert [*Euclides (Madrid)* 7, No. 71, 1]. Boekennoogen (*Verfkroniek* 19, 41) reviewed the composition and distribution of the fatty acids among the glycerides of linseed oil and discussed them with regard to production of factice.

Karnovsky (*J. Soc. Chem. Ind.* 66, 95) suggested several modifications *i.e.* in weight of sample, saponification time, method of extraction, etc., in the Society of Public Analysts' method for determination of unsaponifiable matter so that more accurate results were obtained when the method was applied to oils high in glyceryl ethers such as fish oils. Their results on determination of squalene in the unsaponifiable matter by the Fitelson method showed that slight modification in amount of adsorption medium and solvent was necessary because of the high vitamin A content of the fish oils (*Ibid.* 124). The Society of Public Analysts' method for unsaponifiable matter and the Fitelson method for squalene were recommended for official adoption by the Association of Official Agricultural Chemists (Fitelson—*J. Assoc. Official Agr. Chem.* 30, 489). Cattaneo *et al.* (*Anales asoc. quim. argentina* 33, 85) also investigated the above-mentioned procedures and recorded the effects of method of extraction and of rancidity on the results obtained on olive oils.

A method for determination of moisture in oil was based on the quantitative hydrolysis of acetylenechloride by the moisture (Loury & Piquard—*Oléagineux* 2, 560). A modified Kjeldahl procedure was suggested for the determination of lecithin in soybean oils (McGuire—*J. Am. Oil Chemists' Soc.* 24, 359). Procedures were designed for the spectrochemical determination of traces of aluminum, copper, iron, manganese, nickel, tin, and zinc in oils and fats (O'Connor *et al.*—*Ibid.* 185). Microprocedures appeared for determination of lecithin, solid and liquid fats, and moisture (Gorbach *et al.*—*Fette u. Seifen* 51, 93, 94, 129). Small modifications were recommended for the American Oil Chemists' Society's method for the bleach test (Freyer *et al.*—*J. Am. Oil Chemists' Soc.* 24, 297).

The effects of various factors on the oil produced were topics of some communications. Among various fertilizer ingredients, nitrogenous compounds gave the highest increase of fat in rice (Komatsu & Yamasaki—*J. Chem. Soc. Japan* 62, 1243). The range of the free fatty acid content in the germ end of cottonseed kernels during germination was similar to that in the nongerm end (Hoffpauir *et al.*—*Science* 106, 344). Marcille (*Chim. anal.* 29, 133) recorded that olive oil contained palmitic and arachidic acids in proportions varying according to the variety of olive from which it was extracted. In flax seeds, lower oil content, higher cyanogenetic principle, and greater number of seeds per unit weight were characteristic of varieties grown for fiber, as contrasted to those grown for oil yield (André & Kogane-Charles—*Compt. rend.* 223, 457). A survey of eight varieties of midseason soybeans for the North-Central states showed oil contents of 19.9 to 21.1 and iodine values of the oils 128 to 134 (Woodworth & Williams—*Ill. Agr. Expt. Sta. Bull.* 520, 335). A similar survey was made on four varieties of castor beans grown in

Oklahoma (Webster *et al.*—*Okla. Agr. Expt. Sta. Tech. Bull.* T-27, 18 pp.). There were also some references available to the reviewers in brief abstract form but without data. The originals of these recorded the composition of soybean oils of Korea (Kurata—*J. Chem. Soc. Japan* 62, 1228), of olive oils of Argentina [Cattaneo—*Ciencia e invest. (Buenos Aires)* 3, 38], of sunflower oils of France (Carrière & Pelleron—*Bull. soc. chim.* 1946, 664), of Spanish sunflower oil (Ruiz & Fernández—*Anales fis. y quim. Madrid* 41, 1343), of bonito oil (Aenlle—*Ibid.* 803, 1001), of oils of five Cruciferae (Toyama & Takahashi—*J. Chem. Soc. Japan* 63, 1346), of the oil of *Cocos sclerocarpa* [Diaz—*Rev. sanidad y asistencia social (Venezuela)* 11, 439], and sesame oil of Venezuela (Leon—*Ibid.* 411).

Detergents

MANUFACTURE. A newly designed continuous soap manufacturing plant was quite different from the conventional continuous process (Lachampt & Seemuller—*Inds. Corps gras* 3, 4, 47; *Soap, Perfumery & Cosmetics* 20, 657; *Soap Sanit. Chem.* 23, No. 10, 73; Wigner—*Soap, Perfumery & Cosmetics* 20, 663). Very briefly, this process comprised special proportioning pumps for lye and fat, a reaction conduit, a cooling conduit, a holding tank for crude soap, proportioning pumps for crude soap and brine, a decanter, a holding tank for refined soap, and continuous two-stage equipment for neutralizing the excess alkali. The new developments in other continuous systems were the designing of a combined refining and soap manufacturing plant for use with mixtures of foots and tall oil as the raw material (Clayton—*U. S.* 2,423,638); an improvement in centrifugal separation by the use of an aging step between saponification and dispersion (Sender—*U. S.* 2,411,468-9); a control method for alkalinity which depends on electrical pH equipment having antimony electrodes (Colgate-Palmolive-Peet Co.—*Brit.* 578,278; Hesse—*Ger.* 722,289 *Cl.* 23e); and a continuous countercurrent wash system for soap (*Soap, Perfumery & Cosmetics* 20, 157).

Some improvements were made in batch processes. Mixtures of fat and rosin were converted to suitable soaps by boiling with alkali sulfites (Pavlovich-Volkovyskii—*U.S.S.R.* 66,040). Improved rosin soaps for rubber polymerization were obtained when the rosin acids were first catalytically converted to hydro-acids (Hayes *et al.*—*Ind. Eng. Chem.* 39, 1129). Harva (Suomen Kemistilehti 19B, 77) recommended that tall oil soaps be submitted to 3 or 4 salting-out operations with 7% brine starting at 60-80° for the first and successively lowering the salting-out temperatures to 40-50°; reduction of losses and improvement of quality were then said to be the advantages of the procedure. The tendency of soap to hydrolyze was reduced by chlorinating the fatty raw materials until they contained 13% chlorine and then saponifying (Stiepel—*Ger.* 708,437 *Cl.* 23e). The neutralization of excess alkali in soap with monosodium phosphate was patented (Stiepel—*Ger.* 715,439 *Cl.* 23e).

The equipment and method of the Mazzoni soap drying process were described (Berti—*Soap, Sanit. Chemicals* 23, No. 5, 38). This comprised flash drying of neat soap by spraying into a vacuum chamber, scraping the soap from the chamber walls, and means

for removing soap from the system. A similar process was patented by Webb (*Brit.* 581,203). Another patent described an improved soap mill (Scherl—*Ger.* 709,611 *Cl.* 23e). A new plodding apparatus supplied soap bars having a helical grain from face to face (Garvey & Maseline—*U. S.* 2,414,097-8). An addition of 1% dioxodisiloxane before solidification was said to induce floating properties in soaps (Chem. Fabrik von Heyden A.-G.—*Belg.* 449,078).

Apparatus for manufacturing thin pleated or crimped sheets of soap was developed (Tainsh—*U. S.* 2,429,852). New mechanical means were designed for trimming soap bars (Pease—*U. S.* 2,413,995) and for forming bars containing a desired insignia (Garvey—*U. S.* 2,412,979; Block—*U. S.* 2,423,435; 2,423,576). One soap patent dealt with making novelty soap bars, especially gift type bars (Churchill—*U. S.* 2,420,734).

Many soap patents dealt with incorporating builders or fillers with soap. The non-soap materials in these cases were alkali percarbonates and phosphates (Henkel & Cie G.m.b.H.—*Belg.* 448,841), silicic acid gel (Wigleven—*Dutch* 56,339), special cyclic acetals obtained by condensing aldehydes or ketones with pentaerythritol (Deut. Hydrierwerke A.-G.—*Belg.* 448,363), saponification products of reaction products of monochloroacetic acid and wood (Jahrstorfer—*Ger.* 720,589 *Cl.* 23e), substitution products of formaldehyde with water-soluble cellulose ethers (Sponzel—*Ger.* 712,561 *Cl.* 23e), alkali salts, soluble cellulose, glycolic acid and starch (Sichel-Werke A.-G.—*Belg.* 450,899), special hydrophilic cellulose gels (Alliance Européenne Soc.—*Belg.* 451,725; 451,734; 452,265), sulfite residues of wood pulping (Noll—*Ger.* 714,681 *Cl.* 23e), and egg yolk (Cauchaner—*Brit.* 569,106). Bluish fluorescent dyes were added to laundry soap as an opacifying agent and to improve brightness of the wash (Lever Bros. & Unilever Ltd.—*Brit.* 567,716; 575,406; 584,484). One communication dealt with soap additives and their efficiency in preventing clouding of liquid soaps in glass containers due to dissolving silica from the glass (Kranich—*Soap, Sanit. Chemicals* 23, No. 11, 33). Among organic additives to control clouding, phenols gave excellent results, and some commercial calcium dispersing and sequestering agents were very successful; among inorganic compounds, sodium pyrophosphate was best but led to corrosion of steel equipment; and certain commercial sodium silicates were good but not suitable when the soap products were packed in glass containing aluminum or zinc.

The additives used to improve the efficiency of soaps in hard water were the trialkali metal salt of ethylene diamine tetracarboxylic acids (Bersworth—*U. S.* 2,412,943-5), the reaction product of monoethanolamine and phosphoric acid (Chem. Fabrik J. A. Benchiser G.m.b.H.—*Ger.* 719,734 *Cl.* 23e), and guanidine stearate (Lever Bros. & Unilever Ltd.—*Brit.* 581,799). A mild nonirritating toilet soap comprised a mixture of sulfated oleic acid and sodium stearate (Cunder—*U. S.* 2,414,452). The new methods of dedusting soaps were: coating with soluble silicate salt (Holuba—*U. S.* 2,423,451) or certain mineral oil fractions (Heald *et al.*—*U. S.* 2,423,499-50), or treating the soap in an atmosphere of saturated steam to increase moisture and thereafter redrying (Holuba—*U. S.* 2,423,452). The new antioxidants and preservatives for soap were three hydrocarbon substituted mercaptopropionic acids (Gribbins—*U. S.* 2,416,052),

stannic borate (Lofdahl—*U. S.* 2,411,443), and polyethylene polyamines (McClain—*U. S.* 2,409,056).

Formulas for special detergents were patented. The ingredients of two paste soaps were a mixture of colloidal clay, glycerol, and sodium α -propyl- β -naphthalenesulfonate (van Lindonk—*Dutch* 58,336) and a mixture of trisodium phosphate, sulfated non-soap detergent and hydroxyl-alkylamine (Kamlet—*U. S.* 2,421,703). Cream type soaps were improved by saturation with nitrous oxide (Peter—*Ger.* 711,633 *Cl.* 23e). Some other detergents were special mixtures of alkali salts (McMahon—*U. S.* 2,412,819; Gero—*Belg.* 448,280; N. V. Franken-Donders Vereenigde Aniline-fabrieken—*Dutch* 53,973; Commanditaire Vennootschoop "Ichemex"—*Dutch* 53,989).

The journal literature contained descriptions for the manufacture of some non-soap detergents. A preparation by Uyeno & Anzai (*J. Chem. Soc. Japan* 63, 978) was a sulfonation product of a petroleum-like substance obtained by the dry distillation of sodium oleate. The van An del process for converting the unused fraction from the manufacture of lubricating greases to sulfo-oxygenated soaps was described by Lemaire (*Génie civil* 122, 27). Soap-like materials derived by the action of sulfuryl chloride on oleic and stearic acids were described by Bouquet & Pouquot (*Compt. rend.* 223, 481). References to patents on non-soap detergents will be listed near the end of this section of the review. Publications on uses for non-soap detergents dealt with: use as emulsifiers in the polymerization of vinyl esters (Starek & Freudenberg—*U. S.* 2,422,646), emulsifiers for insecticide sprays (Flenner & Littler—*U. S.* 2,407,486; Dolman—*U. S.* 2,412,720; Maxwell—*U. S.* 2,418,652), and for washing city streets (Morgan—*Soap, Sanit. Chemicals* 23, No. 12, 42).

EVALUATION AND PROPERTIES OF DETERGENTS. The Production and Marketing Administration has modified the American Oil Chemists' Society's methods for soap analysis in the interest of speed in soap deliveries for the government (Hunt & Neustadt—*J. Am. Oil Chemists' Soc.* 24, 1). The alterations were not fundamental, but involved rapid methods of grinding, sampling, drying, filtering, use of mechanical stirrers, etc. Several methods were proposed for determination of silicate compounds in soaps. Silverman's (*Ibid.* 13) procedure comprised oxidation of the sample with perchloric acid, heating the residue with hydrochloric acid, and washing, igniting, and weighing the silica. A volumetric method by Schutz (*Fette u. Seifen* 51, 433) depended on the following reaction: $6\text{NaF} + \text{SiO}_2 + 4\text{HCl} = \text{Na}_2\text{SiF}_6 + 4\text{NaCl} + 2\text{H}_2\text{O}$. A colorimetric procedure was based on converting the silicates to yellow silico-molybdic acid complex which was measured by a Lange universal colorimeter (Gottschaldt—*Ibid.* 432). Zinc was determined in shaving soaps gravimetrically as the zinc ammonium phosphate salt (Grossfeld—*Z. Lebensm.-Untersuch. u. -Forsch.* 86, 260). Silverman (*J. Am. Oil Chemists' Soc.* 24, 410) applied the perchlorate reaction method to determine glycerol in soap. It gave results comparable to those of the dichromate acid method in less time. A new silver-silver soap electrode was designed for use in determination of the pH of soap solutions (Ekwall & Harva—*Finska Kemistsamfundets Festskrift* 1944, 257). As preliminary work on hydrolysis of soap, McBain & Van Tuyl

(*J. Am. Oil Chemists' Soc.* 24, 271) recorded the titration curves of acetic, myristic, and lauric acids.

Igepon T was quantitatively precipitated from strongly acid solutions by benzidine hydrochloride, washed, and could be determined by titration with caustic soda in alcohol solution or gravimetrically by drying (Shiraeff—*Am. Dyestuff Repr.* 36, 313). Brunzell (*Svensk. Farm. Tid.* 51, 101) issued instructions for analysis of dodecyl sodium sulfate based on titration of the acid liberated by acid hydrolysis. Tests for determining the presence of soap and saponin in the detergent were included. Methods for determining carboxyl, sulfate, and sulfonate groups in sulfated oil salts were modified for application in the presence of ammonium salts (Burton & Byrne—*J. Intern. Soc. Leather Trades' Chem.* 31, 100).

A qualitative test for detecting surface active agents was based on solubilization of the dye, Brilliant Oil Blue BMA (Hoyt—*J. Am. Oil Chemists' Soc.* 24, 54). A solution of equal quantities of methylene blue and uraniu was found useful for identifying surface active agents (Göbel—*Rev. quim. ind. Rio de Janeiro* 15, No. 173; 16, 340). With anionic products, the reagent yields a yellowish green to dark green color with fluorescence; with non-ionic product, navy blue with little fluorescence; and with a cationic product, vivid blue to bluish red with no fluorescence.

The Northern New England Section of the American Association of Textile Chemists and Colorists (*Am. Dyestuff Repr.* 36, 91P) rated a large number of detergents according to their efficiencies in a standard detergency test developed by the Association. In general, synthetic detergents showed excellent results in removal of oil but were not as good as soap for lampblack removal. Ten per cent of each detergent, with six per cent sodium carbonate to give a pH of about 11.0, produced excellent results for removal of both oil and lampblack. Tomlinson (*J. Soc. Dyers Colourists* 63, 107) also recommended adding sodium carbonate to improve the efficiency of soap. He discussed this improvement on the basis of inhibiting hydrolysis of the soap by the soda ash. Nieuwenhuis (*Chem. Weekblad* 43, 510) also indicated the theoretical and economic aspect of using soda ash with detergents. He recommended a special mixture of soap, Tylose HBR, and sodium carbonate as a very economical textile detergent.

Miles and Ross (*J. Am. Oil Chemists' Soc.* 24, 23) tabulated the mole ratio of builder to calcium and magnesium hardness required to effectively protect the soaps of several fatty acids with the following builders: $\text{Na}_6\text{P}_4\text{O}_{13}$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{Na}_6\text{P}_6\text{O}_{18}$, $\text{Na}_4\text{P}_2\text{O}_7$, Na_3PO_4 , $\text{Na}_3\text{PO}_4 \cdot \text{Na}_2\text{O}$, and Na_2CO_3 . These varied considerably, depending on each soap, builder, and whether calcium or magnesium salts were used. Soap saving was favored when the builder was added to the hard water prior to adding the soap. Also in a study of the effect of hardness on detergency, Sisley (*Corps gras, savons* 2, 77) rated the calcium soap dispersing power of various detergents. In concluding, he stressed that industry should use softened or purified water, under which conditions soap would retain pre-eminence over non-soap detergents. A device to aid in determining the effectiveness of dairy detergents comprised means of agitating microscopic slides covered with dried milk films in a solution of the cleaner (Fouts & Freeman—*J. Dairy Sci.* 30, 61).

Morgan (*Monthly Rev. Am. Electroplaters' Soc.* 34, 430) showed that the efficiency of acid metal cleaners was improved by the addition of alkyl aryl sodium sulfonate type detergents. Cleanliness of his test specimen was determined by measuring the intensity of fluorescence under ultraviolet radiation. The intensity of fluorescence was proportional to the amount of oil on the surface. A method for evaluating dispersing agents for the rubber industry relied on measuring the dispersing efficiency of the sample for the pigment, Hansa Yellow YT-445-D in water [Tesoro—*Rubber Age (N. Y.)* 60, 319].

Much new data on the phases of soap systems were recorded. Aqueous sodium oleate systems with more than 60% soap displayed phase transitions at 28, 66, 89, and 112° (Vold—*J. Phys. & Colloid Chem.*, 51, 797). Ferguson *et al.* (*J. Am. Chem. Soc.* 69, 141) submitted microscopic, vapor pressure, and x-ray data to indicate that β -sodium palmitate was a solid-solution phase which existed over the range from 0.2 to 2.5% water in a sodium palmitate-water system. A phase study on palmitate soap-alkaline electrolyte-water systems was for the purpose of measuring the salting-out effect of the electrolytes (Merrill & Getty—*Ibid.* 1875). More of the silicious silicates than of the metasilicate or phosphates were required to salt in liquid crystal middle soap or to salt out liquid crystal neat soap. Hexametaphosphate exerted the strongest salting out power of any of the alkaline electrolytes (Merrill—*Ind. Eng. Chem.* 69, 158). Vand *et al.* (*Nature* 159, 507) recorded crystal structure data on three forms of anhydrous and one form of hydrated neutral potassium soaps. The phase behavior of soaps was also evident in data on its flow properties, which were developed in connection with the study of applicability of soaps for grease manufacture (Southam & Puddington—*Can. J. Research* 25B, 125). Buerger *et al.* (*J. Am. Oil Chemists' Soc.* 24, 193) discussed the conversion of one soap phase to another and recorded experimental results obtained in the system sodium myristate-water. A combined x-ray and electron microscope study of sodium stearate fibers showed that they were not round but ribbons with rectangular cross section (Thiessen & Erdmann—*Z. physik. Chem.* 193, 367).

After measuring the streaming double refraction of 4-12% oleate soap solutions, Snellman (*Arkiv. Kemi, Mineral. Geol.* B19, No. 5, 1) interpreted the data to indicate that large crystal micelles did not occur at a definite concentration but over the broad range of 6 to 10% solutions. In similar work, Klevens (*J. Colloid Sci.* 2, 301; *J. Chem. Phys.* 14, 742) correlated micelles formation with definite temperatures and associated the extent of aggregation with changes in refraction, conductivity, and spectral changes of dyes added to the solutions. Mattoon *et al.* (*J. Chem. Phys.* 15, 209) recorded x-ray diffractions which supported their suggestion that micelles consist of only one double layer of soap molecules.

Micelle formation data on anionic detergents, comparable to those of the above on soaps, were also recorded (Gonick & McBain—*Rec. trav. chim.* 65, 601; *J. Am. Chem. Soc.* 69, 334; McBain & Sullivan—*J. Chem. Phys.* 15, 211). Corrin & Harkins (*J. Am. Chem. Soc.* 69, 683), from work with both anionic and cationic detergents, showed that salts lowered the critical concentration at which micelles formed in both types of detergents, and hence micellar aggre-

FAT ACID COMPOSITION

Oil or Fat Source	Common Saturated Acids			Common Unsaturated Acids			Other Fat Acids
	C ₁₄ Myristic	C ₁₆ Palmitic	C ₁₈ Stearic	C ₁₈ (-2H) Oleic	C ₁₈ (-4H) Linoleic	C ₁₈ (-6H) Linolenic	
<i>Argyria speciosa</i> seed ²				33.23	18.17	6.09	C ₂₂ 6.64
Chaulmoogra seed ¹				0.8			Chaulmoogric 73.8, gortic 17.1
<i>Catalpa</i> seed ¹⁶				28			C ₁₆ (-6H) 6, C ₂₀ (-6H) 10, C ₂₂ (-10 or 12H) 23
<i>Thunus orientalis</i>							
Gourd seeds ¹⁸		26	4				
<i>Curcubita digitata</i>		11.5		40.4	37	10	
<i>Curcubita palmata</i>		1.5	8.3	34.0	4.3	12	
<i>Ipomoea ovigera</i> seed ¹⁹		8.7	7.1	39.6	44.6		
<i>Ipomoea muricata</i> seed ²⁰		13.7	22.5	41.0	15.2	3.9	C ₂₂ 22.8
Lard (Canadian) ²¹		45.6		38.6-51.8	4.6-11.3	0.3-0.5	C ₂₀ (-8H) 0.2 - 1.7
Lumbang nut kernel (Australian) ²²		5.5	6.7	10.5	48.5	28.5	C ₂₀ 0.3
Mango seed kernel ²⁴	0.69	8.83	33.96	49.78			C ₂₀ 6.74
Mango seed kernel ²⁵		5.5	7.8	75.8	0.8		C ₂₀ 2.7, C ₂₂ 1.2, C ₂₄ 5.3, C ₁₆ (-2H) 0.9
<i>Moringa oleifera</i>	2.4	41.6	6.3	38.0	9.5	0.4	C ₁₈ (-2H) 1.8
Palm (N'Dian Congo) ²⁶				15.2	16.0	7.0	C ₂₀ 0.5, C ₂₂ 1.5, C ₂₄ 0.8
Rape seed ²⁰	0.2	2.2	0.4	56.01	16.07		C ₁₈ (-2H) 0.1, C ₂₂ (-2H) 53.8, C ₂₂ (-4H) 2.3
<i>Svetenia mahagoni</i> seed ³¹		9.48	18.44	11	1.1	65	
<i>Tetracarpidium-conophorum</i> nut kernel ³²		7	6				
Wild mustard seed ³³				27.2	34.7	8.1	C ₂₀ 0.1, C ₂₀ (-2H) 17.2
<i>Sesuvium</i> trio	0.1	8.7	18.2	34.0	31.8		C ₂₀ 5.8
<i>Rightia tinctoria</i> tree seed ³⁶							

REFERENCES TO CHARTS

1. R. D. Machado. *Bol. divulgação inst. óleo* No. 3, 111.
2. G. M. Kelkar, N. L. Phalnikar, and B. V. Bhide. *J. Indian Chem. Soc.* 24, 83.
3. A. Lacerda. *Rev. soc. Brasil quim.* 15, 57.
4. B. A. Smith and F. G. Dolléar. *J. Am. Oil Chem. Soc.* 24, 52.
5. M. Carrière. *Peintures, pigments vernis* 29, 39; also U. Cuppini. *Olearia* 1, 28.
6. E. André and Madeleine Kogane-Charles. *Ann. agron.* 16, 423.
7. S. G. Quinza and P. R. Anno. *Anales fis. y quim. (Madrid)* 42, 393.
8. F. Palma, M. Donde, and W. R. Lloyd. *J. Am. Oil Chem. Soc.* 24, 27.
9. P. Cattaneo, G. Karman, and L. Uberti. *Anales asoc. quim. argentina* 34, 5.
10. Nora V. Le-Feuvre. *Anales quim. y farm.* 1946, No. 47, 1.
11. Maria da C. P. B. Cavalcanti. *Rev. quim. ind. (Rio de Janeiro)* 16, No. 181, 16.
12. I. Novák. *Magyar Gyógyszerésziud. Társaság Értéktöje* 18, 342.
13. R. D. Machado. *Bol. divulgação inst. óleo* No. 3, 105.
14. Y. Toyama. *J. Chem. Soc. Japan* 63, 905.
15. I. M. Gajjar. *J. Sci. Ind. Research (India)* 5, No. 1 B, 18.
16. C. Hata and T. Kunisaki. *J. Chem. Soc. Japan* 63, 64.
17. Y. Toyama. *J. Chem. Soc. Japan* 63, 893.
18. W. C. Ault, Margaret L. Swain, and L. C. Curtis. *J. Am. Oil Chem. Soc.* 24, 289.
19. C. Hata. *J. Chem. Soc. Japan* 63, 1540.
20. G. M. Kelkar, N. L. Phalnikar, and B. V. Bhide. *J. Indian Chem. Soc.* 24, 87.
21. M. Lewy. *J. Am. Oil Chem. Soc.* 24, 3.
22. H. J. Lips and G. A. Grant. *Can. J. Research* 25F, 63.
23. F. D. Gunstone and T. P. Hilditch. *J. Soc. Chem. Ind.* 66, 205.
24. S. P. Pathak, B. G. Gunde, and N. N. Godbole. *J. Indian Chem. Soc.* 23, 11.
25. H. C. Dunn and T. P. Hilditch. *J. Soc. Chem. Ind.* 66, 209.
26. T. P. Hilditch, M. L. Menara, and O. A. Roels. *J. Soc. Chem. Ind.* 66, 284.
27. W. A. Bush and B. J. Cagan. *Ind. Eng. Chem.* 39, 1452.
28. N. Hasebe. *J. Chem. Soc. Japan* 64, 967.
29. W. Awe and W. Bathe. *Fette u. Seifen* 51, 431.
30. T. P. Hilditch, P. A. Laurent, and M. L. Meara. *J. Soc. Chem. Ind.* 66, 19.
31. D. G. Fishavikar and S. V. Shah. *J. Univ. Bombay Sect. A*, 15, Pt. 3, 17.
32. F. D. Gunstone, T. P. Hilditch, and J. P. Riley. *J. Soc. Chem. Ind.* 66, 293.
33. A. Lacerda. *Rev. soc. brasil. quim.* 14, 113.
34. M. D. Nadkarni, J. W. Airan, and S. V. Shah. *J. Indian Chem. Soc.* 24, 25.
35. J. S. Aggarwal and Karimullah. *J. Sci. & Ind. Research (India)* 5B, 57.
36. D. B. Parihar and S. Dutt. *J. Indian Chem. Soc.* 23, 307.

gation was not governed by ionic strength. They suggested a theory which indicated that a new type of electrolyte occurs in which salt ions of the same charge as the colloid aggregates are repelled to such a distance as to give independence of the magnitude of the charge per ion, with dependence upon only the sum of the charges on all such ions in the formation of the aggregate. These workers (*J. Chem. Phys.* 14, 640) also recorded graphically the effect of several organic solvents on micelles formation of decyltrimethylammonium bromide in aqueous solutions. Since some increased and others depressed the critical concentration of aggregation, the results refute the Ward hypothesis which attributed the initial drop in the critical concentration to absorption of solvent molecules on the surface of micelles. In developing methods for studying micelles formation the above investigators (*Ibid.* 641; *J. Am. Chem. Soc.* 69, 679) tabulated many dyes according to whether they could be used successfully to show micelles formation in cationic, nonionic, or anionic soap solutions by color or fluorescence changes.

Walton and coworkers (*J. Colloid Sci.* 1, 385; *J. Am. Chem. Soc.* 69, 469) determined the concentration for micelles formation for dodecanesulfonic acid, dodecylbenzyltrimethylammonium chloride and sulfamate in aqueous solutions.

Some reports of physical study contained information on water-detergent-insoluble organic compound systems. Increases in the concentration of the detergent did not increase the solubility of an oil above that in water until the critical concentration of micelles was attained (Stearns *et al.*—*J. Chem. Phys.* 15, 496). Above this, the solubility increased more rapidly as the soap concentration increased, *i.e.*, per mole of soap the solubilization was greater in a 25% than in a 5% soap solution. With benzene emulsified in water with potassium oleate, the benzene protected the oleate against oxidation with 0.0005*N* potassium permanganate solution (Cheesman—*Archiv Kemi, Mineral. Geol.* 20A, No. 10, 9 pp.). Rebinder *et al.* (*Kolloid Zhur.* 9, No. 1, 67) tabulated the characteristics of emulsions of kerosene in solutions of sodium, potassium, and lithium oleate with attention to the effect of the relative concentrations of soap and free fatty acids on inversion of the emulsions. Tabulations of the gel strengths and viscosities of gels of soaps and piene were made in connection with studying lubrication (Hattiangdi *et al.*—*Proc. Ind. Acad. Sci.* 24A, 287). Several detergents were rated in regard to their capacity to solubilize the water insoluble dye, Orange OT (Green & McBain—*J. Phys. & Colloid Chem.* 51, 286). The mechanism of the polymerization of rubber was discussed in the light of a new structure for soap micelles (Harkins—*Science* 105, 635; *J. Am. Chem. Soc.* 69, 1428). Particle sizes of synthetic latexes, determined by soap adsorption using various dyes as indicators of surface saturation, agreed with those determined optically (Klevens—*J. Colloid Sci.* 2, 367).

Ralston & Hoerr (*J. Am. Chem. Soc.* 69, 1869) recorded the viscosities, densities, and refractive indexes of solutions of dodecylammonium chloride in various dilutions of ethanol. Their work (*Ibid.* 883) on conductivity of aqueous solutions of mixtures of dodecyl- and octadecylammonium chlorides, and of hexyl- and octadecylammonium chloride, indicated that the hexyl- compound was not included in the

micelles. The lowering of the conductivity of these solutions by nonelectrolytes was interpreted as evidence that the nonelectrolytes were included in the micelles.

Many data on solubility of soaps in mixed solvents, and blending of water with organic solvents by detergents were recorded by Palit (*J. Am. Chem. Soc.* 69, 3120), and Palit and McBain (*J. Soc. Chem. Ind.* 66, 3). The mechanism of improvement of solubility resulting from blends of solvents was discussed.

Several new physical testing techniques were applied to detergents. Carr *et al.* (*J. Phys. & Colloid Chem.* 51, 636) determined the cation activity in solutions of sodium and potassium soaps with the use of negative collodion membrane. A new surface tension apparatus for testing surface active agents measured the force exerted on a rectangular stirrup as it was pulled out of the solution (Matalon—*Compt. rend.* 223, 896). The rate of solution of soaps in water was evaluated by determining the amount dissolved while rotating soap cylinders in water at constant speed and standard temperatures (Miles & Scott—*J. Phys. & Colloid Chem.* 51, 391). An old but rarely used characteristic of soaps, the Krafft point, was the subject of one communication which discussed its theoretical basis and usefulness, and recorded new data for many alkali soaps (Démarecq—*Inds. Corps gras* 2, 341, 370). This characteristic was described as the temperature at which soap solutions become opaque.

Since some non-soap detergents are efficient germicides and sanitizers, many investigators are attempting to rate these for various cleaning uses, to evaluate their germicidal value, and to compare them with other chemicals used for the same purpose (DuBois—*Soap, Sanit. Chemicals* 23, No. 5, 139; Quesno *et al.*—*Ibid.* No. 6, 145; Klarman & Wright—*Ibid.* No. 7, 151; Armbruster & Ridenour—*Ibid.* No. 8, 119; Mueller *et al.*—*Ibid.* No. 9, 123; Eckfeldt & James—*Ibid.* No. 12, 157; Johns—*Can. J. Research* 25, 76; Lawrence—*Chem. Industries* 60, 44; Klein & Kardon—*J. Bact.* 54, 245; Guiteras & Shapiro—*Ibid.* 52, 635; Kenner *et al.*—*Ibid.* 52, 449; McCulloch—*Science* 105, 480; Mueller *et al.*—*J. Dairy Sci.* 30, 519; Spurgeon *et al.*—*Ibid.* 520; Mallmann & Zaikowski—*J. Milk and Food Tech.* 10, 206). In a comparison of the bactericidal activity of C₈ to C₁₂ soaps, the more efficient were those between C₈ and C₁₂ (Roelehe & Reichel—*Z. Hyg. Infektionkrankh.* 125, 666). One report claimed that certain non-soap detergents have a deodorizing effect on perfumes, chemicals, household odors, and perspiration odors (Flett *et al.*—*Am. Perfumer Essent. Oil Rev.* 49, 612). A pharmacological study of synthetic detergents showed that the LD₅₀ in rats for Igepon T was 0.44 mg. per g. and for Igepon A, 0.21 mg. per g. (Jalon & Jalon—*Farmacoterap. actual Madrid* 3, 833).

Organisms named *Micrococcus saponophilus*, *Penicillium crustosum*, *P. flavidorsum*, and a species of *Cladosporium* were isolated from a moldy bar of green soap which was strongly alkaline and contained 18.7% moisture and 35.7% fats [Verona—*Ann. facoltà Pisa (N. S.)* 6, 1].

Many communications on soaps and other detergents provided information on common practices in the industry or described some raw materials or known products. These are most conveniently tabulated below under the name of the subject treated.

Raw materials: synthetic fatty acids, Otter—*Chem. Weekblad* 43, 131; rosin and hydrogenated oils, Fontana—*Ion* 6, 604; use of dairy wastes in the industry, Promtov—*Myasnaya i Molochnaya Prom.* 1946, No. 4, 59; Alginates, Federici—*Soap, Sanit. Chemicals* 23, No. 5, 35; Spanish bentonite, Carbonell—*Ion* 7, 15; perfumes for soap, Bollmann—*Fette u. Seifen* 51, 113; Morel—*Soap, Perfumery Cosmetics* 20, 48; dyes for soap, Marsden—*Perfumery Essent. Oil Record* 37, 366.

Technics: history, Schaefer—*Ciba Rev.* No. 56, 2014, 2025; modern processes, Seaman—*Soap, Perfumery Cosmetics* 20, 245; developments in America and Germany, Bigelow—*Chem. Corps J.* 1, 17; continuous process, McBride—*Chem. Eng.* 54, No. 4, 94, 134; floating soap manufacture, Arend—*Perfumery Essent. Oil Record* 37, 363; manufacture, on the farm, Calzadilla—*Estación exptl. agron. Santiago Vegas, Cuba Circ.* 83, 15 pp.; Lever Bros. & Unilever Ltd. plant at Cheshire, Eng., Anon.—*Soap, Sanit. Chemicals* 23, No. 4, 41; potash soap manufacture, Bachrach—*Am. Perfumer* 50, 265.

Properties: relation of chain length and unsaturation to soap properties, McCutcheon—*Soap, Sanit. Chemicals* 23, No. 1, 40; Lindner—*Fette u. Seifen* 51, 143; emulsification, foaming, and wetting, Lachampt & Dervichian—*Bull. soc. Chim.* 1946, 491, 496; biological properties of cation-active soap, Ripert & Sisley—*Soap, Perfumery Cosmetics* 19, 834; influence of soap hydrolysis on detergent action, Tomlinson—*J. Soc. Dyers and Colourists* 63, 107; properties and classification, Gotte—*Die Chemie* 57, 67.

Synthetic detergents: manufacture, Soderdahl—*J. Am. Oil Chemists' Soc.* 24, 69, Gill—*Cotton* 110, No. 11, 43, Kroch & Tomlinson—*J. Intern. Soc. Leather Trades Chem.* 30, 316; economics of, Parkhurst—*Soap, Sanit. Chemicals* 23, No. 3, 37, Vallance—*Soap, Perfumery, Cosmetics* 19, 829, Anon.—*Soap, Sanit. Chemicals* 23, No. 4, 45; properties and classification, Ackley—*Soap, Sanit. Chemicals* 23, No. 3, 39, Sisley—*Oleagineux* 2, 349, Leslie—*Manufg. Chemist* 18, 449, Chwala & Martina—*Textil-Rundschau* 11, 147, Granacher—*Ciba Rev.* 56, 2039; Sapamine, Solidogene, Soromine, Velan, etc., Boyer—*Rev. prod. chim.* 47, 1; Mersol, Anon.—*Soap, Sanit. Chemicals* 23, No. 4, 81, Groninger—*Ibid.* No. 7, 40, den Otter—*Chem. Weekblad* 43, 211, 276; quaternaries, Varley—*Soap, Sanit. Chemicals* 23, No. 12, 130; Zephirol, Polonovski—*Compt. rend. soc. biol.* 140, 19; Igepons, den Otter—*Chem. Weekblad* 43, 314, 323; sodium lauryl sulfate, Macias-Sarria—*Am. Perfumer* 48, No. 9, 61; alkali metal and nitrogen derivatives of wool-wax acids, Lower—*Ind. Chemist* 23, 274; sulfonated fatty alcohols, Kramarovsky—*Industria y quim (Argentina)* 8, 323.

Uses: in industry, Leslie—*Manufg. Chem.* 18, 449, 539, Lesser—*Soap, Sanit. Chemicals* 23, No. 8, 37, Smith—*Am. Perfumer* 49, 395; in dairy plants, Harding & Trebler—*Food Technol.* 1, 478; for the printer, Kantrowitz & Gosnell—*Printing Equip. Eng.* 74, No. 2, 15; for manufacture of synthetic rubber, Semon—*J. Am. Oil Chemists' Soc.* 24, 33; for fire extinguisher fluids, Zussman—*Chem. Inds.* 61, 994; for washing city

streets, Morgan—*Soap, Sanit. Chemicals* 23, No. 12, 42.

Special products: medicated and cosmetic soaps, Alperin—*Am. Perfumer & Essential Oil Rev.* 49, No. 7, 53; novelty soaps, Lesser—*Soap, Sanit. Chemicals* 23, No. 3, 33; dish washing detergents, Tiedman—*Soap, Sanit. Chemicals* 23, No. 4, 48, Anon.—*Ibid.* No. 5, 36, Lesser—*Ibid.* No. 6, 43; sterilizing detergents for food manufacturers, Resuggan—*Food Manufr.* 22, 485; glass cleaners, Davis & Resuggan—*Proc. Soc. Applied Bact.* 1946, 20, Neidig—*Chem. Inds.* 60, 53; metal cleaners, Buton—*Southern Power & Ind.* 65, No. 6, 55, Vallance—*Mfg. Chemist* 18, 75, 124, Lef-fingwell & Lesser—*Products Finishing* 11, No. 2, 80; floor soaps, Lesser—*Soap Sanit. Chemicals* 23, No. 7, 36; cleaning and polishing cloths, Lesser—*Ibid.* No. 2, 129; bubble bath bases, Molteni—*Am. Perfumer Essent. Oil Rev.* 49, 266.

The newly patented non-soap organic detergents are derivatives of fats or of the by-products of the coal and petroleum industries. These and their methods of manufacture are not discussed in detail in this review, but references to them are partially classified.

Those patents on sulfated or sulfonated organic compounds are:

- American Cyanamid Co.—*U. S.* 2,414,015; 2,415,255.
- Atlantic Refining Co.—*U. S.* 2,413,199.
- Berl—*U. S.* 2,413,855.
- British Celanese Ltd.—*Brit.* 580,383.
- Colgate-Palmolive-Peet Co.—*U. S.* 2,412,909; 2,420,383; 2,422,128; 2,422,613; 2,423,692, 2,424,420; 2,427,576.
- Compagnies réunies Congo Belge et Savonneries Lever Frères—*Belg.* 449,185.
- E. I. duPont de Nemours & Co.—*Brit.* 568,102.
- General Foods Corp.—*U. S.* 2,415,347.
- Globus—*U. S.* 2,424,951.
- Harvel Corp.—*U. S.* 2,412,264.
- I. G. Farbenind. A.-G.—*Belg.* 448,848; 448,971; 449,767; 451,227.
- Petrolite Chemical Products Corp.—*U. S.* 2,413,814.
- Quaker Chemical Products Corp.—*U. S.* 2,419,783.
- G. Schicht A.-G.—*Belg.* 448,551-2.
- Soc. pour l'ind. chim. à Bâle.—*Brit.* 581,985.
- Sun Chemical Corp.—*U. S.* 2,413,161.
- Union Oil Co.—*U. S.* 2,416,192.
- Wyandotte Chemicals Corp.—*U. S.* 2,422,926.

In some cases sulfur-containing detergents were prepared by sulfonating nitrogen derivatives, such as amines, amides, etc.:

- American Cyanamid Co.—*Brit.* 575,608; *U. S.* 2,402,510-14.
- I. G. Farbenind. A.-G.—*Belg.* 449,444.
- J. R. Geigy—*Brit.* 571,369; 581,076.
- National Oil Products Co.—*Brit.* 567,911.
- N. U. Olieraffindery "Zulien"—*Dutch* 55,072.
- Niederl et al.—*U. S.* 2,417,992.
- Soc. pour l'ind. chim. à Bâle.—*Brit.* 578,654; 579,370; 580,641; 582,092; 584,914.

Some detergent amines, amides, and quaternary ammonium compounds were patented:

American Cyanamid Co.—*U. S. 2,413,755*;
2,426,891.

Arnold, Hoffman & Co., Inc.—*U. S. 2,410,788*.

Celanese Corp. of America—*U. S. 2,408,127*.

Commercial Solvents Corp.—*U. S. 2,413,248*.

E. I. duPont de Nemours & Co.—*U. S. 2,414,050*.

General Aniline & Film Corp.—*U. S. 2,426,293*.

Th. Goldschmidt A.-G.—*Belg. 450,966*.

I. G. Farbenind. A.-G.—*Ger. 718,071 Cl. 120*;

Belg. 448,523; *449,417*; *450,587*.

Harris—*U. S. 2,406,329*.

Malkeinus—*U. S. 2,421,707*.

Martin Dennis Co.—*U. S. 2,407,645*.

Nostrip, Inc.—*U. S. 2,419,404*.

Parke, Davis & Co.—*U. S. 2,406,902*.

Rohm & Haas Co.—*U. S. 2,416,264-5*.

Soc. pour l'ind. chim. à Bâle.—*Brit. 581,339*.

Victor Chemical Works—*U. S. 2,406,423*.

Two other detergents were a special phenol-lactone ester (I. G. Farbenind. A.-G.—*Belg. 450,233*) and higher alcohol ester of boron or phosphorus compounds (N. V. Chemische Fabriek Servo & Rozenbroek—*Dutch 56,089*).

A Review of the Technical Applications of Soybean Lecithin*

W. K. HILTY, Ross and Rowe, Inc., New York City

SINCE the introduction of lecithin into this country from abroad some twenty-odd years ago, there has developed a new industry devoted solely to the recovery and marketing of this commodity. The lecithin industry in itself is comparatively small but robust, serving today a host of varied industries. It is a tribute to the few enterprising individuals who, recognizing the potentialities of lecithin, introduced it to American industry.

The acceptance of lecithin by industries who use it advantageously was a slow process. Those who introduced it had to begin with only a limited knowledge of its basic properties and functions. Potential users in most cases adapted it to their processes only after prolonged experimentation. Considerable knowledge of the applications of lecithin has accumulated but, aside from patented uses, relatively little information is to be found in published literature. The recovery and purification of lecithin from solvent extracted soybeans is generally known to this group and will not be considered in this paper.

In the interests of clarity and convenience the applications of lecithin will be segregated into two general classifications:

1. Those based on its surface active properties.
2. Those based on its chemical properties.

The applications based on the surface active properties are most numerous and offer unlimited potential new uses. Lecithin, basically, is a surface active substance, and a clear understanding of what is meant by a surface active agent is fundamental. Fischer and Gans (1) define a surface active agent as a compound which in small relative quantity modifies the physical properties of a heterogenous system by adsorption at an interface. The change is considerably greater than any law of mixtures would predict. The term wetting agent is often used instead of surface-active agent and in a sense further defines a surface-active agent. Bartell (2) states that one of the most commonly occurring phenomena is the wetting of solids by liquids. Processes involving wetting are encountered continually. Life itself is possible only because certain liquids are properly wetting

the different solid constituents of the body. Important technical processes are fundamentally dependent upon the degree of wetting of solids by liquids. Surface active agents are not new; soap, the commonest, has been used for centuries; and sulfonated oils have been used for a long time. However, the greatest advance in development of surface active agents has been since 1925 when a number of synthetic products appeared. With these came a clearer understanding of the functions and properties of surface active agents. Most surface active agents have a fairly large molecular structure having a long chain aliphatic group known as the hydrophobic group and a solubilizing group commonly called the hydrophilic group.

LECITHIN has a molecular structure commonly associated with surface active agents. The long chain fatty acid groups constitute the hydrophobic group, and the phosphoric acid-choline group, the hydrophilic group. Lecithin is generally used in non-aqueous systems since it is not soluble in water. It is widely used in systems composed of solids dispersed in fatty vehicles. Specifically, one of the earliest established uses of lecithin was its use in chocolate coatings. Here we have a heterogeneous mixture consisting of cocoa butter, sugar, and cocoa fiber. Sugar, a hydrophilic solid, is not readily wetted by cocoa butter. Since the introduction of a small amount of lecithin in the order of 0.25% produces thorough wetting of the sugar by the cocoa fat, the viscosity of the mixture is reduced sometimes by more than 50%. Chocolate coatings can be produced with stabilized viscosities and reduced cocoa butter. The confectionery industry uses lecithin as an emulsifying agent in fat containing confections. Thorough emulsification of the fat results in improved eating qualities, facilitates cutting and wrapping, and longer shelf life; 1% of the fat content is used. Lecithin has long been used by the margarine industry where it serves as an antispattering agent and a means of keeping the milk solids from sticking when margarine is used for frying. Here we have a water in oil emulsion in which milk solids are dispersed. When margarine is heated as in frying, water is driven off and the

* Presented at the 21st fall meeting of the American Oil Chemists' Society, Oct. 20-22, 1947, Chicago, Ill.