

Review of Literature on Fats, Oils and Soaps for 1943*—Part 2

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Deterioration

Reviews on spoilage of fats were prepared by Täufel (*Die Chemie* 55, 273), Werner (*Z. Fleisch- u. Milchhyg.* 52, 207) and Mangrane (*Ion* 2, No. 6, 35). These dealt with theories, chemical processes involved, natural causes, antioxidants and analytical methods.

A new analytical test for judging the extent of autoxidation depended on the amount of *a*-diketones present in the oil (O'Daniel and Parsons—*Oil & Soap* 20, 72). The concentration of these was indicated by the depth in color produced by warming to 68° and agitating a mixture of 50 g. of the fat, 50 cc. of alcohol and 20 cc. of a 50% aqueous solution of potassium hydroxide. The data obtained showed that the color and peroxide value increase progressively during autoxidation. The advantage of this test over determination of peroxide value was that the *a*-dicarbonyls were stable under bleaching and deodorizing conditions and hence the extent of deterioration of the fats and oils should be evident in processed samples. Mangold (*Vorratspflege u. Lebensmittel-forsch.* 4, 297) modified the fuchsin-sulfurous acid reagent test used for measuring the aldehydes in rancid fats according to the method of Pritzker and Jungkuz, so that the color developed could be evaluated with the step-photometer. Reimenschneider *et al.* (*Oil & Soap* 20, 169) improved the air-distributing device of the Swift fat stability test apparatus so that only one tube was required for each test sample. This modification allowed carrying out 3 times as many tests as were possible with the original apparatus.

A method for determining active oxygen in fats, based on oxidation of ferrous to ferric iron and the colorimetric determination of the ferric iron as ferric thiocyanate, yielded values twice that by iodometric procedures (Lips, Chapman and McFarlane—*Oil & Soap* 20, 240). This newly proposed method was said to be simple and sensitive; and the calculated absorption of oxygen from change in peroxide value agreed with measurements in the Warburg-Barcroft apparatus when the equivalent weight for peroxide oxygen was assumed to be 8. The usual methods of determining peroxide value were discussed by Sabalitschka and Maas (*Mikrochemie ver. Mikrochim. Acta* 30, 26) and Zinov'ev and Bepalova (*Voprosy Pitaniya* 9, 86).

Some investigators developed stability data on several fats. Barnes, Lundberg, Hanson and Burr (*J. Biol. Chem.* 149, 313) demonstrated that the addition of vitamin E and other sources of fat soluble vitamins

to the diet of a rat did not increase the stability of the depot fat when it already possessed normal stability. However, the keeping time of body depot fat was markedly reduced by diets free of vitamin E or other sources of natural antioxidants. Treatment of moist cottonseed with ammonia prior to storage has been shown to reduce self-heating of seeds and the rate of formation of free fat acids during storage (Altschul *et al.*—*Oil & Soap* 20, 258).

Novikova (*Kholodil'naya Prom.* 19, No. 1, 21) observed carcasses of sheep and geese during a 15-month storage test between -10 and -15°C. Organoleptic changes in the surface fat of suet at -10° became evident at 3 months, they were considerable at 6 months and at 15 months the suet was inedible. At -18°C. the color, odor and taste remained practically unchanged for 15 months. The goose fat did not keep so well. The changes in peroxide value were tabulated. Pearce (*Can. J. Research* 21C, 57) investigated the effect of storage on the development of rancidity in wheat germ. Storage life was considerably extended by holding at low moisture levels and low storage temperatures. Even at -40°C.

sufficient deterioration occurred to reduce the keeping quality of the wheat germ when subsequently stored at higher temperatures. Both packing in nitrogen and compressing into blocks lengthened storage life.

Factors affecting the storage of shortening in glass were investigated by Gudheim (*Oil & Soap* 20, 197). Strong light caused a flavor and odor change which was not characteristic of rancid fat. Light between 325 and 500 m μ was more effective in promoting odor and flavor changes in white shortening than longer wave lengths. Amber colored glass jars almost completely nullified the influence of light on flavor and odor; green and blue colored jars were helpful, while opal glass, even though almost opaque, had little value in minimizing the effect of light. In similar work, Aggarwal (*J. Indian Chem. Soc., Ind. & News Ed.* 5, 121) tabulated changes occurring in several oils stored 1 year in glass, tinned steel and plain steel containers. Oil stored in the glass containers deteriorated least. Ebach (*Z. Untersuch. Lebensm.* 83, 399) also investigated spoilage reactions occurring during storage. His data on several tests, i.e. Lea value, Stamm degree, aldehydes, etc., demonstrated that it was impossible to select a sure chemical test as criterion for spoilage.

Factors affecting the keeping quality of butter fat were studied. Ewbank and Gould (*J. Dairy Sci.* 26, 409) recorded that flash heating of cream above

OUTLINE

- A. General
- B. Technical Treatment
- C. Products (except Detergents)
- D. Deterioration
- E. Biochemical
- F. Characteristics and Composition
- G. Detergents

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100°C. reduced the keeping qualities of the butter oil derived therefrom. Butter oil from cream pasteurized at 90.6°C. was not adversely affected by heating periods of 30 minutes but instead appeared to be stabilized to a slight degree. Schwaibold *et al.* (*Vorratspflege u. Lebensmittelforsch.* 5, 32) analyzed commercial samples of butter for copper, tin, zinc and iron and recorded the effect of these on the stability of butter. Copper promoted spoilage while zinc had a preserving action. Aluminum treated samples of fat developed a bitter taste during storage although only slight chemical changes could be observed; the work emphasized possible effects of utensils and cleaning operations.

The kinetics of the oxidation of tocopherol (vitamin E) during the induction period of animal and vegetable fats were studied photometrically by Golumbic (*Oil & Soap* 20, 105). Tocoquinones appeared as intermediate oxidation products of tocopherols in animal and vegetable fats. Chroman-5,6-quinones developed from oxidation of their precursors which are found in vegetable oils but not in animal oils. These *o*-quinones retarded active oxygen formation in vegetable fats after disappearance of the tocopherols, thus explaining the absence of sharp induction periods in the vegetable fats. Robeson and Baxter (*J. Am. Chem. Soc.* 65, 940) identified the natural antioxidant of Mangana shark liver oil as natural *a*-tocopherol; they considered it to be the major antioxidant present in the oil. An antioxidant comprising wheat germ oil extracted by means of ethylene dichloride and containing added citric acid was found to be very efficient by Lips and McFarlane (*Oil & Soap* 20, 193). Munin (*Fette u. Seifen* 48, 569) recommended additions of wheat germ oil to butter for increasing the stability of the product. Ciusa (*Boll. sci. facoltà chim. ind. Bologna* 1940, 295) recorded that expressed wheat germ oils were more stable than the extracted oils. Bailey *et al.* (*Oil & Soap* 20, 251) fractionated hydrogenated and unhydrogenated peanut oil in a molecular still and found that the anti-oxygenic substances appeared in the fractions collected at intervals between 120 to 200°C.

Crude sources of the B vitamins were demonstrated to have antioxidant activity by György and Tomarelli (*J. Biol. Chem.* 147, 515) and Clausen, Barnes and Burr (*Proc. Soc. Exptl. Biol. Med.* 53, 176). Thiourea and other sulfhydryl compounds, which are good stabilizers for ascorbic acid, proved to be effective with fats, but only in the presence of water (György *et al.*—*Science* 98, 518). Mitchell and Black (*Ind. Eng. Chem.* 35, 50) preferred the use of gum guaiac for lard because it was an excellent stabilizer and was innocuous physiologically. Davies (*J. Indian Chem. Soc. Ind. & News Ed.* 3, 174) fostered the use of antioxidant cereal flour paste as coating on contact wrappers for fatty foods. Täufel and Müller (*Biochem. Z.* 310, 152) believed that phosphatides, proteins and catalase were all concerned in the antioxidant system of cereal flours. Brindle and Pedley (*Quart. J. Pharm. Pharmacol.* 15, 389) recommended Siam benzoin for preservation of lard for pharmaceutical use. Boehm and Williams (*Pharm. J.* 151, 53) reported that propyl gallate was 10 times more effective than Siam benzoin and 30 times more effective than Sumatra benzoin. In investigations by Täufel *et al.* (*Fette u. Seifen* 48, 669) the order of activity of quinones was found to be: quinone <

hydroquinone < quinhydrone. Of the nitro compounds investigated *m*-dinitrobenzene was more active than *a*- or *b*-dinitrophenol.

Nordihydroguaiaretic acid, a compound extracted from the creosote or grease wood bush, has been reported in trade literature as a suitable antioxidant for lard or other fats. Approval for its use in lard and rendered pork fat has been issued (*Meat Inspection Memo. No. 25, Dec. 11*).

The recently patented antioxidants were: a mixture of ascorbic acid with a tocopherol (Mattill and Golumbic—*U. S.* 2,333,655), ascorbic acid with naphthols, quinones and quinols (Mattill and Golumbic—*U. S.* 2,333,656), caffeic acid (Mattill and Golumbic—*U. S.* 2,333,657), hexuronic acid with a cyclic oxy compound such as quinones, hydroquinones, naphthols, chromans, etc. (Mattill and Golumbic—*U. S.* 2,333,658), acetyl methyl carbinol (Simons and Buxton—*U. S.* 2,331,432), a combination of phosphatides and gum guaiac with heating after addition (Musher—*U. S.* 2,314,365), combination of phosphatide and a polyhydroxy benzene (Musher—*U. S.* 2,314,364), use of contact wrapping paper containing deoiled spice residue (Musher—*U. S.* 2,325,624), use of wrapping paper coated with a starch-lecithin mixture (Musher—*U. S.* 2,324,529), use of wrapping paper containing a phenol (Mitchell—*U. S.* 2,309,079), coffee oil (Johnson—*Can.* 412,131; *U. S.* 2,314,988), peroxides of fat acids derived from cacao butter (Kokatnur and Johnson—*U. S.* 2,301,124), Schiff base type compounds in which the carbonyl carbon of each ketone group was doubly bonded to a different nitrogen atom (Downing and Pedersen—*U. S.* 2,301,861), reaction products of amides and ethylene oxide (Ericks—*U. S.* 2,320,225), alkali metal, ammonium, mercury, alkyl or guanidine thiocyanates (Martin—*U. S.* 2,293,350) and reaction products of aliphatic ketones with ammonium thiocyanate (Ter Horst—*U. S.* 2,305,043). The last 3 were developed particularly as soap preservatives. A patented method for facilitating the incorporation of gum guaiac into fats consisted in dissolving the antioxidant in acetic acid before incorporation (Doegey—*U. S.* 2,308,912). The acid was removed by steaming.

Thaler and Eisenlohr (*Biochem. Z.* 308, 88) reported on biochemical rancidity investigations. They measured ketone formation during the action of several molds on saturated acids. Optimum pH and time curves for the reactions were recorded. The results sustain the Wieland theory of dehydrogenation through the steps *a*, *b*-unsaturated acids, *b*-hydroxy acids and *b*-keto acids.

Only meager literature appeared on flavor reversion. Farmer and Sutton (*J. Chem. Soc.* 1943, 119) attributed the development of fishy odor in fish oils to the decomposition products of long chain fat acids. Young and Black (*U. S.* 2,308,848) prevented reversion of revertible fats by completely hydrogenating, oxidizing and then deodorizing. Vollbrecht (*Molkerei-Ztg.* 56, 65) attributed development of oily-fishy taste defect in butter to the use of unsuitable detergents on the dairy utensils.

The thermal decomposition of lard between 200 and 350° was studied by analyses of the products (Larson and Morris—*J. Am. Chem. Soc.* 65, 2301). Decomposition with formation of free acids, acrolein, carbon dioxide, water and unsaponifiable material was greatly accelerated as the temperature approached

350°C. The decomposition was associated with an increase in total free acids and an increase in unsaponifiable material.

Biochemical and Physiological

An excellent review on the literature of fat metabolism for 1942 was compiled by Burr and Barnes (*Ann. Rev. Biochem.* 12, 157). The same authors (*Physiol. Revs.* 23, 256) prepared a comprehensive review on the non-caloric functions of dietary fats.

The increase in use of butter substitutes and the advent of "filled milk" on the market has led to investigations and discussions on the comparative nutritive values of butterfat and butterfat substitutes. The work conducted at the University of Wisconsin supplied new details (Boutwell, Geyer, Elvehjem and Hart—*J. Nutr.* 26, 601; *J. Dairy Sci.* 26, 429). Rats showed superior growth on butterfat or lard as compared to corn, cocoanut, olive, cottonseed, soybean, peanut oils or hydrogenated cottonseed oil when lactose was the sole carbohydrate in the diet. When the sole carbohydrate was sucrose, starch, dextrin or dextrose the superiority of butterfat was not evident. The growth rates on such rations were also greater than when the carbohydrate was lactose. Properly fortified animal margarine fats, with lactose as the sole carbohydrate, were but slightly below butterfat in nutritive value, while the vegetable margarine fats were distinctly inferior. On the mixed carbohydrate diet, such as man ordinarily consumes, there was no conclusive evidence that margarines were inferior to butter; in fact some margarines showed slight superiority. Euler, Euler and Säberg's data (*Ernährung* 7, No. 3, 65) showed that rats fed properly fortified margarine grew much faster than those fed butter. The growth rate was 9.4% faster the first 3 weeks and 40% faster during a second 3-week period. Deuel, Movitt and Hallman's (*Science* 98, 139) experiments indicated that on diets of 68% mineralized skim milk powder and 32% fat with adequate vitamin supplements, butterfat and vegetable food oils were of equal nutritive value for growing rats. They believed that discrepancies between their results and those of others when *ad lib.* feeding was employed were due to rats preferring a butter flavor and eating more of such diets. A preference by rats for food containing diacetyl flavored fats was demonstrated. Boer and Jensen (*Arch. Neerland. Physiol.* 26, 1) believed that butter contains some substances that allow normal growth of animals. Experiments to support the view that margarines and vegetable oils were inferior to butter even after fortification with vitamin A and D were described. The Food and Nutrition Board Committee on Fats of the National Research Council (Maynard, Longenecker, Burr, Elvehjem, Elliot and McCay—*Natl. Res. Council Circular* 118), after review of the present available scientific evidence, reported that when fortified margarine was used in place of butter as a source of fat in a mixed diet, no nutritional differences could be observed. They emphasized that all margarine should be fortified. The Council on Food and Nutrition of the American Medical Association (*J. Am. Med. Assoc.* 121, 1370) reported that no nutritional disturbances occur if oleomargarine is substituted for butter in the ordinary mixed diet of adults provided the oleomargarine contains at least 9000 units of vitamin A per pound. A public relations committee of the New York Academy of Medicine (*Ibid.* 1102)

recommended that oleomargarine be made more freely available to the public as a butter substitute and urged that federal and state laws restricting the manufacture and distribution of oleomargarine be suspended for the duration of the war.

The digestibility studies of fats by Hoagland and Snider (*J. Nutr.* 25, 295; 26, 219) are of particular value because they were well controlled, the physical and chemical characteristics of the experimental fats were determined, and the digestibility data were corrected for the amount of fecal fat of the rats while on a fat free diet. When the diets contained 5% fat the digestion coefficients were: coconut oil 98.9, soybean oil 98.5, corn oil 97.5, butterfat 88.3, mutton tallow 74.6, oleo stock 74, and cacao butter 63.3%. When the diets contained 15% fat the digestive coefficients were: soybean oil 98.3, corn oil 98.3, coconut oil 96.5, butterfat 90.7, oleo stock 86.7, mutton tallow 84.8, and cacao butter 81.6%. There was no consistent relationship between the melting points of the fats and their digestion coefficients. The work with pure saturated fat acids showed that stearic and palmitic acids were poorly utilized while myristic and lauric acids were practically 100% digestible when the fat mixtures contained 5 to 15% of either acid. Tristearin was very poorly utilized; tripalmitin was much more digestible, while trimyristin and trilaurin were thoroughly absorbed. Better utilization of fat on high fat diets was also confirmed in experiments on poultry by Whitson *et al.* (*Poultry Sci.* 22, 137). Nitschke (*Ber. Naturforsch. Ges. Freiburg Breisgau* 37, 43) studied fat absorption with rats by feeding the fat-depleted animals for several days on a diet containing 30% of the test fat. Olive oil caused the greatest deposition of fat. Synthetic fats were uniformly inferior to natural fats. In the work of Smith (*Ohio State Med. J.* 39, 425) comfort of humans during assimilation was interpreted as indicating digestibility. His subjective tests favored foods cooked with hydrogenated vegetable oils over those prepared with animal fats. The quality, physical and chemical characteristics and the amount of fat ingested or assimilated were not determined and hence were not correlated with the conclusions. The work of Wikoff *et al.* (*Am. J. Digestive Dis.* 10, 266, 395) was a more accurately controlled investigation of this type, using dogs as the experimental animals. At 20% levels lard, cottonseed oil, olive oil and Crisco were without effect on intestinal elimination. Some fats with low iodine value, such as cacao butter, bayberry tallow, tripalmitin and tristearin, caused constipation at 10 and 20% levels. Glycerides of lauric, capric, caprylic, caproic and butyric acids had a laxative effect, which varied in intensity inversely with the number of carbon atoms. In a study of the ability of fats to produce gastric inhibition Tidwell *et al.* (*Bull. Johns Hopkins Hosp.* 70, 362; *Proc. Trans. Texas Acad. Sci.* 25, 33) observed that the fats that were most completely absorbed pass from the stomach most slowly. High fat diets were found to accelerate fat metabolism (Roberts and Samuel—*J. Biol. Chem.* 151, 267). A very early fasting ketosis was given as support to this theory.

The mechanism of increased red blood cell destruction on high fat diets remained rather puzzling. Both the investigations of Loewy *et al.* (*Am. J. Physiol.* 138, 230) and of Longini and Johnson (*Ibid.* 140, 349) demonstrated that although red blood cell de-

struction in test animals was abnormally large no anemia occurred. The former believed that normally functioning hematopoietic tissue was able to compensate for losses which were due to the high fat diet. The latter suggested that the physiological mechanism which delays the absorption of fat and its entrance into the blood stream was probably significant in the prevention of anemia. Investigations on normal children showed that this effect of high fat diets was independent of the type of fat fed (Joseph *et al.*—*Bull. Johns Hopkins Hosp.* 71, 84). Turner and Miller (*Proc. Soc. Exptl. Biol. Med.* 54, 177) recorded that the acid fraction of beef liver lipids contained 2 substances that stimulate building of red blood cells.

Investigations on the metabolism of synthetic fats dealt principally with the absorption of odd and branch chain fat acids (Keil *et al.*—*Z. physiol. Chem.* 274, 175, 186; 276, 26). Rats, dogs and goats were used as test animals. Growth and development were the same when the animals were fed coconut oil or butterfat or a synthetic fat containing odd and even number carbons in the fatty chains. Feeding C_{10} to C_{23} fatty acids led to C_{13} to C_{17} fatty acids in depot fat and the odd numbered carbon chain acids amounted to 33% of the total depot fat acids. The feeding of triglycerides of branched chain fatty acids caused an increase in the amount of acid metabolic products in the urine; ethyl branch chain acids were inefficiently attacked and were eliminated, whereas those with methyl branches were not excreted in significant amounts.

Fat metabolism studies under pathological conditions have yielded new information. In the work of Bavetta (*Am. J. Physiol.* 140, 33) adrenalectomized rats did not absorb long chain fat acids as well as normal rats. The observation was said to supply additional evidence in the support of the hypothesis that the adrenal glands play a role in the absorption of long chain fat acids. According to Giroud *et al.* (*Compt. rend. soc. biol.* 135, 836) inhibiting the secretion of adrenal cortical hormones into the blood stream by iodoacetic acid poisoning completely checked the absorption of olive oil from the intestinal tract. Remington and Harris (*J. Nutr.* 25, 203) believed that the function of the thyroid gland is not related to the metabolism of fat because enlargement and edema of the gland had no effect on fat metabolism. Pancreatectomy produced varying degrees of impairment of absorption of neutral fat, but some animals still absorbed 75% or more of the fat in the diet (Vermeulen *et al.*—*Am. J. Physiol.* 138, 792); impairment in absorption of free fat acids was very definite. Rekers, Abels and Rhoads (*J. Clin. Invest.* 22, 243) observed that patients with intestinal carcinoma absorbed about 93% of the fat ingested; however, in cases of gastrectomy only 27% of the ingested fat was absorbed. Conrad *et al.* (*J. Am. Med. Assoc.* 121, 237) cautioned against the use of sesame oil as a carrier for injecting drugs; this oil has been found responsible for painful and disabling tumors at the sites of injection.

The effect of dietary fat on calcium metabolism was considered in 2 communications. In one (Bunkfeldt and Steenbock—*J. Nutr.* 25, 479), calcification of bones in rats decreased uniformly and in proportion to the amount of oil fed; the other (French and Elliott—*Ibid.* 17) presented evidence to show that oleo oil diminished the retention of calcium.

In one study on metabolism of fats, ethyl esters of fat acids containing 2 bromine atoms in various positions on the carbon chain were fed to rats and the total fat acids in the liver and their bromine content were determined (Arton and Swanson—*J. Biol. Chem.* 148, 633). The highest liver fats were obtained with 9,10-dibromostearic ester followed in order by the 6,7- and 2,3-isomers. These results were believed to indicate that isomeric fat acids were utilized at different rates. Most of the acids that accumulated in the liver had already lost their bromine.

The problems of intermediate metabolism of fats seem mainly to involve the liver. Using deuterium labeled fats, Stetten and Grail (*J. Biol. Chem.* 148, 509) found the half-life of depot fat in the liver to be 2.6 to 2.8 days. The presence or absence of choline had no significant effect on the rates of disappearance of deuterium from body or liver fat acids. Gavin, Patterson and McHenry (*Ibid.* 275; *Federation Proc.* 2, 63) compared the effect of choline, inositol and lipocaic toward decrease of fat in fatty livers. Choline was effective for thiamine fatty livers, and partially effective with the cholesterol type, but showed little activity with biotin fatty livers. Inositol and lipocaic were effective with the latter. Inositol differed from lipocaic in being effective against fatty livers caused by feeding cholesterol with a high fat diet. Additional evidence of the lipotropic action of inositol and its increased effect with choline was presented by Forbes (*Proc. Soc. Exptl. Biol. Med.* 54, 89). Handler and Bernheim (*J. Biol. Chem.* 148, 649) suggested that the development of fatty livers in choline deficiency occurs only when all other dietary factors permit the growth of the whole rat. Vitamin B complex deficiency prevented the appearance of fatty livers due to choline deficiency probably because of impairment of the over-all metabolism of the test animals. Simultaneous mineral deficiency with a fatty liver producing diet also slowed the deposition of fat in the liver (Handler—*Ibid.* 149, 291). Engel's work (*Proc. Soc. Exptl. Biol. Med.* 52, 281) emphasized that rats differ in their requirements of dietary choline, due to hereditary factors, thus demonstrating that variations in genetic stock may affect experiments. The same author's (*J. Nutr.* 25, 441) analytical information showed that animal organs, egg yolk and nervous tissue were considerably better sources of choline than plant materials. Poultry investigations by Berry *et al.* (*Poultry Sci.* 22, 442) indicated that soybean oil meals were deficient in choline. Lipocaic prevented accumulation of fat in the liver produced by injection of ketogenic hormone in fasting guinea pigs (Julian *et al.*—*Am. J. Physiol.* 138, 264). Abrine, a compound that promotes growth of rats on a tryptophane-deficient diet did not prevent accumulation of fat in livers of animals on a choline deficient diet (Cahill and Kotalik—*J. Nutr.* 26, 471). Glutamic acid exerted a lipotropic effect on cholesterol but not on fat-fatty livers (Channon *et al.*—*Biochem. J.* 37, 483).

Artom and Fishman (*J. Biol. Chem.* 148, 405, 413, 423) determined total lipids, noncholine and choline phospholipids and other lipid fractions in muscle and liver of rats. On an adequate mixed diet the total choline and non-choline phospholipids remained remarkably constant when expressed on the basis per gram of lipid-free tissue. Diets containing casein

reduced the choline phospholipids of the liver, whereas muscle phospholipids were only slightly affected. Choline, glycine, cystine, or *dl*-methionine were ineffective in raising the liver content of the choline phospholipids. Dietary factors other than choline or choline precursors may be involved in maintaining normal liver phospholipids. Schulte (*Biochem. Z.* 313, 78) recorded that phosphorus poisoning reduces the phosphatide content of the liver. However, using injections of inorganic radioactive phosphorus Fishler *et al.* (*J. Biol. Chem.* 50, 47) obtained analytical evidence suggesting that plasma phospholipids were formed mainly in the liver. Histological investigations of fatty livers produced by a high sugar diet were recorded by Deane (*Anat. Rec.* 84, 171). Fasting after such dietary regimes produces an immediate additional increase in liver fat. The liver returned to normal within one week after return to normal diets. Chaikoff *et al.* (*Am. J. Pathol.* 19, 9) developed liver cirrhosis in dogs by feeding diets high in fat. Greene (*J. Am. Med. Assoc.* 121, 715) believed that vitamins were also involved in liver cirrhosis and encouraged use of high protein and high vitamin diets in the treatment of the condition.

Kaucher *et al.* (*Arch. Biochem.* 3, 202) tabulated the cephalin, lecithin, sphingomyelin, free and combined cholesterol, cerebroside and neutral fat distribution in beef organs and muscles, in the muscles of other warm and cold blood animals and in eggs. His discussion of the data points out relations between the distribution of these lipids and the functions performed by the individual tissues.

Experimental evidence in support of the belief that the composition of the fat of the animal body appears to be characteristic of the species was developed by Visscher and Corley (*J. Biol. Chem.* 147, 291). The kinds of fat acids stored by the rat were essentially the same on a diet low in lipids as on diets supplemented with 5% palmitic acid, with or without additional linoleic acid. Hilditch and Jaspersen (*Biochem. J.* 37, 238) recorded the effect of the fat in the feed on the composition of butterfat produced by cows. Feed fats high in oleic acid led to increased amounts of oleo glycerides, and some decrease of butyric-decanoic glycerides in the milk fats. Hydrogenated fats increased stearo glycerides. Ingestion of palm-kernel oil increased the proportions of lauro and myristo glycerides and slightly diminished both palmito and oleo glycerides in the fat produced. The production of milk fat almost identical with control milk fat after ingestion of more completely hydrogenated fats was interpreted to suggest that the highly saturated fat was relatively unassimilable. Loosli and Lucas (*J. Dairy Sci.* 24, 291) were unsuccessful in attempts to raise milk fat production by adding thiamine supplements to cattle rations. Butter fat or milk production was not altered by feeding grain mixtures varying from 2.69 to 4.89% fat (Monroe and Krauss—*Ohio Agr. Expt. Sta. Bull.* 644).

The work of Fraps (*Poultry Sci.* 22, 421) should encourage investigations on development of livestock rations with most favorable fat producing ingredients. He showed that the fat content of poultry could be altered by changes in the fat, protein and carbohydrate content of the feed. For example, substituting cottonseed oil for part of the corn meal ration increased fat deposition and high protein diets de-

creased it. He suggested that such data should be developed so that the diets to produce chickens of highest quality could be determined.

Essential fat acid potency of several seed oils (Anthony, Quackenbush, Ihde and Steenbock—*J. Nutr.* 26, 275) and fish oils (Bailey—*J. Fisheries Res. Board Can.* 6, 109) were evaluated. Both communications revealed that the activity of the fats in curing rat acrodynia was not simply a function of their unsaturation. In the work on seed oils the anti-acrodynic potency was found to be in direct proportion to their linoleic acid content unless considerable amounts of linolenic acid were present. In the presence of linolenic acid the curative effect was greatly reduced. Hansen and Wiese (*Proc. Soc. Exptl. Biol. Med.* 52, 205) produced essential fat acid deficiency in dogs by feeding diets low in fat. The symptoms were also associated with a lowering of the iodine value of acetone soluble fraction of the blood serum fat acids. Bodman and Felix (*Med. Press. & Circ.* 105, 331) prepared case reports of industrial dermatitis patients that were cured by ointment rich in unsaturated fat acids. A brief treatise on the subject by Besancon and Laroche (*Presse med.* 50, 373) dealt with the role of linoleic acid in metabolism and its clinical importance.

Some details on the chemistry and physiology of fat soluble vitamins have been developed. Heinrich and Mattill (*Proc. Soc. Exptl. Biol. Med.* 52, 344) recorded some alterations in the lipids of rats deprived of tocopherol (vitamin E). The cholesterol content of muscle and brain tissue was significantly increased. The total lipids of the muscle were less markedly increased. The data generally parallel those reported for rabbit tissue but were not so striking. Miller (*J. Nutr.* 26, 43) recommended that partially hydrogenated oils be substituted for lard or unhydrogenated oils in experimental diets, to increase the stability of the vitamin E in the diet. Hydrogenation did not destroy the vitamin E in vegetable oils. Vitamin E deficiencies readily occurred in chicks on diets containing 5% fresh cod-liver oil and slightly rancid cod-liver oil; and to a lesser extent on diets containing similar proportions of lard or fat acids from linseed oil (Dam—*Proc. Soc. Exptl. Biol. Med.* 52, 285). The symptoms did not occur with thoroughly rancid cod-liver oil or if the diet was rigidly freed of fats. The data were interpreted to indicate that the appearance of symptoms depends upon the presence of highly unsaturated fat acids in the vitamin E deficient diet, and that rancidity of the dietary fat did not contribute to the development of the symptom. Investigations on corn by Richter and Rice (*Am. J. Physiol.* 139, 147) indicated that white corn was deficient in vitamin A as well as another factor which was also lacking in yellow corn. Both factors were provided by a cod-liver oil supplement. Other evidence suggested that yellow corn contained some factor lacking in white corn and not present in cod-liver oil. A mixture of corn germ oil and cod-liver oil was recommended by Grandel (*Vorratspflege u. Lebensmittelforsch.* 4, 304) as a good stable source of all fat-soluble vitamins. Grollman and Harrison (*Proc. Soc. Exptl. Biol. Med.* 52, 162) discovered that fish oils contain substances effective for reducing blood pressure of hypertensive rats. The effectiveness of the oils was increased by oxidative procedures which destroy vitamin A. Rodahl

and Moore (*Biochem. J.* 37, 166) attributed the toxicity of bear and seal livers to the presence of excessive amounts of vitamin A. Sachs (*Arch. Path. Anat.* 309, 712) reported that the vitamin A of liver increased whenever its fat content was normally increased, whereas in fatty degeneratoin processes vitamin A diminished. New analytical data on fat-soluble vitamins included reports on the vitamin D content of subdermal dolphin and cod-liver oils (Lapina—*Voprosy Pitaniya* 9, 79), vitamin D content of Florida shark liver oil (Rusoff and Mehrhof—*Poultry Sci.* 22, 47) and the vitamin A potency of South Indian marine animal oils of medicinal value. The stability of vitamin A added to several commercial fats with and without antioxidants was evaluated by Morgal, Byers and Miller (*Ind. Eng. Chem.* 35, 794).

Enzymes associated with the biological oxidation of fat received some attention. Munoz and Leloir (*J. Biol. Chem.* 147, 355) prepared an enzyme system from liver which oxidized lower saturated fat acids but in vitro oxidation of acetone by liver and muscle tissue could not be demonstrated (Krauel and Gibson (*J. Iowa State Med. Soc.* 33, 183). Shapiro and Wertheimer (*Biochem. J.* 37, 102) demonstrated the presence of an enzyme, which desaturated fat acids, in liver, muscle, heart, testes and adipose tissue but not in brain. Schwartz (*J. Gen. Physiol.* 27, 113) determined the effect of temperature on the rate of hydrolysis of some triglycerides by pancreatic lipase.

Characteristics and Composition

New analytical data on many fats and oils have been tabulated to simplify their inclusion in this review. Many of these data were developed in searches for new fat sources or for fats for particular uses. Such contributions also contained details regarding availability, ease of production and behavior in manufactured products. Some investigators applied improved technic in identifying constituents; as for example, Jamieson and Rose's work on prickly poppy-seed oil suggests that there is no ricinoleic or linolenic acid in the oil although these have been reported by others. Tabulated reports similar to that on elderberry oil should be of botanical interest to show differences or likenesses in character or composition of the members of the same or related species. Many analyses made on liver oils, human depot fats, butterfat produced under different feeding regimes, etc., were useful in the development of physiological and biochemical knowledge of fats and oils. The preceding section of this review contained discussions on some data of this type which are therefore not included in the tabulations.

Certain miscellaneous data are of general interest. Boekenooen's (*Olïen Vetten Olïezadan* 26, 143) statistical calculations indicated that the distribution of fat acids in world-wide commercial oils was oleic 34, linoleic 29, palmitic 11, lauric 7, linolenic 6, myristic 3, erucic 3, stearic 3 and all others 4%. Analyses of 227 samples of food fats by Andrews and Richardson (*Oil & Soap* 20, 90) showed that the average percentage of glyceride derived from linoleic acid increased in the order: butterfat, margarine, lard, hydrogenated shortening and blended shortening. A deposit occurring in avocado pulp oil after standing contained according to Asenjo and Goyco

(*J. Am. Pharm. Assoc.* 32, 259: palmitic acid 56.6, oleic acid 28.9 and unsaponifiable matter 0.5%.

Variations in climate, soil and variety were shown to affect the amount and character of seed oils. Hancock (*Tenn. Agr. Expt. Sta. Circ.* 79, 7 pp.) found an inverse relationship of the oil to the protein content of cottonseeds. A wet cloudy season was favorable to oil but unfavorable to protein. This was confirmed in similar work on 4 varieties of flax by Dillman and Hopper (*U. S. Dept. Agr. Tech. Bull.* 844, 69 pp.). In addition they recorded that an unusually dry season reduced the size of seeds and the iodine value of the oil. The oil content of large-seeded varieties of flax was 2-3% higher than that of the small-seeded varieties, and the iodine values of the oils of the latter were higher. Four flax varieties were investigated by Painter and Nesbitt (*Oil & Soap* 20, 208). Composition and unsaturation were affected by variety and location, and single varieties in same locations in different crop years showed wide ranges. Eckestein's analyses (*Industria y quim.* 5, 25-34) of several oils from different parts of Argentine also confirmed the observations of other investigators as to the effect of climatic conditions on the iodine value of the oils. Krug and Menders (*Bragantia, Sao Paulo* 2, 155) called attention to the need of selection and improvement in castor oil cultivation; the oil content of the seeds presently marketed varies from 39 to 54% oil. Venezia (*Ricerca sci.* 11, 260) analyzed many varieties of Italian grape seeds; in general the oil content of the black seeded varieties was slightly higher. Analytical data on 10 varieties of soybeans grown in New South Wales compared favorably with American, South African and Manchurian beans (Bryant and Morrison—*J. Australian Inst. Agr. Sci.* 8, 117). Frost damage of soybean seeds was accompanied by increases in the phosphate acidity, oil acidity, amino-acid acidity, nonprotein nitrogen, reducing sugar and internal aerobic microfloral content of seeds (Milner *et al.*—*Oil & Soap* 20, 265).

Directions for sampling and for preparation of samples for determination of oil were issued for peanuts (Cox—*Oil & Soap* 20, 213) and tung fruit (McKinney—*Oil, Paint, Drug Repr.* 144, No. 3, 3, 69). Mixing coarsely ground peanuts with diatomaceous earth before passing through a mill for very fine subdivision yielded prepared samples that did not lose oil during the milling and did not require re-grinding during extraction. The sampling directions for tung fruit called for sampling from 25 bags per load.

Several innovations in methods of fat determination were suggested. A new German method (Schloemer *et al.*—*Z. Untersuch Lebensm.* 83, 289; 84, 202; Grossfeld *et al.*—*Ibid.* 83, 322; 84, 193) comprised hydrolyzing the sample with hydrochloric acid in the presence of trichloroethylene or carbon tetrachloride, cooling, shaking with 40 cc. benzene and determining the fat in a 25 cc. aliquot. Tables for calculation of the fat content were devised. Details of the method for application to cheese, buttermilk and dried eggs were developed. Another method (Schwarze—*Fette u. Seifen* 49, 774) which was suitable for control work in oil milling comprised shaking a 2 g. sample with 20 c.c. trichloroacetic acid and 5 cc. benzene, centrifuging, separating the benzene solution of the oil and determining oil either gravimetrically or refractometrically. The transparencies

CHARACTERISTICS OF FATS AND OILS REPORTED DURING THE YEAR (Continued)

Oil or fat source	% Oil or fat	Specific gravity	Refr. index	Acid No. or (% free fat acids)	Sapon. No.	Iodine No.	(SON) No.	Diene No.	Acetyl No.	R-M No.	Polenske No.	% Unsapon.	Melting point	Solidification point	Hexa-bromide No.	Carbonyl No.
Silkworm chrysalis ³⁰	5.7	0.9206 ³⁰	1.4739 ³⁰	5.87	212.2	145.7						2.4				
<i>Phaenacia synthlipsis</i> ricini																
Soursop or guanabana seed ⁴⁰	23.9	0.9178 ^{30,35}	1.4709 ³⁰	2.29	197.0	87.8			12.6	0.81	0.56	1.02				
<i>Annona muricata</i>	3.12	0.9255 ¹⁵	1.4727 ³⁰	4.4	189.5	124.4						11.8				
<i>Spinacia oleracea</i> seed ¹	32.6	0.9266	1.4770 ³⁰	6.1	186.8	151.2	85.5		7.51	0.31	0.20	1.62			2.6	
Stinging nettle seed ¹	16.8		1.4703 ¹		211	111				1.0	0.8	1.97				
Subterranean clover seed ¹		0.9208		0.24		127							-16			
Sunflower (Uruguay) seed ¹⁴		0.9236 ¹⁵				130							-18			
<i>Taeniopoda auricornis</i> (an insect) ⁴⁵																
Female	2.76	1.4733 ²⁵		3.8	185	101.3				12.76	1.4					
Male	2.52		6.16	196.5	111.5								
Turkey depot ⁶		1.4615		(0.17	182.1	78.8	59.2		1.9							
<i>Tetrasturus mizukurii</i> ⁶	3	1.4625 ⁴⁰		0.28)	193.3	87.9	66.8		4.3							
Road thistle seed ⁷		0.9216 ²⁵		0.9	157.8	130.2						20.0				
<i>Onopordum acanthium</i>	16.1	0.8897 ^{15/4}		4.3	193.4	143.3	84.5			1.4	0.4	1.6				
Tropical almond (talisay) ⁴	54.6	0.9024 ^{25/25}		7.39	187.6	71.3			4.67	0.08	0.12	0.65				
<i>Terminalia catappa</i>	38.5	0.9515 ²⁴		3.98	191.0	88.72			5.66	1.5	0.46	0.95	50			
<i>Vanuaria spinosa</i> seed ⁴⁰																
Watermelon seed ³⁰				1.8	190.5	123.6	67.5			0.2		0.59	-11			0
<i>Citrullus vulgaris</i>																

FAT ACID COMPOSITION

Oil or fat source	Common saturated acids			Common unsaturated acids			Other fat acids
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Arrow wood bush seed ⁷	0.35	4.5	1.1	54	19		C ₁₅ (-2H) 3.6
<i>Pithecellobium dentatum</i>		10.9		71.7	17.7		
Bear (No. Am. Black) ¹		26.5	12.6	54.0	2.0		
<i>Ursus americanus</i>							
Bone marrow of reindeer ⁶		11.6		5.4	7.6		Licanic 73.3, Elaeostearic 1.6
Cacahuanahe seed kernel ¹							
<i>Lycium arborea</i>		2		56	6		Ricinoleic 31
Dingili seed ³		8.5		10.7	35.1	45.7	
<i>Cephalocroton cardofolius</i>		8.4		2.4	42.7	46.8	
Dutch night violet seeds (2 samples) ¹⁴							C ₂₀ 0.6
<i>Asperula matronalis</i>							
Elderberry seeds ¹⁰		5.3	2.6		92.1		
<i>Sambucus canadensis</i>							
Flaxseed ³				12.1-27.6 (21)	13.4-22.4 (16.7)	42.5-61.3 (52.9)	
Redwind variety		8.6-10.2 (Av. 9.4)		17.6-33.5 (25.8)	11.7-22.6 (17.9)	34.7-54.5 (46.4)	
Bison variety		8.5-11.7 (Av. 9.9)		14.2-26.1 (21.5)	15.6-26.8 (19.7)	42.9-61.8 (50.6)	
Linnata variety		7.2-9.2 (Av. 8.2)		14.2-31.2 (23.6)	9.1-21.1 (15.6)	41.8-53.2 (48.4)	
Bio variety		8.9-14.5 (Av. 12.4)					
Fungus or Behurda kernel ¹⁵				27.1	8.6		Elaeostearic 48.8
<i>Parinarium campestris</i>		14.5		27	3		
<i>Gnetum scandens</i> seeds ³⁰		14					
Human depot ¹	2.6-3.9	24.7-25.7	5.2-8.4	44.8-46.9	8.2-11.0		C ₁₂ 0.1-0.9, C ₁₄ (-2H) 0.2-0.6, C ₁₆ (-2H) 5.0-7.6, C ₂₀ (-8H) 0.4-1.0, other C ₂₀ 0.3-2.2
Lycopodium spores ²⁵							
<i>Lycopodium clavatum</i>							
Papaya seed ¹	4.57	12.79	1.78	91.7	8.3		
<i>Carica papaya</i>				80.03			
Prickly poppy (Mexican) seed ³⁴							
<i>Arymenes mexicana</i>	0.3	11.1	1.8	21.3	58.6		
Physic nut kernels ¹⁵				97.1	40.3		
<i>Jatropha curcas</i>		16.9	5.7	33	61		
Safflower (Indian) seed ³⁶		3	1				
<i>Carthamus tinctorius</i>				61.01	12.11		
Soursop or guanabana seed ⁴⁰	0.34	16.99	5.76	11.55	73.66	1.71	
<i>Annona muricata</i>							
Stinging nettle seed ¹		6.98		95.1	17.9		
Tropical almond (talisay) ⁴	0.65	36.5	3.8				
<i>Terminalia catappa</i>							
Watermelon seed ³⁰							
<i>Citrullus vulgaris</i>		10.7-10.8	9.6-9.7	12.7-13.9	60.1-61.9		

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formed on evaporation of solvent from a drop of an oil solution on a ground-glass surface were the basis for another oil determination method (Edeler—*Ind. Eng. Chem. Anal. Ed.* 15, 282). The use of this principle for quantitative purpose was patented (Lippke—*Ger.* 711,444 *Cl.* 42, 1).

Both Bull (*Oil & Soap* 20, 94) and Schloemer *et al.* (*Z. Untersuch. Lebensm.* 83, 305) pointed out that variable amounts of lipids could be removed from materials by analytical methods and they emphasized that the lipid content should always be defined on the basis of a definite standard procedure. Bull showed that heating soybeans with methyl alcohol or denaturing the proteins in water vapor affected the amount of lipids that could be extracted. Schloemer's contribution contains a review of the literature on the factors affecting the amounts of extractable triglycerides and phosphates and indicates the possible differences which may occur with the various procedures. The American Oil Chemists' Society method for determining oil in seeds and oil meals gave results averaging 0.25% higher than those of the Association of Official Agriculture Chemists (Taylor—*J. Assoc. Off. Agr. Chem.* 26, 74).

Various devices and changes in procedures shortened the fat determination. Tobie (*Ind. Eng. Chem. Anal. Ed.* 15, 122) supported the Soxhlet thimble on a glass stopper so as to diminish the volume of solvent

that accumulates in the device. The innovation promoted more frequent siphoning and faster extraction. The determination of fat, nonfat, moisture, salt and acidity of butter on one sample was made possible with an apparatus consisting of a glass filter crucible suspended over a small cup (Korpácy and Ersek—*Z. Untersuch. Lebensm.* 83, 218). Moen (*Tids. Kjem. Bergvesen Met.* 2, 20) issued details for applying modified Babcock procedures to the determination of fat in herring. A Minnesota Babcock method, which was originally intended only for the analysis of skim milk for butterfat, was found unreliable when applied to concentrated milk products and ice cream (Brown and Thurston—*J. Milk Tech.* 6, 136) Brüchner (*Chem. Ztg.* 66, 229) devised a procedure and supplied the necessary data for applying the refractometric method to cacao products. Control methods for determining fats in confections were compared by Finogenov (*Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Konditerskoi Prom.* 1941, No. 4, 5). He preferred the refractometric method for chocolates, Gerber procedure for milk products and a modified Gottlieb-Rose extraction for candies and cakes.

Parsons (*Oil & Soap* 20, 256) called attention to the need of good laboratory tests for commercial evaluation of the qualities of tallow and greases for soap making. A refining and bleaching test was recommended and his work indicated that a "Pikes Peak" brand of active earth gave more uniformly good bleaches on these products than other earths now commonly used as standards.

Shuey (*Oil & Soap* 20, 244) proposed improving the standard methods of determining the free fat acids in fats by adopting the use of cotton filters in place of asbestos, adding 10 cc. petroleum ether before addition of alcohol and using isopropyl alcohol. Petroleum ether facilitated the titration, so that simply whirling the flask instead of shaking sufficed. A more definite end-point appeared when isopropyl alcohol was used. In a comparison of the iodometric and alkalimetric acid determinations the latter was preferred because it was more simple and rapid (Schmalfuss and Stadie—*Fette u. Seifen* 49, 779). An electrical conductivity apparatus for determining moisture in butter and margarine was patented (Raardt & Co.—*Brit.* 508,783).

Work on solidification curves and crystallization temperatures yielded information of both analytical and commercial interest. Schuette *et al.* (*Oil & Soap* 20, 263) prepared solidification point curves of binary mixtures of C₂₄ to C₃₀ fat acids and discussed the possibility of using these to analyze wax acid mixtures. Analysis of Chinese insect wax was unsuccessful because ester fractionation of the acids into binary mixtures failed. A discussion on this type of procedure in the identification and analysis of fat acids was presented by Schuette and Vogel (*Fette u. Seifen* 48, 368). Anthony, Quackenbush and Steenbock (*Oil & Soap* 20, 53) analyzed fat acid mixtures by quantitative crystallization from acetone at -40°C. and determination of the linolenic, linoleic and oleic acid content of the liquid portion from iodine and thiocyanate values. Handschumaker, Thompson and McIntyre (*Ibid.* 133) used crystallization from acetone to prove that hydrogenated fats did not contain trisaturated glycerides. Dilatometric, melting point and solidification data on cacao butter were plotted by Fincke (*Kazett.* 30, 254, 271, 286). Practical infor-

mation such as comparison with other fats, formation of crystals, effect on density of chocolate, etc. was included. The data on specific heat and heat of melting of milk fat were also prepared for practical purposes (Jack and Brunner—*J. Dairy Sci.* 26, 169). The relation between the degree of solidification of fat in cream and its churning time, values for the percentage of solid fat in cream at various temperatures, and amount of heat necessary to add or remove for processing and cooling, respectively, were some of the useful contributions of this paper. Davis (*Ind. Eng. Chem.* 35, 105) prepared a solidification-point nomograph for fat acids. In a new cold test method by Bailey (*Fisheries Res. Board Can. Prog. Repts. Pacific Sta. No. 55*, 16) the oil in a 4 oz. sample bottle was cooled to a temperature sufficiently low to produce clouding in from 2.5-5 hours. The test rapidly measured the limiting value of the cold test and was useful in control of winterizing operations.

During viscosity measurement work on oils with a rotational viscosimeter, Weltman (*Ind. Eng. Chem. Anal. Ed.* 15, 424) noted that the oils exhibited thixotropy. Capillary number data on several oils were tabulated by Marcelet (*Chimie Industrie* 45, No. 3, 201). He pointed out that, in mixtures of refined olive and refined residual olive oils, the capillary value decreased with lower content of the latter. Other physical data of interest were a refractive index nomograph for liquid fat acids (Davis—*Ind. Eng. Chem.* 35, 1302) and a tabulation of the solubility of hydrogen, oxygen, air, nitrogen and carbon dioxide in butter oil, cottonseed oil and lard (Schaffer and Haller—*Oil & Soap* 20, 161).

The intensity of the yellow to red color produced by the reaction of tetranitromethane with fats in carbon tetrachloride solution formed the basis of a new procedure for determining the amount of unsaturation (Kaufmann—*Ber.* 75B, 1201). When read with a Pulfrich photometer the intensity of the color rose with the iodine value of the sample. Values determined by the method were within ± 5 of those determined bromometrically. This reagent was also a good elaidinization and polymerization catalyst and with suitable procedures it served for oxidizing fat acids and other organic compounds in investigations regarding their structure.

The rapid methods for determining iodine value of fats by Jasperson (*J. Soc. Chem. Ind.* 61, 115), and Norris and Buswell (*Ind. Eng. Chem. Anal. Ed.* 15, 258) included the use of mercuric acetate as a reaction catalyst. The former applied it to the bromometric method. Norris and Buswell improved the rapidity of both the Wijs and Hanus procedures, but the latter method, with mercuric acetate as catalyst, was unsuccessful with conjugated fats and castor oil. In comparable work with the ordinary Hanus, Wijs and Hübl methods on castor oil, the Hanus method was most satisfactory, although values were as much as 8% low (Lo and Chu—*J. Chinese Chem. Soc.* 8, 218). Montequi and Doadrio (*Inst. espan. oceanograf.*, *Notas y resúmenes. Ser. 2*, No. 111, 5) compared 7 well-known procedures for iodine values on olive, castor, cod-liver and sardine oils. The Hanus and Kaufmann methods were most generally useful and a modified Winckler was most desirable for industrial control purposes. In a study of the best procedure for polymerized food oils, Nergaard and Jakobsen (*Tids. Kjemi, Bergvesen Met.* 1, 177) recorded that

Waller's method gave low results, Kaufmann's did not give a definite end-point and the Wijs method gave the most reproducible results. Hartweg's (*Kraftsstoff* 18, 42) recommendation that the Hanus iodine value method be modified so that titrations are made arsenometrically was intended for conserving iodine, which is now scarce in Axis countries. A procedure named the "Woburn iodine absorption method" makes use of iodine bromide in 1.6 to 2 times the concentration of Hanus solution for determining total unsaturation (Mikusch and Frazier—*Ind. Eng. Chem. Anal. Ed.* 15, 109). A differential between the iodine value by this method and a "partial iodine value" with Wijs solution limited to a 2-minute contact at ice temperatures compared well with maleic anhydride diene values and was in good agreement with calculated diene values.

The thiocyanogen absorption value was studied to show the importance of controlling the concentration of reagent, absorption time and amount of reagent (Painter and Nesbit—*Ind. Eng. Chem. Anal. Ed.* 15, 123). With refinements in the method, analyses of linseed oils showed more oleic and linolenic acids and less linoleic acid than have formerly been recorded. Lund (*Fette u. Seifen* 48, 361) applied thiocyanogen and iodine value determinations to an investigation on whale oil. The thiocyanogen values were 40 to 60% of the iodine values on raw oil. He believed that thiocyanogen addition occurred at the 2-4, 2 or 3-5 or 3-6 double bonds. He further found that during hydrogenation the hydrogen added preferentially to those double bonds which do not add the thiocyanogen. Hydrogenation produced fat acids with 2 or 3 double bonds which had the same iodine and thiocyanogen values. The data were significant to the application of unsaturation values for determining the fat acid composition of oils. Mitchell, Kraybill and Zeheile (*Ind. Eng. Chem. Anal. Ed.* 15, 1) proposed spectroscopic methods for the direct determination of linoleic and linolenic acids in fats. This method together with the iodine value determination was said to be more rapid than analysis based on the Kaufmann thiocyanogen procedure.

Rieman (*Ind. Eng. Chem. Anal. Ed.* 15, 325) eliminated a blank in determining the saponification number of fats by the use of double indicators. First excess caustic was titrated to a phenolphthalein indicator change and by adding bromophenol blue and 10 cc. of benzene the soap formed during saponification could be titrated. The method checks standard methods for all oils except acetylated castor oil and palm oil samples. Kiczales (*Soap* 19, No. 3, 57) increased the rapidity of the saponification value determination by adding petroleum ether to the saponifying medium.

A stirring device illustrated by Van Zile *et al.* (*Oil & Soap* 20, 47) was designed for improving the rapidity and ease of separating and washing fat acids for titer and other determinations.

Several investigations concerned the separation of pure fat acids and determining some of their physical properties or structure. Walker and Mills (*J. Soc. Chem. Ind.* 62, 106) isolated linoleodilinolenin from linseed oil by chromatographic technique. Their investigations on linseed oil fractions indicated a thiocyanogen value of 163.2 for linolenic acid. Graff and Skau (*Ind. Eng. Chem. Anal. Ed.* 15, 340) described chromatographic means of separating unsaturated from

saturated fat acids of the same number of carbon atoms. Two saturated acids differing in chain length by 4 carbon atoms could also be separated by the technic.

Brown and coworkers (*J. Am. Chem. Soc.* 65, 252, 415) isolated the linoleic acids from several oils by crystallization and purification of the bromides followed by debromination. The properties of the acids were compared and suggestions were made regarding their structure. Work by Arcus and Smedley-Maclean (*Biochem. J.* 37, 1) on the structure of normal linoleic and arachidonic acids suggested that the double bonds are, respectively, in the 9, 12 and 5, 8, 11, 14 positions. Dorée and Pepper (*J. Chem. Soc.* 1942, 477) isolated erucic acid from rape oil and prepared oxidation products of it and its elaidinized isomer. The properties of the derivatives were recorded. Hoback (*J. Am. Chem. Soc.* 65, 1606) recorded the physical properties of several alcohol esters of the lower saturated fat acids. Daubert, Longenecker and co-workers (*Ibid.* 2142, 2144) synthesized mono-oleo-disaturated and dioleo-monosaturated triglycerides and determined some of their physical properties. Tutiya (*J. Chem. Soc. Japan* 61, 867, 1188; 62, 10) identified parinaric acid in the seed oil of *Impatiens balsamina*, and a highly unsaturated acid of formula $C_{16}H_{24}O_2$ in sardine oil. Baldwin and Parks (*Oil & Soap* 20, 101) found evidence of the presence of a 9-10 and an 11-12 oleic, an octadecatetrenoic, 11-12 eicosenoic and eicosapentenoic acids in menhaden oil. Fractionation was by crystallization and methyl ester distillation.

Heating curves of tristearin and trilaurin were prepared by Ravich (*Compt. rend. acad. sci. U.R.S.S.* 36, 275; 38, 331). The curves demonstrated a thermal effect during changes from one solid form to another. Trilaurin had an additional unexplained thermal effect of small magnitude at 46°.

Several reports concerned the phosphatide constituents of oils. Rewald's data (*Oil & Soap* 20, 212) indicated 0.76, 0.55 and 0.31% for the respective phosphatide content of red currant, raspberry and plum seed oils. Woolley (*J. Biol. Chem.* 147, 581) isolated an inositol-containing phosphatide from soybean phosphatides. Rewald's analyses (*Biochem. J.* 36, 822) indicated that the phosphatides separated from oil seed cakes contained $\frac{1}{3}$ lecithin except for sesame cake, whose lecithin content was greater. Analytical work by Hilditch and Zaky (*Ibid.* 815) indicated differences between the fat acid content of the phosphatides and the corresponding glycerides. The phosphatides contained highly saturated C_{20} and C_{22} acids which were not present in the glycerides: palmitic formed a greater proportion of the saturated acids in the phosphatides than in the glycerides and linoleic was the most characteristic acid of the phosphatides; in the majority of samples it formed 45 to 55% of the total phosphatide fat acids.

Investigation on nonglyceride constituents of fats was fairly active. Bauer and Moll (*Arch. Pharm.* 35, 37) identified *a*- and *b*-amyrin, caritene and parkeol ($C_{30}H_{50}OH$) in the unsaponifiable material of shea nut oil. King *et al.* (*J. Am. Chem. Soc.* 65, 1168) isolated *b*-amyrin from alfalfa seed and leaf oils.

According to Schmidt-Neilson and Artum (*Kgl. Norske Videnskab. Selskabs. Skrifter* 1940, No. 2, 45 pp.) both the unsaponifiable substances and the squalene content were highest in male black shark oils and lowest in fetuses; the data for females were

intermediate. The fat alcohols, selachyl, chimyl and batyl alcohols, were highest in the fats of the female sharks. The authors suggested that it was impossible to arrive at any conclusions as to the physiological role of squalene. Dimter (*Z. physiol. Chem.* 270, 247) suggested that squalene might be a precursor for the synthesis of cholesterol in organs. Kuhn and Gerhard (*Deut. Apoth-Ztg.* 56, 589) obtained 0.46% squalene from raw liver oil and 0.00053% from a distilled product. Fitelson's (*J. Assoc. Off. Agr. Chem.* 26, 506) tabulations on the squalene content of 23 fats ranged from none in cocoa butter to a maximum of .708% in one olive oil. Since it was present in the fats of 15 vegetables and 4 land animals he suggested that the current conception that it occurs only in marine animals fats should be modified.

Progress in the determination of vitamin A in oils concerned refinement of the existing procedures or adapting them for the analyses of particular products or oils (Jones and Haines—*Analyst* 68, 8; Tompkins and Bolomey—*Ind. Eng. Chem. Anal. Ed.* 15, 437; Coy, Sassaman and Black—*Ibid.* 441; Oser, Melnick and Pader—*Ibid.* 717, 724; Gemeinhardt and Jeglinski—*Vitamin u. Hormone* 1, 341; 2, 44). One method for determination of carotene in vegetable oils without saponification was based on adsorption on aluminum oxide and eluting the carotene with 2% acetone in petroleum ether (Bickoff and Williams—*Ind. Eng. Chem. Anal. Ed.* 15, 266). Analytical results on Wisconsin butters indicated that average vitamin A potencies were 10,500 I. U. per pound in January, 9,500 for March and 18,000 for July and September (Berl and Peterson—*J. Nutr.* 26, 527). In summer butters, about 75% of the total natural butter pigment was found to be carotene, in winter butters 60 to 65%. Data on the vitamin D content of fish liver oils by Ewing *et al.* (*Ind. Eng. Chem. Anal. Ed.* 15, 301) were developed by a chromatographic adsorption method. Results were in fairly close agreement with those of the United States Pharmacopoeia procedure for oils ranging upward in potency from 5,000 units per gram.

Several communications described work on detection of specific fats or oils or methods of determining adulteration. A method of approximating the amount of swine fat in beef and mutton fat by Viollier and Iselin (*Mitt. Lebensm. Hyg.* 32, 180, 197), depended on the amount of vaccenic acid in the samples. Vaccenic acid, an isomer of oleic acid, occurs only in relatively small amounts in swine fat. A method of detecting adulteration of animal fat with vegetable fat or vice versa depended on the separation of cholesterol and phytosterols and identifying these (Artun—*Kgl. Norske Videnskab. Selskabs Forh.* 14, 67). Curves showing the relationship between season and refraction of butterfat were prepared by Schloemer (*Z. Untersuch. Lebensm.* 82, 128; 83, 55) as a basis for judging butters. Zeisset and Grossfeld (*Z. Untersuch. Lebensm.* 83, 385) tabulated the physical and chemical characteristics of 169 goat butter samples, for use as a basis for adulteration detection. There appeared to be no significant difference in samples from different breeds. When the Grossfeld equation for determining the amount of coco fat in cow butterfat was applied to the pure goat butterfats it indicated an average apparent coconut oil content of 43%. Fachini and Dorta (*Fette u. Seifen* 48, 547) claimed they could establish the identity of an

olive oil from its refractive index and that the deviation of the ratio of this characteristic with iodine value was a clue to the possible presence of residual or spoiled olive oils. Marcelet (*Chimie & industrie* 45, No. 3, 201) considered the emulsion number a valuable characteristic for identifying various grades of olive oil. Peleni (*Ann. chim. applicata* 32, 189) encouraged work on isolating coloring, fluorescent and luminescent substances from olive oil. Fitelson (*J. Assoc. Off. Agr. Chem.* 26, 499) proposed determining the squalene content of oils as means of detecting olive oil in edible oil mixtures. Vorhies and Bauer (*Oil & Soap* 20, 175) evaluated several new procedures proposed for determining peanut oil. The basis of the tests, *i.e.*, separation of arachidic acid, was not quantitatively accurate for peanut oil in vegetable oils. The best results for mixtures of peanut and soybean oils were obtained by the American Oil Chemists' Society method. Argemone oil, a toxic oil, could be identified in food oil mixtures by the formation of an orange-red precipitate on treatment with ferric chloride in the presence of strong hydrochloric acid and ethanol (Sarkar—*Ann. Biochem. Exptl. Med.* 1, 271).

Additional activity on characteristics and analysis of fats and oils was displayed in committee reports of fat and oil organizations. The standards of specifications among these were on olive oil for the Norwegian food-preservation industry (Mathiesen—*Seifensieder-Ztg.* 68, 376) and the American Oil Chemists' Society standards for palm kernel, sunflower, coconut and palm oils (Lauro—*Oil & Soap* 20, 163). Other American Oil Chemists' Society Committee reports which contain results of research work on methods were on uniform methods planning (Vollertsen—*Ibid.* 35, 214), on color (Agee—*Ibid.* 162; Mehlenbacher—*Ibid.* 226) and on refining of soybean oil (Mitchell—*Ibid.* 179). Portugal's official methods for analysis of fats were translated into English (*Oil & Colour Trades J.* 104, 130). The principal methods for analysis of all types of fats were made available in Canadian literature by Schierhaltz (*Can. Chem. Process Ind.* 26, 725; 27, 42).

Detergents

A meager supply of technical fats was responsible for the interest displayed in the use of rosin in soap. Experiments at the Hercules Powder Co. (Mayfield—*Soap* 19, No. 4, 21; Van Antwerpen—*Chem. Eng. News* 21, 376; Farquhar—*Chem. & Met. Eng.* 50, No. 4, 108) showed that up to 15% rosin could be used in powdered soap, and that bar soap containing 3% rosin compared favorably in appearance with commercial rosin-free soaps. The advantages listed for rosin as soap stock were: low price, availability, good detergent action, rapid and lasting suds, reduction of dusting in powdered soap and suitability for all types of soap. Its disadvantages were: low titer, tendency to darken, higher unsaponifiable and absence of glycerol. Borglin *et al.* (*Oil & Soap* 20, 77) using a "Launder-Ometer" detergency test method found that, over the range of rosin concentrations normally used, the rosins maintained the high detergent action and enhanced this property in the base soap. "Staybelite," an hydrogenated rosin, in a white high-titer tallow soap improved the detergent action in both hard and soft water, while regular rosin had no effect. Soap products from oxidized

paraffin hydrocarbon stock were rendered non-sticky and capable of yielding a powdered product by treating aqueous solutions of the soaps with adsorbent earths (Lauer and Gärtner—*Ger.* 719,539 Cl. 23d).

Developments of soap builders and substitutes concerned means of incorporating builders, improvements in the products and a few new soap stretching agents. Patents assigned to I. G. Farbenindustrie A-G. (*Ger.* 720,776 Cl. 8i; 720,945 Cl. 22g) claimed the use of water-free metasilicate containing 10-15% free caustic as a builder for powdered soap and described a procedure for incorporating these in spray dried soaps. Bergell (*Ger.* 700,226 Cl. 23e) saponified fats with concentrated metasilicate solution. Schwartz (*U. S.* 2,303,397-400) added barium, strontium, mercuric, antimony or lead salts to detergents containing alkali silicates and intended for metal cleaning. The salts were for the purpose of inhibiting corrosion. Specially prepared mixtures of alkali silicates and phosphates for dry detergents were patented by Robinson (*U. S.* 2,333,443-4). Patents on methods of incorporating metaphosphates in soaps were assigned to I. G. Farbenindustrie (*Ger.* 725,820 Cl. 8i). Other fillers appearing in patents were water-soluble ethers of cellulose (Sponsel—*Ger.* 712,561, Cl. 23e), miscellaneous builders with alkali salts of high molecular weight polymers (Gröner and Trommsdorff—*Ger.* 719,348, Cl. 23e), gelatine, agar-agar and dextrin (Walsh and Newman—*Brit.* 551,369), cellulose, starch and other carbohydrates (Nüsslein and Pauser—*U. S.* 2,335,194) and ester products of haloacetic acids and alkali-treated wood (Jahrstorfer and Kling—*Ger.* 720,589 Cl. 23e). "Mersol" and "Mersol" sulfonates were promoted in Axis literature as substitutes for soap, but none of the available abstracts of this literature published the composition or source of the products (Thomas—*Seifensieder-Ztg.* 69, 22; Widaly—*Ibid.* 106, 130). An abrasive detergent patented by Ruthruff (*U. S.* 2,318,555) was small silica particles coated with sodium silicates.

Bactericides in new germicidal soaps included halogenated phenol (Endres—*U. S.* 2,326,933), 2,2-dihydroxy halogenated diphenyl methane (Kunz and Gump—*Brit.* 545,648) and aromatic chlorosulfonamide crystals coated with mineral oil (Smith—*U. S.* 2,296,121). A colored detergent composition contained trisodium phosphate, sodium hypochlorite and a small amount of metal permanganate (Hull—*Can.* 408,243). The active ingredients of a new soap which indicates the presence of mercury fulminate were triethanolamine and diphenylthiocarbozone (Mason and Botvinick—*U. S. Pub. Health Repts.* 58, 1183). This soap was useful for aiding in reduction of mercury fulminate dermatitis in the explosive industry. In presence of traces of mercury salts the soap changes from orange to purple. Andersen (*U. S.* 2,324,347-8) perfumed soap with a mixture of perfume and antioxidants. This step was said to preserve the original character of the perfume. Foulon (*Allgem. Oel- u. Fett-Ztg.* 38, 441) remedied the ill effect of certain aldehyde and ester perfumes on the stability of soap by adding zinc white.

Two letters patents on the mechanical phase of soap making described improvements in equipment layout and procedures for the Sharples Corp. (*U. S.* 2,335,457, 2,336,893) system. A double saponification system by Stiepel (*Ger.* 710,952 Cl. 23e) made use of alkali carbonates for the first saponification and alkali

hydroxides for the second. The same inventor (*Ger. 708,437, Cl. 23e*) also patented a soap making process in which the fats were first chlorinated and saponification was conducted until total or partial splitting of the chlorine occurred. Soap was recovered from soap nigre containing excess alkali by saponifying the alkali with fat acids and then removing the insoluble impurities (Sander and Wilson—*U. S. 2,321,947*). Refinery-foots containing excess alkali was converted into good soap by adding saponifiable material, heating to break down odoriferous substances and deodorizing with superheated steam (Clayton—*U. S. 2,327,502*). Scherl (*Ger. 709611 Cl. 23e*) recovered curd-soap waste by melting it into liquid curd soap.

A creamy lather which was said to give a thick, fine-bubbled lather was made by passing nitric oxide through a soap solution for as long as it was absorbed (Peter—*Ger. 711,633 Cl. 23e*). Heald and Schulerud (*U. S. 2,316,689*) manufactured a bar soap containing an unusually large amount of builder, which was suitable for the grinding type of dispensers. The dry soap was mixed with 25 to 55% borax, milled and plodded into bars.

A soap spray drying apparatus was designed particularly for the production of soaps containing per-compounds such as sodium perborate (Mertens—*U. S. 2,308,992*). A rotating-disk atomizer for soap drying equipment was described by (Buhler—*Seifensieder-Ztg. 69, 90*). Joyce and Lindhardt (*U. S. 2,332,727*) produced a powdered soap by introducing soap with 6-30% moisture content and at a temperature of about 260°F. into a vessel and rolling heavy rollers on it while it cooled. The hardened soap was broken into fine particles. A newly invented plodder contained agitators and special devices which expelled the soap under uniform pressure (Pease—*U. S. 2,335,306*). Bodman and Pease (*U. S. 2,310,931*) manufactured soap bars containing weakened zones so as to facilitate splitting the bars. Two methods of de-dusting powdered soap appeared, one (Maxwell and Atwood—*U. S. 2,328,568*) concerned equipment for blowing out objectionable fine particles and the other (Bodman—*U. S. 2,329,694*) superficially coated the soap particles with polymerized ethylene glycol.

Publications on soap defects treated stability of the product. A treatise by Simmons (*Soap, Perfumery, Cosmetics 16, 157*) on spontaneous heating and charring of powdered or milled soap attributed the condition to the oxidative decomposition of the soap. The remedies considered were selection of good quality raw material, protection against oxidation-accelerating influences and inclusion of antioxidants. Zajev (*Seifensieder Ztg. 67, 142*) studied the effect of iron and copper salts on the stability of soaps. Soap boiled with 0.001% ferric oxide or copper oxide became rancid in 4 weeks. Other data showed the darkening effect of small amounts of iron impurities.

The following communications were of general nature, giving reviews, discussions, formulas, etc., and were most conveniently included in this review in the form of classified listing. The communications of historical type were on:

Surface active agents. Snell—*Ind. Eng. Chem. 35, 107*.

Wiesbaden and Roman soap balls. Fritz—*Seifensieder-Ztg. 69, 5*.

Synthetic detergents. Sunde—*Soap 19, No. 7, 30*.

Application of soap in paper making. Leffingwell and Radin—*Paper Ind. Paper World 24, 1035*.

The following references contained manufacturing instructions:

Plant layout. Downie—*Mfg. Chemist 14, 12*.

Soap factory equipment. Weir—*Soap, Perfumery, Cosmetics 15, 378, 422, 549, 659*.

Manufacture of cold process soap in Ceylon. Child—*Ibid. 16, 457*.

Army's G. I. soap. *Soap 19, No. 1, 28*.

Fat acid soap process. Treffler—*Ibid. No. 9, 32*.

Fat acids for soap. Reimold—*Can. Chem. Process Inds. 26, 632*.

German standard soap. Braun—*Deut. Pärfum-Ztg. 27, 271*.

Floating soaps. Widaly—*Seifensieder-Ztg. 69, 55*.

Potassium and sodium soap. Lindner—*Wäscheri-Ber. 9, 197*.

Hand cleansers. Davidsohn and Davidsohn—*Soap, Perfumery, Cosmetics 15, 382*.

Abrasive hand soaps. Editorial—*Soap 19, No. 3, 28*.

Abrasive cleaners. Editorial—*Ibid. No. 4, 30*.

Following three references are on soap stretchers:

Saponines as washing agents. Kind—*Fette u. Seifen 49, 708*.

Proteins for soap making. Wittka—*Allgem. Oel-u. Fett-Ztg. 38, 309*

Soap builders. Foulon—*Ibid. 37, 307*.

Some general communications discussed the mechanism of detergency and the characteristics of detergents:

Detergent power, formation and mode of action of the foam. Leimdörfer—*Seifensieder-Ztg. 68, 437, 462, 474, 487, 499, 512, 526, 543*.

Definitions, physical tests, etc., for detergents. Fischer—*Soap 19, No. 12, 28*.

Detergency. Snell—*Paper Trade J. 116, No. 7, 128*.

Body-cleansing. Hebestreit—*Fette u. Seifen 48, 491*.

Soap. Leffingwell—*Chem. Industries 52, 337*.

Naphthenic acid soaps. Renoldi—*Laniera 55, 527*.

The publications on synthetic detergents contained listings, descriptions and uses:

Commercially available surface active agents. Van Antwerpen—*Ind. Eng. Chem. 35, 126*.

"Santomerse" or dodecylbenzene sodium sulfonate. Harris—*Soap 19, No. 8, 21. Am. Soc. Testing Material Bull. 125, 25*.

Characteristics of some common non-soap detergents. Snell—*Soap 19, No. 10, 27; No. 11, 31*.

Salt-water soap. Ruckman *et al.*—*Ibid. No. 1, 21*.

Pigment dispersion with surface active agents. Fischler and Jerome—*Ind. Eng. Chem. 35, 336*.

Sulphonated fish oils. Application to fat liquoring of chrome leather. Das *et al.*—*J. Internatl. Soc. Leather Trades Chem. 27, 217*.

Textile assistants. Fischer—*Färber u. Chemisch-rieger 1942, 51*.

Acid soaps from petroleum products. Profft—*Fette u. Seifen 49, 868; van An del—Chem. Weekblad 39, 314*.

Some general communications treated the uses and selection of soaps:

Soap in the rubber program. Leffingwell and Radin—*Rubber Age* (N. Y.) 52, 235.

Detergents for the dairy industry. Parker—*Food Industries* 15, No. 9, 66; Minor—*Southern Dairy Products J.* 32, No. 5, 22.

Wetting agents in food processing. Mitchell—*Food Industries* 15, No. 7, 81; Feinberg—*Ibid.* No. 1, 61.

Wetting agents for cleaning hog hair. Mitchell—*Natl. Provisioner* 109, No. 10, 23.

The dermatitis producing effect of various soaps was studied. Schnorr (*Arch. Gewerbepath. Gewerbehyg.* 10, 409) listed skin cleansers which raised the normal pH of the skin and those which did not. Those producing a final rise in pH after an intermediate fall were suitable for all but sensitive skins. Those producing an uninterrupted rise such as highly basic pumice soaps should be used only occasionally. In a continuation of this work by Schnitzler (*Ibid.* 422) it was demonstrated that increasing the alkalinity of the skin resulted in removal or emulsification of cutaneous lipoids, and caused swelling of the horn cells, with closing of follicles and inclusion of foreign particles and bacteria. According to Kooymann and Synder (*Arch. Dermatol. Syphilol.* 46, 846) the irritating and sensitizing effects of soaps can be measured by patch and arm immersion tests.

Miller *et al.* (*Proc. Soc. Exptl. Biol. Med.* 54, 174) reported that some cation soaps deposited an invisible film on the hands. This film retained bacteria underneath it and was very resistant to mechanical injury. Such films have low bactericidal power on the inner surface and a strong germicidal action on the outer surface. Valette and Liber (*Compt. rend. soc. biol.* 135, 851) believed that the antiseptic action of soaps depended upon the degree of hydrolysis. According to Ordal and Deromedi (*J. Bact.* 45, 293) two synthetic detergents, lauryl sulfonate and dioctyl ester of sodium sulfosuccinate, enhanced the germicidal action of some phenolic compounds. The use of synthetic detergents in hypochlorite sterilizing solution was patented (Kalusdian—*U. S.* 2,320,280). Stock and Francis (*J. Exptl. Med.* 77, 323) determined the effectiveness of soaps in inactivating one virus strain. Aerosol OT, duponols PC & La, zephiran, chaulmoogric, linolenic, linoleic, myristic, oleic and ricinoleic acids were effective in 0.001 mole concentrations. Aerosol MA, laurylsulfuric, palmitic and undecylenic acids were effective in concentrations of 0.01 mole but not at 0.001 mole. Epstein *et al.* (*Oil & Soap* 20, 171; *Proc. Soc. Exptl. Biol. Med.* 53, 238) demonstrated that among a number of homologs of quaternary ammonium derivatives the C₁₄ homolog had the highest bactericidal activity. Wright (*Soap* 9, No. 8, 31) discussed and illustrated diagrammatically the amounts of bacteria destroyed in various commercial laundry steps. Similar information was prepared by Walter (*Wascherei-Ber.* 9, 183), who also recommended addition of active oxygen compounds in white laundering because the soap and the temperatures used in common practice are of low bactericidal action.

Ferguson *et al.* (*Ind. Eng. Chem.* 35, 1005) and McBain and Lee (*Ibid.* 917; *Oil & Soap* 20, 17) discussed the phase transformations that occur during

soap processing. Vapor pressure measurements indicating the important soap phases were graphically represented. New data on this subject recorded the x-ray diffraction patterns of pure lauric and palmitic acid soaps obtained at temperatures from 25° to 155°C. (McBain *et al.*—*J. Phys. Chem.* 47, 528; *J. Am. Chem. Soc.* 65, 1873). Galloway and Puddington (*Can. J. Res.* 21B, 202, 211) showed that the phase behavior of soaps was unaffected by nonpolar inert diluents. Density-temperature relationship, melting point and cooling curves of sodium stearate and sodium oleate were the data recorded in these communications.

The phase behavior of several sodium and potassium soaps with water and electrolytes were illustrated in many charts by McBain *et al.* (*Oil & Soap* 20, 221). The data showed the effect of small amounts of salts such as are retained in commercial soap systems upon the boundaries of the strict binary phase diagram. Similar data on lithium palmitate with water and with lithium chloride and water were developed by Vold (*J. Am. Chem. Soc.* 65, 465). Water sorption curves prepared by McBain and Lee (*Ind. Eng. Chem.* 35, 784) demonstrated that anhydrous soap takes up 1 or 2% water according to physical sorption mechanism. Except for sodium oleate, the curd or super-curd phases then suddenly form hemihydrate, which again takes up water until another phase forms. At low humidity the higher hydrates revert to hemihydrates. Similar investigations by Buerger *et al.* (*Proc. Natl. Acad. Sci. U. S.* 28, 526, 529) yielded indications that alpha, beta, and gamma forms of sodium stearate contained respectively, 1/2, 1/8 and 0 moles of water per mole of soap.

Physical and chemical measurements on soap solutions are always useful as a basis for manufacturing procedures or selection of soaps fitted for specific needs. Some of the newly recorded information included the surface tension of solutions of certain sodium soaps (Cavier—*Compt. rend.* 212, 1146), interfacial tensions of sodium laurate solutions with heptane (Davis and Bartell—*J. Phys. Chem.* 47, 40), effect of sodium hydroxide on the solubility of soap (Snell *et al.*—*Soap* 19, No. 11, 63), freezing points of solutions of soaps, sulfonates, sulfates, and bile salts (Johnston and McBain—*Proc. Roy. Soc. London A* 181, 119) and the pH of detergents and soap builders at 25°, 40° and 60°C.

In investigations on detergency tests, new soiling compounds and methods were devised and standard procedures for testing different types of fabrics were submitted (Crowe—*Am. Dyestuff Repr.* 32, 237; Holland and Pertrea—*Ibid.* 537; van Zile—*Oil & Soap* 20, 55). Determinations of the detergent action of soap builders by Vaughn and Vittone (*Ind. Eng. Chem.* 35, 1094) gave the following decreasing order of effectiveness: a proprietary product containing alkali silicate and carbonate; a proprietary product containing alkali silicate, carbonate and pyrophosphate; modified soda; sodium bicarbonate; sodium silicate; a builder containing alkali silicate and pyrophosphate; sodium carbonate and sodium hydroxide.

Foaming tests are often applied to soap solutions. A new procedure comprised causing standardized quantities of a liquid to fall in successive volumetric additions from a definite height into a pool of liquid to be tested in a special container which was supplied with a means for measuring the foam formed (Ross

and De Wayne—*U. S.* 2,315,983). A review of the methods for measuring foam was prepared by Ross (*Ind. Eng. Chem. Anal. Ed.* 15, 320) and he recorded (*J. Phys. Chem.* 47, 266) the foam stability data of "Aerosol OT" and laurylsulfonic acid as determined with a Stiepel-type apparatus. Miles and Ross (*Ind. Eng. Chem.* 35, 1221) attributed the decrease in foaming and detergent properties of mixtures of sulfated detergents, soap and calcium salts to the formation of complex salts of calcium with fat acids and the synthetic detergent.

Sufficiently accurate fat acid determinations in soaps were possible in 10-15 minutes after weighing by a method described by Schroder (*Kem. Maanedssblad* 21, 159). The sample of soap was treated with excess 4 *N* sulfuric acid, 20 cc. of alcohol were added and the solution was titrated electrometrically with 0.5 *N* caustic to a definite pH and the titration continued to a second pH value. The difference between the 2 readings corresponded to the caustic consumed by the fat acids. A refractometric procedure for analyzing soap for fat acids was published by Steichen (*Seifensieder-Ztg.* 67, 283). The fact that in the determination of iodine value of fats, half the iodine used adds to the fat while the other half forms hydrogen hypoiodite and in the presence of resin acids the added iodine also splits off, formed the basis of a rosin determination without weighing (Ruziczka—*Chem.-Ztg.* 66, 344). Factors utilized for calculating the rosin present have been developed from tests.

A new method for determination of bicarbonates in soaps depended on removing the alcohol insoluble material and determining the carbon dioxide content on a dried sample of the residue and on a sample of the residue after ignition at 260°C. (Blank and Boggie—*Oil & Soap* 20, 125). The percent carbon dioxide in the alcohol insoluble before ignition minus the percent carbon dioxide after ignition times 3.8184 was equal to the sodium bicarbonate in the alcohol insoluble. For determining hydrocarbons in soap products, Van Zile *et al.* (*Oil & Soap* 20, 13) devised two types of distillate traps, one for determining volatile hydrocarbons lighter than water and the second for those heavier than water.

The "American Society for Testing Materials" methods of analysis and tentative specifications for soap were published (Trevithick—*Proc. Am. Soc. Testing Materials Preprint No.* 70, 7 pp.). Lucentini and Picozzi (*Ann. Chem. Applicata* 32, 163) devised analytical methods for the analysis of Italian war soap, which contains insoluble mineral matter, builders and rosin acids as stretchers.

Unusual new uses for non-soap type detergents were for the wetting and loosening of wall paper (Wassell—*U. S.* 2,317,505), for washing and delimiting of limed hides (Bertsch *et al.*—*U. S.* 2,318,454) and for the treatment of fish to remove objectionable odor (Chemische Fabrik. Stockhausen & Cie.—*Ger.* 722,429-30 *Cl.* 53g).

The patents on non-soap type detergents and methods for their manufacture are listed with only a slight attempt to classify them.

Those on sulfonated compounds derived from fats were:

- Allied Chem. & Dye Corp.—*U. S.* 2,316,194, 2,326,772, 2,327,182, 2,333,830.
Am. Cyanamid Co.—2,296,767.

Böhme Fettchemie-G.m.b.H.—*Ger.* 709,088 *Cl.* 8o.

Chemische Fabrik. Stockhausen & Cie.—*Ger.* 721,991 *Cl.* 12o.

Colgate-Palmolive-Peet Co.—*U. S.* 2,290,583, 2,307,953, 2,307,995, 2,321,020, 2,325,320.

Deutsche Hydrierwerke A.-G.—*Ger.* 706,122 *Cl.* 8o.

E. I. du Pont de Nemours & Co.—*U. S.* 2,308,841.

General Aniline & Film Corp.—*U. S.* 2,315,375.

I. G. Farbenind. A.-G.—*Ger.* 710,169 *Cl.* 8i, 712,372 *Cl.* 8i, 721,809 *Cl.* 8o.

Lever Bros. & Lever Ltd.—*Brit.* 547,688.

Ottokar Linhart & Co.—*Ger.* 724,117.

Mathieson Alkali Works, Inc.—*U. S.* 2,320,279.

National Oil Products Co.—*U. S.* 2,328,931, 2,336,166.

Palmolive Binder & Ketels G.m.b.H.—*Ger.* 709,276 *Cl.* 12o.

Shell Development Co.—*Can.* 409,249.

Solvay Process Co.—*U. S.* 2,290,167, 2,313,719.

Many amino, amide and quaternary ammonia derivatives of fat acids were patented for detergent purposes:

Alrose Chem. Co.—*U. S.* 2,334,852.

Am. Cyanamid Co.—*U. S.* 2,293,027, 2,310,045.

Böhme Fettchemie-G.m.b.H.—*Ger.* 708,428 *Cl.* 12o.

Chemische Fabrik. J. Benckiser G.m.b.H.—*Ger.* 719,734 *Cl.* 23e.

Com. Solvents Corp.—*U. S.* 2,320,707.

E. I. du Pont de Nemours & Co.—*U. S.* 2,313,741.

Emulsol Corp.—*U. S.* 2,290,880-1, 2,328,021.

J. R. Geigy A.-G.—*U. S.* 2,315,765.

General Aniline & Film Corp.—*U. S.* 2,296,225, 2,312,135, 2,313,573.

I. G. Farbenind A.-G.—*Ger.* 719,817 *Cl.* 12q.

Montclair Research Corp.—*U. S.* 2,333,623.

National Oil Products Co.—*Brit.* 547,189.

Ninol Development Co.—*U. S.* 2,325,062.

Petrolite Corp. Ltd.—*U. S.* 2,293,494.

Procter & Gamble Co.—*U. S.* 2,334,517.

Roche Products Ltd.—*Brit.* 547,057.

Unichem. Chemikalien Handels A.-G.—*U. S.* 2,310,109.

Venkataraman *et al.*—*Brit.* 545,496.

Winthrop Chem. Co.—*U. S.* 2,317,999.

Some detergents contained a fat acid radical, a nitrogen radical (amine, amide, etc.) and a sulfate radical:

Alien Property Custodian—*U. S.* 2,332,906.

Am. Cyanamid Co.—*U. S.* 2,322,202.

Böhme Fettchemie-G.m.b.H.—*Ger.* 710,680 *Cl.* 12s.

Celanese Corp.—*U. S.* 2,323,980.

Emulsol Corp.—*U. S.* 2,307,047.

General Aniline & Film Corp.—*U. S.* 2,313,695.

J. R. Geigy A.-G.—*U. S.* 2,312,395; *Brit.* 547,569.

National Oil Products Co.—*U. S.* 2,329,086.

Solvay Process Co.—*U. S.* 2,324,199.

Some organic detergents were derived from non-fat sources. Most of these were petroleum derivatives usually sulfonated; however, some contained nitrogen radicals and a few were special esters of petroleum or coal by-product hydrocarbons:

- Allied Chemical & Dye Corp.—*U. S.* 2,291,778, 2,314,255, 2,314,929, 2,317,986, 2,330,922, 2,334,500.

- Am. Hyalsol Corp.—*U. S.* 2,288,181.
 Am. Cyanamid Co.—*U. S.* 2,314,846.
 E. I. du Pont de Nemours & Co.—*U. S.* 2,318,036, 2,321,890, 2,334,764.
 J. R. Geigy A.-G.—*U. S.* 2,328,159; *Swiss* 211,789 *Cl.* 36a.
 Harvel Corp.—*U. S.* 2,324,300.
 Kalle & Co. A.-G.—*Ger.* 721,719 *Cl.* 8i.
 Märkische Seifen-Industrie—*Ger.* 722,591 *Cl.* 12o.
 Röhm & Haas Co.—*U. S.* 2,313,621.
 Solvay Process Co.—*U. S.* 2,336,387.
 Sonneborn Sons, Inc.—*U. S.* 2,308,743.
 Standard Oil Development Co.—*U. S.* 2,314,450.
 Standard Oil Co.—*U. S.* 2,334,532.
 Unichem. Chemikalien Handels A.-G.—*U. S.* 2,288,702.

During the year very little was published on glycerol. Weir (*Soap, Perfumery, Cosmetics* 16, 40, 92) described equipment and procedures for recovery

of glycerol in a small scale plant. A recently patented still was described (Ittner—*Ger.* 722,956 *Cl.* 23e). Mattikow and Cohen (*Oil & Soap* 20, 135) found a 4% destruction of glycerol during a 7-minute period at 550°F. for each per cent of sodium hydroxide present; the rate of destruction was doubled for a 25°F. rise in temperature. Raecke and Wolter (*Ger.* 722,407 *Cl.* 12o) recovered di- and polyglycerol from glycerol pitch by esterifying with C₄-C₉ fatty acids and refined these water-insoluble esters by washing with water. The di- and polyglycerols were then freed by splitting. A fermentation process for the manufacture of glycerol from molasses was patented by Hildebrandt (*U. S.* 2,315,422-3).

The analytical activities on glycerol were the development of an evaporation method suitable for control analysis of soap lyes (Gowan—*Ind. Eng. Chem. Anal. Ed.* 15, 260) and a publication giving experiences which indicated that the pyridine acetylation method for determining glycerol was as accurate as the dichromate oxidation method.

A. O. C. S. Refining Committee Meeting

Palmer House * Chicago, Illinois

October 5, 1943

Present at the meeting: Members—Mr. G. W. Agee (alternate for Mr. E. R. Barrow), Mr. M. M. Durkee, Dr. E. B. Freyer, Mr. E. M. James, Mr. Arthur Kiess, Mr. R. R. King, Mr. Lamar Kishlar, Mr. N. F. Kruse, Dr. R. T. Milner, Mr. H. S. Mitchell (Chairman), Mr. H. E. Moore, Mr. J. H. Sanders (alternate for Mr. C. B. Cluff), Mr. H. T. Spannuth (alternate for Mr. G. A. Crapple). Visitors—Mr. R. E. Bass, Mr. R. J. Houle, Mr. H. F. Ory, Mr. S. J. Rini (Acting Secretary), Mr. N. W. Ziels.

The meeting was called to order by Chairman Mitchell, who then read the resolutions passed by the Committee at the previous meeting and excerpts from the minority report of the Task Committee appointed by OPA covering the reproducibility of the methods for expeller, hydraulic, and extracted oils.

Dr. Milner presented a report on the reproducibility of the A.O.C.S. refining methods which was, in part, as follows:

Since the July 7-8 meeting, six additional oils from Mr. James have been studied both at Hammond and the Northern Regional Research Laboratory. A comparison of results from the two laboratories on all thirteen oils of this series are given in Table I. The agreement between the two laboratories is excellent on the average, with average deviations between laboratories of .23 and .34 percent for maximum and 2/3 maximum, respectively. Three other oils (hydraulic) were refined by both the Northern Regional Research Laboratory and Procter and Gamble, using both hydraulic and expeller procedures. The results are shown in Table II. Three oils are too few to draw significant conclusions, and it can only be noted that the average difference between laboratories is rather large considering both hydraulic and expeller pro-

cedures, but is much smaller (.43 and .23 percent) for the expeller procedure alone.

Table III shows the collected results from 15 samples (five for three years) as determined by official chemists and collaborators for the Referee Committee of The American Oil Chemists' Society. Twelve of these soybean oil samples were expeller type, two hydraulic, and one was extracted. The average values and standard deviations are shown for each sample and an average of these values for all expeller samples calculated. It is apparent that two of these expeller oils caused great difficulty in the refining tests and the average of the standard deviations are markedly different if these two samples are omitted. However, the results for all twelve oils confirm again that the refining test on expeller oils has given reproducible results.

Over the past six years, results on 15 collaborative samples have been published by the Refining Committee, 7 of which were expeller oils, 7 extracted, and 1 hydraulic. The standard deviations have been calculated for each sample in two ways (Table IV). Averages and standard deviations were calculated first for all collaborators reporting, and then recalculated for a "select" group, omitting from 1 to 3 in cases in which obvious errors in procedure, strength of alkali used, or calculation of alkali, had been made. It is apparent on examining the averages of the standard deviations that the select group were in much better agreement, and, as in Table III, the average of the standard deviations for expeller oils (for the select group) is about .4. It is believed that further collaborative samples of expeller or extracted oils, run by the same methods, would give the same results.