

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

REPORT OF THE LITERATURE REVIEW COMMITTEE*

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

Physiology and Biochemistry

REVIEWS. The general discussion and review communications concerning the text of this division are on the following subjects: fat metabolism (Frazer—*Ann. Rev. Biochem.* 21, 245), interrelations of lipide and carbohydrate metabolism (Block—*Ibid.* 273), chemistry and metabolism of the steroids (Samuels & Reich—*Ibid.* 129), biological oxidations (Chance & Smith—*Ibid.* 687), fat soluble vitamins (Kemmerer—*Ibid.* 333), evolution of animal fats (Shorland—*Nature* 170, 924), the essential fatty acids (Kaufmann—*Fette u. Seifen* 54, 69; Lang—*Ibid.* 53, 731; Finzi—*Policlinico (Rome) Sez. med.* 58, 285, 408, 416), lipotropic action of polyunsaturated acids (Schulintz—*Pharmazie* 7, 9), value of synthetic fats in nutrition (Scheunert—*Ibid.* 6, 652), chemistry of phosphatides and cerebrosides (Celmer & Carter—*Physiol. Revs.* 32, 167), metabolism of fat in the mammary gland and foetal tissue (Popjak—*Nutr. Abs. & Revs.* 21, 535), synthesis of fat from small molecules (Popjak—*Brit. Med. Bull.* 8, 218), and diet and lipotropic agents in arteriosclerosis (Gofman—*Bull. N. Y. Acad. Med.* 28, 279). A group of seven lectures given at a symposium on lipide metabolism is abstracted in the supplement pages of the second issue of *Biochemical Journal*, volume 51. These contain general information on intestinal absorption, defective absorption, body fat synthesis, milk fat synthesis, oxidation, and essential fatty acids.

FAT NUTRITION. The problems on fats studied by nutritionists pertain to desirability in the diet, amount compatible with good nutrition, essential fatty acids, nutritive value, and relation to other dietary constituents. Nutritive value studies on the effect of proportion of fat in diets indicate that for rats diets containing 5-8% fat (Hoagland *et al.*—*J. Nutr.* 47, 399) and for dogs diets of 4-8% fat (Siedler & Schweigert—*Ibid.* 48, 81) no significant differences in food or caloric efficiencies are evident. Similar work with mice shows a better efficiency of food utilization (growth) with certain strains but not in all strains of the test mice (Fenton & Carr—*Ibid.* 45, 225). On high (23%) fat diets female rats produce smaller number of lighter weight young than at moderate levels of fat intake (Fench *et al.*—*Ibid.* 48, 91). The high-fat diet does not impair lactation; but lactation on the diet may be improved by adding carbohydrates, particularly sucrose. Tests by Venkatasubramanian & De (*Indian J. Physiol. and Allied Sci.* 6, 24) show that rats fed solely on peanut oil survive longer than rats fed solely on various carbohydrates; however, survival is considerably longer on mixtures of the oil with carbohydrates. Either feeding of fat or sugar alone increases coagulability of blood; but when sugar is fed with fat, the clotting time does not decrease as much as when the fat is fed alone (Waldron *et al.*—*J. Applied Physiol.* 4, 761).

The protein sparing action of dietary fat is demonstrated by Fox & Swanson (*Federation Proc.* 11, 442) by means of studies on protein-depleted rats. A similar technique is used to show that high-fat diets reduce vitamin B₁ requirements of rats (Balakrishnan & De—*Indian J. Physiol. and Allied Sci.* 6, 1). In reducing diet tests, clinical syndromes develop under restricted fat intake, whereas reducing diets containing fat may cause only a slight drop in serum lipide levels (Pomeranze—*Bull. N. Y. Acad. Med.* 28, 611). In other weight reducing tests with moderate fat diet the cholesterol and lipide values of the plasma at the end of an eight and a half week reducing period are within normal limits (Young—*J. Am. Dietet. Assoc.* 28, 410, 529).

Rats utilize dietary calcium better with a diet containing 20% lard than when cocoa butter is the fat (Beadles *et al.*—*J. Nutr.* 45, 399). The inhibiting effect on calcium utilization in this work is accounted for by greater formation of insoluble calcium soaps. Among rats treated with sublethal doses of X-irradiation at weekly intervals, those receiving fat in their diet are more resistant and survive longer than those on fat-free regimen (Cheng *et al.*—*Ibid.* 48, 161).

The new work on the so-called essential fatty acids concerns nutrition and effect of other dietary material on its action. Greenberg *et al.* (*J. Nutr.* 45, 521, 535) record data on the potency of fatty acids to alleviate deficiency symptoms, their re-

quirements for rats and their distribution in food fats. Methyl arachidonate is three and a half times more biopotent than the linoleate. When the pure compounds are compared with natural oils for curing essential fatty acid deficiency, weight gain by rats is greater with the oils. The essential fatty acids content of margarine is higher than that of butter. Incidentally, in this work it is observed that highest efficiency of food utilization (growth) occurs on a 30% fat diet. Rats on diets deficient in fat to the point where reproduction is affected show deficiency in the essential fatty acids but not in fat *per se* (Kummerow *et al.*—*J. Nutr.* 46, 489). Essential fatty acids deficiency symptoms on low-fat diet are brought about in rats more rapidly by addition of mineral oil to the diets at levels over five percent (Bacon *et al.*—*Ibid.* 47, 383). Sensitivity to essential fatty acids deficiency has been observed to differ among different strains of mice (Cerecedo *et al.*—*Ibid.* 48, 41). Among deficiency symptoms of essential fatty acids, growth and fat synthesis are stimulated at a greater rate when pyridoxine is administered with a linoleate; but dermal symptoms are not relieved at a more rapid rate under these conditions (Witten & Holman—*Arch. Biochem. & Biophys.* 41, 266). In other tests, no relation between linoleate and vitamin E requirements could be demonstrated (Anisfeld *et al.*—*J. Nutr.* 45, 599; Dam *et al.*—*Acta Path. Microbiol. Scand.* 31, 172). Methyl linoleate and cottonseed oil administration protect immature rats against growth retardation when the rat is fed a fat-free, sucrose-casein diet to which thyroid has been added (Greenberg—*J. Nutr.* 47, 31). Marked reduction in prostate and seminal vesicle weight is recently recorded as another symptom of essen-

TABLE OF CONTENTS

- A. INTRODUCTION
Statistics, outlook, substitutes, microbiological fats and oils, new comprehensive literature.
- B. PRODUCTION PROCESSING
Animal fats, fish oils, vegetable oils, by-product oils, refining, bleaching, deodorization, natural alcohols, phosphatides, vitamins, sterols, winterizing, splitting, fractionation, hydrogenation, esterification, interesterification.
- C. FATTY PRODUCTS (except detergents)
Household fats, emulsifiers, demulsifiers, fatty esters, acids, ketones, nitrogen-containing derivatives, hydrocarbons, flotation agents, core binding, drilling fluids, protective coatings, resins, plastics, heavy metal soaps, lubricants.
- D. DETERIORATION
Reviews, tests, mechanism, factors affecting stability, flavor reversion, microbiology and fat deterioration.
- E. PHYSIOLOGY AND BIOCHEMISTRY
Reviews, fat nutrition, absorption, intermediate metabolism, cholesterol metabolism, lipides under diseased conditions, microbiology and lipides.
- F. CHARACTERISTICS AND COMPOSITION
General and comprehensive, fat sources, evaluation tests, chemical characteristics, detection of adulteration, physical characteristics, composition.
- G. DETERGENTS
Manufacture, constituent analyses, physical properties, performance tests.

*LITERATURE REVIEW COMMITTEE

E. W. BLANK
J. B. BROWN
E. A. GASTROCK
M. M. PISKUR,
Chairman

tial fatty acids deficiency (Greenberg & Ershoff—*Proc. Soc. Exptl. Biol. & Med.* 78, 552).

When a prooxidant is fed with a linoleate, conversion to hexaenate is greatly increased (Witten & Holman—*Arch. Biochem. & Biophys.* 37, 90). In this work it is observed that toxic effects of prooxidants, e.g., benzoyl peroxide, is inhibited when fed with essential acids; and the combination promotes greater gain in total body fat. Destruction of essential fatty acids in aqueous solutions by X-irradiation is said to result from production of conjugated bond systems and in the accumulation of peroxides (Mead—*Federation Proc.* 11, 257).

Rancid lard in a diet low in vitamin A much accelerates the onset of vitamin A deficiency signs, and this is entirely prevented by addition of vitamin A palmitate or a "lard factor" (Stoerk *et al.*—*Arch. Path.* 53, 15). In the presence of enough vitamin A the rancid lard is not harmful. This and similar observations with other essential factors has suggested that rancid fats destroy some vitamins and other factors; whereas normal fats supply substitutes for necessary essentials or stimulate the production of some factors by the intestinal flora (Kaunitz *et al.*—*J. Nutr.* 46, 151). Liver contains a pigment which destroys fat peroxides but is itself destroyed in the process (Dubouloz *et al.*—*Bull. soc. chim. biol.* 33, 1740).

Several investigations were made to compare nutritive values of fatty materials. Isoöleic acids appear to be normally metabolized, but fats high in these constituents may not be digested as readily as lower melting fats (Bose & Subrahmanyan—*Ann. Biochem. & Exptl. Med. India* 10, 53). During fasting, deposited isoöleic acids disappear more rapidly from body stores than do saturated or average body fats. Replacement of milk fat in whole milk for calves with soybean oil or hydrogenated soybean oil considerably increases fat content of hair and feces of the calves (de Man—*Tijdschr. Diergeneeskunde* 76, 175). Refined finbuck whale oil is as nutritious as soybean oil when judged from growth attained by white rats fed diets of 20% oil (Sakurai *et al.*—*J. Japan Soc. Food Nutr.* 3, 155). Polymerized whale oil is harmful to the rats. Tests on human subjects with whale, shark, sardine, bran, and hydrogenated products of these at 40 grams per day indicate that utilization of each of these is about the same, i.e., digestibility ranges from 92 to 95% (Matsumura—*J. Japan Biochem. Soc.* 23, 26).

Pigs heavily fed whale oil have depot fat resembling whale oil in composition (Garton *et al.*—*Biochem. J.* 50, 517). Icteric swine contain yellow fat but the composition is normal rather than that of the yellow fat produced on unsaturated fat diets (Dugan Jr. *et al.*—*J. Am. Oil Chem. Soc.* 29, 161). Turkey carcass fat also is influenced in composition and stability by dietary fat (Klose *et al.*—*Poultry Sci.* 31, 354). High unsaturated acid content and poor stability of body fats is associated with diets containing soybean, linseed, or sardine oils, whereas corn oil, beef fat, and low fat dietary induced more stability in the turkey carcass fats.

FAT ABSORPTION. The general popularity of Frazer's hypothesis with regard to emulsification as a factor in fat absorption and the increasing commercial interest in emulsifiers in foods have resulted in many investigations on relation of emulsification to fat absorption. New communications along this line of work tell of enhanced fat and vitamin A absorption by infants on emulsification (Morales *et al.*—*Pediatrics* 6, 86, 644), improvement of growth and health of calves whose diet included glycerol monostearate as an emulsifier in the synthetic milks (Huff *et al.*—*J. Dairy Sci.* 34, 1056), and growth acceleration in chicks (Ely—*U. S. 2,604,402*; Ely & Schott—*Worlds' Poultry Sci. J.* 8, 133). However, some new investigations could not confirm an improvement in fat absorption by exogenous emulsifiers (Tidwell & Nagler—*Proc. Soc. Exptl. Biol. & Med.* 81, 12; Dasher—*Science* 116, 660).

In absence of bile, only from 50 to 80% of the dietary fat appears to be absorbed (Bernhard *et al.*—*Helv. Physiol. et Pharmacol. Acta* 10, 68). "Tween 80," a commercial emulsifier, at two- to four-gram daily doses with 15-40 grams of fat did not alter the high fecal fat excretion in dogs caused by absence of bile (Annegers—*Proc. Soc. Exptl. Biol. & Med.* 81, 277). Hence, the emulsifier does not improve absorption even when some of the natural emulsifiers, bile acids, are absent.

The mechanism of absorption of fat is the subject of some investigations. Most comprehensive studies are with the use of labeled fats. In work where the glycerol moiety is labeled with C¹⁴ and the fatty acids contained conjugated double bonds the following observations are made: 25-45% of the ingested glycerides are completely hydrolyzed during absorption; the remaining 55-75% are hydrolyzed to monoglycerides; hydrolyzed glycerol is not utilized for resynthesis of lymph glycer-

ides but follows an independent metabolic pathway; and half the phospholipide formed from ingested fat utilizes the hydrolyzed fatty acids and endogenous glycerol (Reiser *et al.*—*J. Biol. Chem.* 194, 131). Comparable work in which the fatty acid and glycerol are labeled with deuterium is in practical agreement, since 24-53% of the fat is hydrolyzed during absorption; fed glycerol does not participate in the reesterification of intestine fat; and only slight deuterium concentrations are found in the lymph and lymph fats after administration of tagged glycerol or triacetin (Bernhard *et al.*—*Helv. chim. Acta* 35, 1404). Borgstrom *et al.*'s (*Acta Chem. Scand.* 5, 643; *Acta Physiol. Scand.* 25, 120, 140, 322) approach on the subject has been to compare C¹⁴ labeled fatty acids alone, together with glycerides, and esters of the labeled acids as the ethyl ester, triglyceride, phosphatide or cholesterol ester. With the fatty acid alone, fatty acids mixed with fat, as a glyceride, or fatty acids as a phosphatide, the absorbed fat is transported via lymphatic channels, 90% as neutral fat and 10% in the phospholipides. The fat seems to be absorbed by organs before being mixed with corresponding lipides of the plasma. In measurements of the total recovery of labeled acid from administration as acid, glyceride, and cholesterol ester, the lymph contains respectively, 58.7, 43.7 and 48.9% of the acids of each fed and the distribution of these in the lymph averages 87% as glyceride, 11% as phospholipide, and 2% as cholesterol ester. The tritium-labeled technique is used to demonstrate that absorbed cholesterol is conveyed into the systemic circulation by the lymph of the thoracic duct (Biggs *et al.*—*Proc. Soc. Exptl. Biol. & Med.* 78, 641). The C¹⁴ labeled fat technique is used by Kiyasu *et al.* (*J. Biol. Chem.* 199, 415) to demonstrate that short chain fatty acids are transported mainly by the portal pathway, and long chain saturated acids via the lymph. Mead *et al.* (*J. Nutr.* 46, 499) demonstrate that eleostearic acid from tung oil can serve as a means of measuring absorption and distribution of absorbed fat. Some work on digestion of glycerides is aimed at definitely demonstrating that they are hydrolyzed to mono- and diglycerides (Mattson *et al.*—*J. Nutr.* 48, 335, *Chem. Eng. News* 31, 159; Desnuelle *et al.*—*Biochem. et biophys. Acta* 5, 56; 7, 25; *Compt. rend. soc. biol.* 144, 1182).

In the above review on absorption of fats only the direct observed results are briefly annotated. However, the reports contain various interpretations. In general most seem to confirm the Frazer hypothesis on absorption of fats. Some point out the futility of adding emulsifiers to dietary fat because the partial glycerides naturally produced together with bile salts produce surface conditions such that increase of surface active material has nothing to add. The fact that partial glycerides naturally occur in the digestive system is relevant to suitability of using prepared partial glycerides in food preparations.

Taylor *et al.* (*Can. J. Med. Sci.* 30, 303, 453) has studied absorption of fats with regard to effects on serum lipases. Because synthetic diets containing fats increase activity of phosphatase and tributyrinase, it is suggested that the lipases are concerned with intestinal absorption of fatty acids. On starving, phosphatase levels drop. Tributyrinase values rose to levels which suggest that this enzyme is concerned with mobilization of fat during periods of fasting.

Intravenously injected fat is studied for its transport and effects. A study of its appearance in the thoracic duct lymph indicates that transport from the blood stream to the lymph system is partly by direct transfer through the blood capillaries of the liver, intestine, and adipose tissue where fat is desaturated, joining the thoracic lymph via their respective lymphatics (Meng—*Am. J. Physiol.* 163, 335). Johnson *et al.* (*J. Lab. Clin. Med.* 39, 414) have recorded the rate of disappearance of the fat from patients and animals. There is less elevation of the blood fat in cirrhotic patients and in Eck-fistula dogs than in normal controls on administration of the fat. Thyrotoxicosis accelerates removal of the infused fat. In diabetic dogs insulin administration accelerates removal of the fat from the blood. In a report preliminary to the above (*Ibid.* 176) stability, pyrogenicity, and effects produced by four emulsions are recorded. Ten percent emulsions injected for 24 days are well tolerated, whereas at 20% fat content platelet count decreases and prolonged bleeding time appears in from one to eleven days.

INTERMEDIATE METABOLISM OF FATS. The communications on intermediate metabolism of fats concern such aspects as biological synthesis, blood and liver lipides, biological oxidation, and mobilization.

Various aspects of fat synthesis in the body have been studied. Human feces partially hydrogenate triolein or olive oil (Chipault—*Ann. Rept. Hormel Inst. Univ. Minn.* 1950-51,

27). In one study of the mechanism of fatty acid synthesis it is demonstrated that C_2 units add to the carboxy carbon to lengthen the chain of the fatty acids (Anker—*J. Biol. Chem.* 194, 177). This interpretation is based on determining the position of the C^{14} in the palmitic acid biosynthesized from $1-C^{14}$ myristic acid.

Various factors which may affect fat synthesis have been studied. Synthesis of fat from carbohydrates is unaffected by thiamine deficiency (Gruber—*Acta Physiol. et Pharmacol. Neerland.* 2, 411). In experimental biosynthesis of fatty acids from labeled acetate by pigeon liver homogenate both the supernatant liquid and particulate matter are necessary for the activity (Brady & Gurin—*Arch. Biochem. Biophys.* 34, 221). Pancreatectomy inhibits and hypophysectomy stimulates the fat synthesis by liver slices (Brady *et al.*—*J. Biol. Chem.* 193, 459). In this work growth hormone and cortisone have antagonistic and insulin stimulating actions on fat synthesis. Mammary gland slices synthesize fatty acids from acetone alone; such synthesis is unaffected by insulin unless glucose is present; whereas synthesis from the acetate is accelerated (Balmain *et al.*—*Biochem. J.* 52, 301). Cortisone inhibits this synthesis (Balmain *et al.*—*Nature* 169, 447).

A general increase in capacity to synthesize phospholipides develops in the tissue and plasma of dogs on depancreatization (Silversmit & DiLuzio—*J. Biol. Chem.* 194, 673). This is interpreted as being compatible with the hypothesis that phospholipides are intermediates in fat oxidation. The capacity of the rat to incorporate short chain fatty acids into phospholipide molecules is demonstrated in a test in which $1-C^{14}$ -lauric acid is administered and then isolated from the body phospholipides (Stevens & Chaikoff—*Ibid.* 193, 465).

The work on metabolism of fats in the liver concerned mostly factors which modify the amount of liver fat. Data on fatty changes and damage induced by varying levels of protein and fat in diet of rats are recorded by McLean & Beveridge (*J. Nutr.* 47, 41). In general protein as casein should be above four percent of the diet to prevent damage, increasing fat levels produce concomitant damage, and variation of carbohydrates has no effect. In experimental fasting or protein depletion followed by repletion in rats excess fatty infiltration in liver can be inhibited by administration of choline (Hale & Schaefer—*J. Nutr.* 46, 479). Inhibiting fatty liver in such experiments with choline permits much faster weight regain on refeeding. Prolonged exercise also increases fatty infiltration of liver (Yakovlev—*Fiziol. Zhur. S.S.S.R.* 38, 332). The observations that animals on high-fat diets lose body weight and gain liver fat, that these deviations from normal are partially inhibited by choline, and that on high carbohydrate diets they gain weight without marked effect on liver fat is interpreted to suggest that choline has no role in the synthesis of fats from carbohydrates (Raman—*Biochem. J.* 52, 320). The lipotropic work with amino acids indicates that methionine is the only essential amino acid that is effective (Eckstein—*J. Biol. Chem.* 195, 167), that high protein diets repair the deficiency symptoms better than either methionine or choline (Plough *et al.*—*J. Exptl. Med.* 90, 221) that protein may support growth without controlling liver fat (Litwack—*Proc. Soc. Exptl. Biol. & Med.* 81, 441), and that the action of methionine is in some manner different from that of choline in lipotropic action (Waldstein & Steigmann—*Am. J. Digestive Dis.* 19, 323). In a symposium on physiology and biochemistry of the liver, various aspects of liver lipides are reviewed (Schwiegk—*Deut. Z. Verdauungs- u. Stoffwechselfkrankh., Suppl.* 1952, 85; Kühnau—*Ibid.* 104). In this series of papers, Lang (*Ibid.* 121) states that methionine acts differently than choline in curing fatty livers in that the former also favors growth; cystathionine is also effective but large amounts are required. Increase in neutral fat and decrease in phospholipides during fatty infiltration of livers are interpreted as meaning that the organ is unable to build phospholipides (Schulze—*Ibid.* 133; Harman—*Ibid.* 134). "Amellin" a protein-like substance extracted from plants prevents fatty infiltration in the liver (Nath *et al.*—*Nature* 169, 711).

Certain vitamins and hormones also may have an influence on liver fat. Vitamin B_{12} acts both as a growth promoter and fatty-liver preventative in methionine- and choline-free diets containing homocystine (Bennett *et al.*—*J. Biol. Chem.* 193, 285). Similar observations with combinations of vitamin B_{12} and folacin are interpreted to suggest that the materials promote efficiency of betaine, dimethylaminoethanol, and other compounds as replacements for dietary choline (Strength *et al.*—*J. Nutr.* 45, 329). An extract of heart tissue, corhormone, prevents fatty infiltration in liver but, unlike choline, it cannot mobilize fat already deposited (Emmrich & Petzold—*Arch. exptl. Path. u. Pharmacol.* 214, 333). Crude pituitary extracts

of adrenotropic hormone induce fatty livers which can be prevented by glucose or prior adrenalectomy (Levin—*Intern. Congr. Biochem. Abstrs. Commun. 1st Congr. Cambridge 1949*, 393).

Tests with liver slices show that phospholipides are synthesized from labeled inorganic phosphorus, but this action is considerably modified by dietary of rats from which the livers are obtained (Artom & Swanson—*J. Biol. Chem.* 193, 473). Low protein diets and high protein diets to which choline was added slow the phospholipide synthesis in livers. Choline, added to livers resulting from low protein diet, stimulates the phospholipide synthesis. Similarly, the labeling technique is used to demonstrate that phospholipide turnover in the liver takes 8-9 hours and that non-phospholipide choline of liver is not a precursor for the choline of the phospholipides (Tolbert & Okey—*J. Biol. Chem.* 194, 755). A quick method of recognizing fatty livers is based on staining with the dye, Sudan IV (Hartmann & Fleck—*Klin. Wochschr.* 30, 652). No staining occurs at fat contents less than 18-20%.

The work on biofatty acid oxidation pertains to the ability of various tissues to oxidize fats and to the mechanism of some of the oxidations. The ability of rat diaphragms to oxidize fat is affected by diets of rats; high carbohydrate diet stimulates, whereas high fat diet inhibits the fat oxidizing power of the isolated diaphragms (Hansen & Rutter—*J. Biol. Chem.* 195, 121). A difference in enzymes is presumed to be involved. According to Sabeldir (*Ukrain Biokhim. Zhur.* 20, 57) higher fatty acids, stearic and palmitic, are oxidized by the diaphragm, but not by ground heart, muscle, or liver, whereas lower fatty acids are oxidized by all the tissues. Wertheimer & Ben-Tor (*Biochem. J.* 50, 573) demonstrate that fat acids are not used up by muscle in absence of glucose but the utilization is normal when glucose content of the serum is normal. In this work pyruvic acid and acetoacetate also inhibit the decrease of fatty acids. The oxygen consumption and the carbon dioxide production of different tissues of cats have been recorded by Stary & Tekman (*Bull. fac. med. Istanbul* 15, 257). In this work the oxidation of fat in tissues from which fat is normally consumed slowly during starvation, is the same as that of easily mobilized perirenal and mesenteric fat depots.

Studies on cleavage products of biooxidation of fats are made mostly with labeled fat. Chaikoff and coworkers (*J. Biol. Chem.* 191, 523; 192, 453; 195, 567) administered palmitic and stearic acid labeled at 1-C and 6-C and record data on recovery of the labeled carbon as carbon dioxide, body fats, and glucose. A little more of the $1-C^{14}$ is recovered as carbon dioxide than is the $6-C^{14}$. Part of the stearic acid is converted to palmitic acid. With $1-C^{14}$ palmitin the urinary glucose recovered from diabetic rats is found to have C^{14} at 3- and 4-C; and with $6-C^{14}$ palmitin 10% of the C^{14} appears in 3- and 4-C of glucose and the remainder is equally distributed among the other four carbons. 9,10-Dihydroxy and diketostearic acids are oxidized in dogs to azelaic acid (Bernhard & Gloor—*Helv. chim. Acta* 35, 608). Azelaic acid is not a product of oleic acid biooxidation. Tamemasa (*J. Pharm. Soc. Japan* 71, 1015) studies stearic acid metabolism by preparation of 2-phenylstearic acid and observing cleavage products formed from this in rabbits. Recovery of α -phenyladipic acid is interpreted to indicate that one ω - and six β -oxidations occur. Other material recovered indicates that dehydrogenation also may occur.

CHOLESTEROL METABOLISM. Biggs and coworkers (*Arch. Biochem. Biophys.* 36, 430; *Proc. Soc. Exptl. Biol. & Med.* 78, 641; *Circulation* 6, 359) have demonstrated that tritium-labeled cholesterol is very suitable for studying metabolism of cholesterol and, together with C^{14} , double labeling is available. Their investigations demonstrate that exogenous cholesterol is absorbed and may be deposited in atherosclerotic aorta. The absorption of exogenous cholesterol is 9.3-19.2% of that in the test diets and is conveyed into the systemic circulation by the lymph of the thoracic duct; little or no transport occurs via the portal venous system.

The metabolism of cholesterol has been studied with regard to factors that modify various phases of the process. In livers of animals pre-fed high cholesterol diet, synthesis is depressed on a low fat diet for about eight days then returns to normal (Alfin-Slater *et al.*—*J. Biol. Chem.* 195, 311). However, with high fat diet synthesis remains normal, but, less newly formed cholesterol appears in the plasma of the high-fat diet animals than in controls. Some of the data are interpreted to indicate that high fat diets are efficient for removing cholesterol which has accumulated in the liver during preexperimental cholesterol feeding. Feeding of soybean lecithin, a source of choline, is said to decrease the concentration of cholesterol esters in the livers of cholesterol-fed mice (Schettler—*Klin. Wochschr.* 30,

627). The excess deposition of fat in the liver of animals on hypolipotropic diet containing much cholesterol can be controlled by administration of choline and inositol but liver cholesterol increases to amounts considerably above normal (Ridout *et al.*—*Rev. can. biol.* 11, 78, *Biochem. J.* 52, 79). Microorganisms of the intestines normally destroy a considerable amount of dietary cholesterol, but this capacity of the microorganisms is inhibited when antibacterial drugs, sulfasuxidine or streptomycin, are added to the diet (Wainfan *et al.*—*Arch. Biochem. Biophys.* 33, 187). This suggests that microorganisms of the intestines are primarily responsible for destruction or modification of consumed cholesterol. The hypercholesteremia caused by biliary obstruction may be a measure of hepatic synthesis of cholesterol (Friedman & Byers—*Am. J. Physiol.* 168, 292). In investigations on esterification of serum cholesterol it has been observed that the process is less active on aging, it is increased with soybean lecithin and the coexistence of a heat labile component of serum, and is reversed by induced hypercholesterolemia (Wagner *et al.*—*J. Lab. & Clinical Med.* 40, 321, 324, 334). Thyroid substances decrease plasma cholesterol, but with biliary obstruction an accumulation in the plasma takes place (Rosenman *et al.*—*Circulation* 5, 589). The latter observation suggests either rapid manufacture or rapid discharge from the liver.

Conversion of cholesterol to vitamin D₃ in the body takes place in the intestinal walls (Glover *et al.*—*Biochem. J.* 51, 1). This process is reversible.

Chaikoff and coworkers (*J. Biol. Chem.* 194, 407, 413; 196, 569; 198, 93, 105, 111) studied the synthesis of cholesterol in rats by measuring the ability to incorporate C¹⁴ labeled acetate in the compound, and studied its metabolism by tracing the fate of C¹⁴ from administered C¹⁴ cholesterol. During fasting the rat is unable to synthesize the cholesterol from administered acetate. The synthesis is restored by feeding glucose, protein hydrolyzate, or fat. On feeding of ring-labeled cholesterol 22-49% is absorbed, 70-90% of this appears in the lacteal lymph and 50% of this is esterified. Bile is an obligatory requirement for passage of cholesterol from the intestinal tract to the lymph. During oxidation of cholesterols labeled at 4- and 26-C, respectively, 31% of the chain carbon is eliminated as carbon dioxide whereas none of the ring carbon appears as carbon dioxide. The body cholesterol excreted is in the form of nonsaponifiable compounds, i.e. cholesterol, coprosterol, or dihydrocholesterol. In another study of synthesis of cholesterol from 2-C¹⁴ acetate five of the side chain carbon atoms are found to be derived from methyl groups of acetic acid and three from acetate carboxyls (Wuersch *et al.*—*Ibid.* 195, 439). Here the possibility, that five carbon units related to isoprene are intermediates in the biosynthesis from acetic acid is discussed.

Other aspects of cholesterol metabolism are discussed in this review under lipides under diseased conditions.

LIPIDES UNDER DISEASED CONDITIONS. Much information on lipide metabolism in atherosclerosis is in the various papers of a symposium on atherosclerosis. Here Allen (*Circulation* 5, 98) and Keys (*Ibid.* 115) seem to disagree with the current recommendations that patients should be sharply restricted in fat and cholesterol intake; Katz (*Ibid.* 101) points out that metabolism of lipides is at fault in the disease, and Gofman *et al.* (*Ibid.* 119) discuss the physical characteristics of the serum lipides in the disease.

In the past years, much work has been done in associating giant lipoprotein molecules, so called S₁ 10-20 lipoprotein, with atherosclerosis. Many studies on atherosclerosis recorded during the year under review are on this aspect. Heparin administration or rigid decrease of fat intake is said to decrease concentration of giant lipoproteins in blood and relieve angina pectoris (Lyon *et al.*—*Arch. Internal Med.* 89, 421). In alloxan-diabetic rabbits the serum cholesterol is principally carried in the large lipoprotein molecules, and this correlates with extent of atherosclerosis (Pierce—*Circulation* 5, 401). Low serum cholesterol occurs in obesity, but the major portion of this cholesterol is in the large lipoprotein molecules (Gofman & Jones—*Ibid.* 514). This relation of large lipoproteins with obesity is suggested to explain association of obesity with atherosclerosis. Treatment of atherosclerosis in humans with adrenocorticotrophic hormone or cortisone does not alter the large lipoprotein in their blood (Bloom & Pierce—*Metabolism* 1, 155). A study of the concentration of large lipoprotein in relation to total serum cholesterol in children has indicated that a significant correlation exists (Kempe *et al.*—*J. Pediatrics* 40, 11). Pollak's & Wadler's (*J. Gerontol.* 6, 358) studies on this large molecule theory are by observing the fate of intravascularly injected cholesterol sols. Maintenance of dys-

colloidity, large molecules, in this work is associated with atherosclerotic intimal alterations.

Clinical observations of 529 cases of hypercholesterolemia show that 72.5% have arteriosclerosis (Priddle—*Ann. Internal Med.* 35, 836). In these, serum cholesterol is lowered by low-fat diets but the results are not marked or consistent. In advanced diabetic atherosclerosis serum cholesterol is depressed with testosterone, but not with inositol or choline (DeWind *et al.*—*Ibid.* 37, 344). However, other investigators report that such lipotropic substances as soybean phosphatides (Pottinger Jr. & Krohn—*Am. J. Digestive Dis.* 19, 107) and betaine (Goldbloom & Pomerance—*Ibid.* 281) reduce hypercholesterolemia. Soybean sterols are also reported as effective (Peterson *et al.*—*Proc. Soc. Exptl. Biol. & Med.* 78, 143). Low choline diets on the other hand induce atherosclerosis (Friedman *et al.*—*Ibid.* 81, 393). In normal rats, however, severe hypercholesterolemia can be produced by conditions atherogenic in other animals but aortic or coronary atherosclerosis does not appear (Page & Brown—*Circulation* 6, 681).

The majority of patients with atherosclerosis have a serum phospholipide:cholesterol ratio of less than one whereas the reverse is found in normal subjects (Morrison—*J. Lab. & Clinical Med.* 39, 550). In similar study on normal subjects a ratio over one is encountered mostly in old individuals (Goldbloom—*Am. J. Digestive Dis.* 19, 9). However, in this work the ratio of phospholipide to cholesterol varies too much to be considered absolutely suggestive of atherosclerosis.

Tuttle (*Geriatrics* 7, 37) suggests that treatment of atherosclerosis should be by a dietetic approach. He recommends exclusion of animal sources of cholesterol and hydrogenated fats; whereas, sunflower seed oil is approved. Principles of designing low-fat diets for hypercholesterolemia patients are discussed by Hildreth *et al.* (*Circulation* 4, 899). Moses (*Am. J. Med Sci.* 224, 212) demonstrates, however, that reduction of cholesterol in blood is only achieved by complete elimination of all lipides from the diet. Experimental atherosclerosis is inhibited in test animals with administration of estrogen (Pick *et al.*—*Circulation* 6, 276, 858), or by injection of oleic acid (Keeser—*Arch. intern. pharmacodynamie* 87, 371).

A mechanism of cholesterol deposition on arterial walls proposed by Bjorksten (*Proc. Soc. Exptl. Biol. & Med.* 81, 350) suggests chemical changes occur in artery walls, which become cholesterophilic and that the intima proteins cross-link with the cholesterol compounds.

An investigation of consecutive unselected patients coming to a clinic has indicated a 5.5% incident of hereditary hypercholesterolemia (Adlersberg *et al.*—*J. Lab. & Clin. Med.* 39, 237). Incidence of hereditary hypercholesterolemia is high among Jewish families and seems absent among nonwhites.

Chung *et al.* (*Pediatrics* 7, 491) find fat absorption is proportional to fat intake in idiopathic celiac disease and cystic fibrosis of the pancreas. They, therefore, question the current restriction of fat in the diet in the light of the above evidence and because fats have noncaloric necessary functions. In such diseases and in sprue, Weyer (*Intern. Congr. Biochem. Abs. Commun. 1st Congr.* 198) finds that lower and unsaturated acids are much better absorbed than higher saturated acids. Also working with sprue patients, Asenjo (*Am. J. Trop. Med. & Hyg.* 1, 344) finds that their fat excretion averages 12.5 grams per day as compared to four grams for normal individuals.

A study of 52 patients with multiple sclerosis shows no abnormalities of concentration of cholesterol and lipide phosphorus or percentage of combined cholesterol in the blood serum (Chiavacci & Sperry—*Arch. Neurol. Psychiat.* 63, 37). Serum lipides, fatty acids, total cholesterol, and phospholipides are within normal limits in patients with acne vulgaris (Kalz *et al.*—*J. Invest. Dermatol.* 17, 273). Lipides from follicle orifices of persons with acne are no different from those from normal persons (Schmidt-Nielson *et al.*—*Ibid.* 281). The comedones contain a higher proportion of water than do normal sebaceous material.

Kaufmann & Budwig (*Fette u. Seifen* 54, 156) apply paper chromatography to the analysis of blood and skin lipides as a means of diagnosis of various diseases. The behavior of blood lipides of cancer patients in specific tests is described.

The administration of 40% fat emulsions by mouth is advised in gastrectomy, jejunostomy, and other abdominal surgery (Goldberg *et al.*—*J. Am. Med. Assoc.* 150, 1665; Van Itallie—*Metabolism* 1, 80). This feeding inhibits weight loss and is well tolerated. Fats made from the odd chain fatty acids derived from oxidation of olefin hydrocarbons are said to be useful nutrients for diabetics because they are less ketogenic than natural fats (Gebhart & Ross—*U. S.* 2,585,129).

LIPIDES IN RELATION TO MICROBIOLOGY. Much of the information on microbiological lipides is discussed in other divisions of this review. Synthesis of fats by microorganisms is reviewed in the introduction of this communication. Information on bacterial spoilage of fats is found at the end of the section on deterioration. Microbial control with surface-active fat derivatives is to be found in the section on detergents. Some information on enzymes and bacteria in relation to fats is not classifiable into the other sections.

Ramakrishnan & Banerjee (*J. Univ. Bombay Sect. A20*, Pt. 3, 111; *J. Am. Oil Chemists' Soc.* 29, 596) have prepared lipases from several molds found on oil seeds and have recorded conditions for their optimum activity. Procedures for study of hydrolysis of fats by bacteria of the *Pseudomonas* genus developed by Goldman & Rayman (*Food Research* 17, 326) are characterized by emulsifying the fat in as fine a state as possible to provide highly effective surfaces for bacterial action. A method for determining esterase in animal or plant tissue depends on hydrolysis of phenolphthalein dibutyrate and measuring freed phenolphthalein colorimetrically (Purr—*J. Am. Oil Chemists' Soc.* 29, 409).

In aerobic oxidation of fatty acids by *Serratia marcescens* bacteria 2,4-dinitrophenol blocks or inhibits oxidation of lower acids, and where oxidation occurs, the acids are completely oxidized without accumulation of unoxidized fragments (Silliker & Rittenberg—*J. Bact.* 64, 197). This is interpreted to suggest that β -oxidation of fatty acids is not the mechanism utilized by *S. marcescens*. Mukherjee (*Arch. Biochem. & Biophys.* 35, 23) points out evidence which indicates that processes compatible with both the β -oxidation theory and dehydrogenation mechanism occur during metabolism of fats by mold.

Rancid corn oil and lard inhibit the germination of spores of putrefactive anaerobes, whereas nonrancid samples at the same concentration have no effect (Roth & Halvorson (*Ibid.* 63, 429). This experiment has been done with *Clostridium botulinum*, *Clostridium pasteurianum*, *Bacillus subtilis*, and *Bacillus stearthermophilus*. The possible relationship of this inhibition to the phenomenon of dormancy is discussed. An inactivating action by oxidized fatty acids on the activity of many oxidative enzymes is demonstrated by Bernheim *et al.* (*Arch. Biochem. Biophys.* 38, 177). Quercetin, which inhibits oxidation, prevents the inactivation. The inhibiting action of rancid milk on *Streptococcus lactis* has been found to be due to the presence of free lower fatty acids in the milk (Castilow & Speck—*J. Dairy Sci.* 34, 1104, 1119). The principal acids involved in the inhibition are caprylic, capric, and lauric acids. These same acids are fungistatic to *Trichophyton mentagrophytes* (Sing & Verhagen—*Dermatologica* 99, 139). Stearic, oleic, vaccenic, and linoleic acid inhibit respiration of washed suspensions of *Bacillus subtilis*; but treatment with any one acid produces resistance against any of the other acids (Laser—*Biochem. J.* 51, 57). Oleic acid is required for optimal activity of both the formic hydrogenase enzyme systems of *Escherichia coli* (Lichstein & Boyd—*J. Bact.* 62, 415).

Characteristics and Composition

GENERAL AND COMPREHENSIVE. The communications dealing principally with composition and analytical methods are reviewed in this section. Some information on composition and tests such as compositions given when new sources of fats are fostered, analysis of soap, and determination of rancidity seem more pertinent to and are found in other divisions of this review.

Among the comprehensive reports, the Uniform Methods Committee of the American Oil Chemists' Society has made slight changes in several analytical procedures (Andrews—*J. Am. Oil Chemists' Soc.* 29, 47); the revised analytical methods of the German Society for Fat Science are published (Kaufmann & Baltes—*Fette u. Seifen* 54, 257, 402, 445); oil, fat, and wax analytical methods of the Society of Leather Trades Chemists are issued (Burton & Robertshaw—*J. Soc. Leather Trades Chemists* 35, 391); the German machines and equipment for testing lacquer are discussed (Schwarzhofer—*Fette u. Seifen* 54, 473); and linseed oil specifications of various nations and new methods for testing linseed oil are reviewed (von Mikusch—*Farbe u. Lack* 57, 91, 532; *Ind. vernice Milan* 6, 15).

FAT SOURCES. Correlations of agronomic characters, climate, and variety of soybeans with seed compositional characteristics are recorded by Weiss *et al.* (*Agron. J.* 44, 289; *U.S.D.A. Tech. Bull. No. 1017*). Among analyses of seeds from five dates of planting the significant correlations are: large seed size and high oil content with low iodine value, lateness of maturity and

high protein content with low oil content, lateness of maturity and low mean temperature between flowering and maturity with high iodine value, and number of days between flowering and maturity and high temperatures with high oil content. Grindley (*J. Sci. Food Agr.* 3, 82) compares a summer and a winter crop of sunflower seed grown in Sudan. Increasing temperature during the period of ripening of the seed leads to a very much reduced linoleic acid content in the oil. Because of cooler climate, the almond oil produced in England has a greater iodine value and contains more polyunsaturated acids than normal for this oil (Meara—*Chemistry & Industry* 1952, 667). In composition it mostly resembles sesame oil. In work on olive oil, Pastor, (*Anales bromatol., Madrid*, 4, 63, 67) records differences found in the pulp oils of five different species of olives, and for one species the character of the pulp, seed, and seed bone oils is recorded. The oil content of yew seed is twice that of fir seed (Nemec—*Sbornik Ceskoslov. Akad. Zemedelske* 24, 419).

In New Zealand butterfat, there is an increase of C_6 - C_{14} saturated acids beginning in July up to November and thereafter a slow decline (Hansen & Shorland—*Biochem. J.* 52, 207). The C_{18} unsaturated acids and the C_6 - C_{14} constituents vary in the reverse direction. The fat globules in sows' milk, unlike that of the cow, do not cluster or clump, and hence the milk "creams" at a slow rate (Whittlestone—*J. Dairy Research* 19, 127). Grey seal milk resembles whale milk in that its fat content is of the order of 10 times that found in milks of land animals (Meara—*Biochem. J.* 51, 190). The fat acid composition of the seal milk is similar to that of blubber oil.

The saturated acid contents of Antarctic, Atlantic fin, and pike whales are respectively 28, 23, and 15-17.8%. The figures differ very little with season and different catching regions (Pedersen—*Hvalradets Skrifter, Norske Videnskaps-Akad. Oslo No. 34*, 1). Thus determination of saturated acids may be useful for distinguishing pike whale oil from oils of large species. Analyses of oil from dolphin body by Cmelik (*Bull. soc. chim. Belgrade* 15, 173) indicate that subcutaneous fat does not contain highly unsaturated acids such as clupanodonic acid, and that the jaw oil fatty acids are chiefly esters of myristyl alcohol and those of head oil esters of palmityl alcohol.

Fish oil analyses of interest because of geographical location or source are on 12 marine fish oils of Bombay (Patakoot *et al.*—*J. Univ. Bombay* 19B, Pt. 3, No. 28, 18), on Indian freshwater fish oils (Pathak & Agarwal—*Biochem. J.* 51, 264), and on oil from body and liver of Japanese swell-fish (Kaneko *et al.*—*J. Japan Chem.* 3, 23).

Several investigations on moisture determination in oil seeds are recorded. The comparisons by de Janvry & Francois (*Bull. mens. ITERG* 6, 117) indicate that where the oven method is not obligatory the Carl Fisher method is recommended; precision with infrared ray heating is within one percent; whereas conductometric and dielectric behavior methods are inconsistent. Similar work on tung fruits and kernels by McKinney and collaborators (*J. Am. Oil Chemists' Society* 29, 425, 604) agrees in that the oven and Carl Fisher methods are most reliable. In these works values obtained by distillation or with vacuum oven differ a little from values of the above methods. For rapid determination of moisture in tung fruit they recommend forced draft drying for 15 minutes at 126.7° and adding 1.35% to bring results in agreement with the oven method. Radio frequency meter moisture methods require much standardization with the individual materials and wet fruit exceeds the range of the instruments. Infrared ray equipment for rapid moisture determinations is demonstrated by Pasquier & Francois (*Bull. mens. inform. ITERG* 6, 280) and Fauve & Lacoste (*Ibid.* 70). In tests with a dielectric apparatus, precision is best if samples contain over six percent moisture (Massoni & Desnuelle—*Ibid.* 39).

The work on fat determination methods pertains to developing rapid methods or to improvements in accuracy of existing procedures. Special flasks are designed with which semiskilled control operators determine fat in olive pulp (Rousseau—*Oleagineux* 6, 651). These flasks have a side bulb to separate an aliquot of clear solvent-oil solution for transfer to tared weighing dishes. Dielectric equipment for determination of oil in soybeans comprises a mill for simultaneous grinding and solvent extraction and a special unit for measuring the dielectric properties of the solvent-oil solution (Hunt *et al.*—*J. Am. Oil Chemists' Soc.* 29, 258). The rapidity of the grease determination in leather is increased over the Soxhlet technique with a new apparatus and use of chloroform as the solvent (Lollar—*J. Am. Leather Chemists' Assoc.* 47, 7). Heating and extraction conditions have been worked out for using digestion methods of fat determination for many foods (Stoldt—*Fette u. Seifen* 54, 206). Hadorn & Jungkunz (*Mitt. Lebensm.*

Hyg. 43, 197) in tests with various methods for fat in pastry find that those using acid digestion gave the best results.

Fat data from aged cream by the Rose-Gottlieb and Gerber methods are, respectively, considerably higher and lower than those obtained with fresh cream (Lehmann—*Schweiz Mülchztg.* 78, 122). Better preservation of cream samples intended for analysis is recommended. Since Babcock test results are usually a little higher than those of other methods, more legally acceptable, changes such as altering size of sampling pipet or use of glymol are being considered to induce results agreeing better with those of more acceptable procedures (Herreid *et al.*—*J. Assoc. Off. Agr. Chemists* 35, 202). For fat determination in ice cream with use of mixture of perchloric and acetic acids for digestion, the method is standardized into two procedures, one more applicable to samples of low fat content and the other for high fat samples (Rexach & Tracy—*Ice Cream Field* 58, No. 5, 60).

In an investigation on releasing fat from milk for fat determination, 20 out of 69 organic liquids have been found effective (Patton—*J. Dairy Sci.* 115, 324). In this work, *n*-butylamine and *n*-butanol are found to be exceptional demulsifiers for normal milks, ice cream, evaporated, and dry whole milks. A new single-solution detergent-method for determining butterfat in milk makes use of a mixture of tetra decyl desoxyethyl-ethylene, dioctyl sodium phosphate, oil Red-O-dye and methanol as the demulsifier (Schain—*Proc. 43rd Ann. Mtg. Milk Ind. Foundation Lab. Sect.* 1950, 46).

The fat content of rats has been determined *in vivo* by measuring the cyclopropane taken up by animals in a closed gas system (Lesser *et al.*—*Am. J. Physiol.* 169, 545). A technique to measure fatness and carcass value on live hogs is based on measurements with a probe of thickness of fat back at a certain location on the back (Hazel & Kline—*J. Animal Sci.* 11, 313). A similar method for hog carcasses is based on analysis of a core taken from the back at a position near the fifth or sixth rib (Auman & Winters—*Ibid.* 319). Methods of calculation of percentage of fat in carcass, primal cuts, and lean tissue are explained.

A method for determination of plasma lipides in biochemical work is based on extraction, saponification, hydrolysis, purification of fatty acids, and titration (Kaiser & Kagan—*Anal. Chem.* 23, 1879). In another method for biochemical work acid-soluble tissue is removed with a 10% trichloroacetic acid solution containing 0.4 M magnesium chloride before lipide extraction (Johnson & Dutch—*Proc. Soc. Exptl. Biol. & Med.* 78, 662). A histochemical technique for blood lipides is applied to plasma infiltrated into frozen-dried tissue (Haek—*Anat. Record* 112, 275).

Special extraction apparatus is designed for exhaustive extraction of lipides from various materials (Lips—*J. Am. Oil Chemists' Soc.* 29, 300). The purpose of the apparatus is to completely extract the lipides for study of their characteristics and composition.

Doadrio & Montequi (*Anales real soc. espan. fisica y quim.* 48B, 69) have issued an oxidation procedure for determination of monoglycerides. It is a slight modification of the periodate method now most commonly used. The presence of monoglycerides in lard and bread has been proven by isolation and identification by spectrophotometry and chemical tests (Kuhrt *et al.*—*J. Am. Oil Chemists' Soc.* 29, 261).

EVALUATION TESTS. Eight methods of grading soybean oil are compared by Freyer & Shelburne (*J. Am. Oil Chemists' Soc.* 29, 403, 408). Acetone insoluble, acid heat break, centrifugal foots, phosphorus, ash, free acidity, and moisture plus volatile matter are determined with respect to finding a laboratory refining loss approximation which closely simulates commercial wash kettle refining. The centrifuge foots test originally developed for linseed oil seems best and it is modified for application to soybean oil. Another comparison of acid foots, heat break, sludge, and centrifugal foots tests refers to determination of non-oil constituents of raw linseed oil (Shaw *et al.*—*Ibid.* 99). The tests classify the oils in the same groups but values are unrealistic as a measure of non-oil constituents. The Wesson refining loss determination is applied to refined oils as a measure of degree of refining (Hartman & White—*Ibid.* 177). This work included a comparison of laboratory refining methods for that purpose. Another comparison of methods proposed for determining non-oil constituents of crude oils shows that results are not comparable; hence it is suggested that the oil be extracted with ligroine, then with ether to determine residue, and that this be used together with moisture and acidity determinations. (Marini—*Olii minerali Grassi e saponi, colori e vernici* 28, 105). An oil refining test suitable for oils of either low or

high acidity is based on neutralization with potassium hydroxide, salting out soap with a mixture of water, alcohol, and salt, and extraction with ether (Accinelli—*Ibid.* 76).

Suitable solvents, indicators, and procedures for determining acidity and saponification value of oils are discussed by Anders (*Deut. Farben-Z.* 6, 133). A procedure for acid value suitable for dark oils is by potentiometric titration of samples emulsified in water (Narsimhan & Saletore—*Anal. Chem.* 23, 1315). The hydrolyzing tendency of the soap produced by the reaction is kept at a minimum by the emulsification. Apparatus and procedure for a micromethod of acid value determination is developed by Flaschka & Lackner (*Fette u. Seifen* 54, 141).

New modifications for the free fatty acid determination in milk by Breazeale-Bird procedure comprise substitution of *n*-propanol-Skellysolve-B mixture for the petroleum solvent, and absolute methanolic-potassium hydroxide for ethanolic-potassium hydroxide as the titration medium (Tucker & Bird—*J. Dairy Sci.* 34, 1170). In investigating butters for fitness of cream from which it was made, the determination of water insoluble acids may serve for sorting samples on which official but more tedious procedures should be applied (Hillig—*J. Assoc. Off. Agr. Chemists* 35, 748).

Koetschau (*Fette u. Seifen* 54, 337) points out that the color of transparent oils is a linear function of the wave number and applies the Pulfrich-photometer for color grading.

Lectures and communications by Hilditch and co-workers (*Chemistry & Industry* 1951, 846; *J. Sci. Food & Agr.* 2, 543; *J. Oil and Colour Chemists' Assoc.* 34, 354) on grading of oils emphasize that specifications for fatty oils should be based on actual composition, especially linoleic acid content. A classification called "linoleic-rich oil" is an oil whose acid mixtures contain over 67% linoleic acid.

The vitamin A content of oils such as those of fish liver may be the main criterion for evaluation; whereas in margarine vitamin A measurements are for the purpose of judging whether fortification is up to specifications. The spectroscopic properties of vitamin A and effect of interfering material as kitol, epoxide, anhydrovitamin A, etc., are recorded by Cama *et al.* (*Biochem. J.* 50, 48) in work to improve accuracy in analysis of fish oils. Dalvis & Morton's (*Ibid.* 43) work on the same procedures involve preparation of neovitamin A and neoretinene, observing their chromatographic behavior and ultraviolet absorption in order to develop corrections for the spectroscopic assay of fish-liver oils. A survey of British Columbia whale-liver oils for vitamin A indicates that the sperm whale-liver oils are the most potent (Schmidt—*Fisheries Res. Board Can. Progress Repts.* No. 33, 28). The method of Kuhn-Brockmann for vitamin A in seed oils has been adapted to semimicro and micro work (Gorbach & Pfudl—*Fette u. Seifen* 54, 334).

Work to standardize the estimation of vitamin A includes comparison of existing methods with bioassays, adoption of sorting and control methods, and development of adjustments for neovitamin A, annatto margarine color, etc. (Melnick *et al.*—*J. Am. Oil Chemists' Soc.* 29, 104, 121, 174, 321). In a new vitamin A procedure the margarine is saponified and in the extraction of vitamin A for spectroscopic measurement a mixture of alcohol, petroleum ether, and ethyl ether is used (Jampoler—*Roczniki Panstwowego Zakladu Hig.* 2, 190). Of three layers formed in each extraction only the upper one is collected and analyzed.

A method for the determination of α -, β -, γ -, and δ -tocopherols in oils, designed by Brown (*Biochem. J.* 51, 237; 52; 523), is based on isolation of unsaponifiable, concentration by absorption on active earth, elution, and separation by paper chromatography.

CHEMICAL CHARACTERISTICS. The various procedures for determination of iodine value are reviewed and critically discussed by Alonso (*Pr. Montevideo*, 1, No. 2, 39). Data on variations caused by varying weight, Hanus reagent strength, reaction time, and temperature with the application of the U. S. Pharmacopeia iodine procedure to lanolin have indicated that most rigid adherence to the directions is necessary (Punnett & Rebarber—*J. Am. Oil Chemists' Soc.* 29, 414). Basu (*Indian Soap J.* 17, 216) has designed an iodine value procedure for commercial fats using hypochlorous acid as the reagent. This procedure is modified for application to biological lipides (Mukherjee—*J. Am. Oil Chemists' Soc.* 29, 97). The Hanus procedure is modified for application to very small biological samples (Grunbaum & Kirk—*Mikrochem. ver. Mikrochim. Acta* 39, 268). A modified bromine-vapor gravimetric method is published by Atmore & Hawke (*J. S. African Chem. Inst., N.S.*, 3, 23). Investigations of the well known method of this type, Winkler method, indicate that at high iodine values the results are lower than those from other methods,

(Lindner Jr.—*Magyar Kém. Folyóirat* 56, 441). The Woburn procedure and an explanation of calculations for obtaining iodine, partial iodine, and diene values are written in the Italian literature (Bonilauri—*Olii minerali grassi e saponi, colori e vernici* 28, 89). A procedure developed for determination of the iodine value of fat containing conjugated double bonds is based on using pyridine bromide as the reagent (Tsuchiuiya et al.—*J. Nippon Oil Technol. Soc.* 4, 30). Oils with conjugated double bonds give higher iodine values with the Rosenmund Kuhnemann method accelerated with mercuric acetate than with the Hanus method (Dupin—*Bull. mens. ITERG* 5, 469). Application of amperometric apparatus for the titrations in the iodine value determinations of Hanus, Benham-Klee, and Wijs is said to improve accuracy (Duke & Maselli—*J. Am. Oil Chemists' Soc.* 29, 126). On finding that linoleic acid increases, and oleic and saturated acids decrease very regularly with increase in iodine value in cottonseed oils, Stansbury & Hoffpauir (*Ibid.* 53) developed equations for approximating the composition of cottonseed oils from iodine value and percent unsaponifiable.

The activities on determination of iodine value by measuring hydrogen absorbed during hydrogenation include a design of new apparatus for the procedure (Pack et al.—*J. Am. Oil Chemists' Soc.* 29, 227; Savaccol & Ulyot—*Anal. Chem.* 24, 715) and an evaluation of precision of a semimicro method (Vandenheuevel—*Ibid.* 847).

Determination of conjugated double bonds, i.e., the diene value, with *p*-benzoquinone gives a higher value than when maleic anhydride is the reagent used (Tamayo & Estada—*Anales real soc. espan. fis y quim., Madrid* 47B, 815). In estimating diunsaturated acid, linoleic acid, as the insoluble tetrabromides, higher values are obtained with *n*-pentane and *n*-heptane as solvents in place of petroleum ether (White & Brown—*J. Am. Oil Chemists' Soc.* 29, 292). In this work the composition determinations on seven oils agree favorably with those by thiocyanometry. Chatfield (*Paint Manuf.* 22, 90, 247) has discussed iodine, thiocyanogen, and diene values with regard to usefulness in the paint industry for approximating composition of oils. He says that they do not always accurately measure drying and polymerization properties of an oil.

Meier (*Farbe u. Lack* 57, 437) has reviewed the faults of common hydroxyl value determination and has designed a modified procedure for the purpose. A dielectricometric hydroxyl value determination is described by Oehme (*Chem. Tech., Berlin* 3, 171). The hydroxyl value determination is unreliable as a measure of the dehydration of castor oil because substantial amounts of estolides and partial glycerides develop during the dehydration (Phillips—*J. Oil & Colour Chemists' Assoc.* 33, 395).

An improvement in the combined procedure for Reichert-Meissl and Polenske values comprises repeating distillation five times adding 110 cc. of water to the flask before each distillation (Vizern & Guillot—*Oleagineux* 6, 409). The method permits detection of addition of oils containing lauric acid to butter, and the determination of C₁₀ and lower acids on a five-gram sample more readily and faster than the conventional method.

In the saponification value determination, errors due to glass of apparatus using up potassium hydroxide vary with the temperature, flask, and vigor of boiling (Sandermann & Klein—*Fette u. Seifen* 54, 269). Rhodium-plated copper flasks are recommended for obtaining accurate results. Other activities on saponification value are the development of a microprocedure (van Etten—*Anal. Chem.* 23, 1697) and design of procedure for analysis of fatty sulfochlorides (Weber—*Fette u. Seifen* 54, 201).

In general discussion on constants of fats and oils it is pointed out that acid, saponification, and hydroxyl values are reported in mg. KOH/g. and iodine, thiocyanogen, and similar values in percent iodine; consequently a plea is made to standardize to an equivalent system so that results will be comparable (Meier—*Farbe u. Lack* 57, 483). Values in equivalents are easily converted into molecular equivalents giving better insight as to the composition of the oil.

In a polemic communication on unsaponifiable matter determination, Williams (*Chemistry & Industry* 1952, 379) maintains that the British Standard Method does not give high values. A continuous method for extraction of unsaponifiable matter in analytical work is designed by Sherman & Dillistone (*Ibid.* 130).

Among communications on miscellaneous chemical tests for fats and oils, two are on determination of trichloroethylene solvent residue (Sallee—*J. Am. Oil Chemists' Soc.* 29, 197; Thomson—*Ibid.* 43); a method for determination of iron in red oil is issued (Francois & Juillard—*Bull. mens. ITERG* 5,

578); a scheme for identifying dyes of butter or margarine is based on chromatographic segregation of the dyes (Thaler & Scheler—*Z. Lebensm.-Untersuch. u. Forsch.* 95, 1); and a colorimetric method is recorded for detection of contamination of fatty material with the pesticide, 1,1,1-trichloro-2,2-bis(*p*-methoxyphenol) ethane (Claborn & Beckman—*Anal. Chem.* 24, 220).

DETECTION OF ADULTERATION. A method of detecting sheep butter in cow butter by Isidoro & Bonarelli (*Boll. lab. chim. provinciali, Bologna* 1, No. 2, 19) is based on interpretations derived from Reichert-Meissl, Polenske, iodine, and refractive index values. Analytical data are given for the fats concerned. Ambrosetti's (*Ibid.* 2, No. 1/2, 9) procedure for detecting adulteration of butter assumes that hydrogenated oil is the adulterant and the procedure is based on determination of isooleic acid. In India the best criterion for detection of adulteration of buffalo milk fat is the determination of the linoleic acid content (Venkitasubramanian & Banerjee—*Indian J. Vet. Sci.* 19, 301). The pure fresh fat never contains over two percent linoleic acid; whereas all adulterants commonly used in India contain much more.

The hydrochloric acid, acid-furfural, tin chloride colorimetric tests for sesame oil are investigated for possible effects from other oils and dyes (Anselmi & Cesari—*Ann. Chim., Rome*, 41, 573). The acid-furfural color reaction seems most specific for the sesame oil. Other communications on detection of sesame oil are two descriptions of acid-furfural colorimetric test (Isidoro & Pavolini—*Boll. lab. chim. provinciali, Bologna* 1, No. 4, 18; Bühler—*Anais assoc. quim. Brasil* 9, 95), and one description of the concentrated hydrochloric acid reaction with the oil (Hahn—*Ciencia, Mex.*, 11, 80).

The procedures written on detection of peanut oil in other oils are based on determination of the Bellier index (Amato & Almieda—*Engenharia e quim., Rio de Janeiro*, 4, No. 3, 7; Musso—*Actas y trabajos Congr. peruano quim. 3rd Congr.* 2, 525; Mitra—*Current Sci., India*, 20, 158; Isidoro—*Boll. lab. chim. provinciali Bologna* 1, No. 1, 18), and on isolation and microscopic examination of arachidic and lignoceric acids (Al-lavena—*Olii minerali, grassi e saponi, colori e vernici* 28, 57).

Argemone oil treated with concentrated hydrochloric acid fluoresces with a pink color under ultraviolet light. This serves to detect the oil in mustard oils (Sarkar & Nandi—*Current Sci., India*, 20, 232).

Spectroscopic detections of adulteration are based on analyses for highly unsaturated acids. Morris et al.'s (*Anal. Chem.* 24, 1396) screening of margarine and cottonseed oil from butter and olive oil, respectively, is based on the latter two containing conjugated tetraenic acids which are detected spectroscopically. Theirs and Dugan's & Petherams' (*J. Assoc. Off. Agr. Chem.* 35, 767) recommendations for detection of horse fat in pork or beef fat are also dependent on determining the amount of trienoic fatty acids present. Horse fat contains 11.4% linolenic acid whereas pork or beef fat has insignificant amounts.

The critical separation temperature of fats from aniline is used to identify several food fats. Brunink (*Chem. Weekblad* 43, 97) has investigated this technique for application to determining the purity of beef fat. He records deviations caused by rancidity and by admixing other fats. In applying the technique to determining the purity of cacao fat in nut chocolate confection, van Voorst (*Chem. Weekblad* 47, 595) finds that oil exuding from nuts into the chocolate may affect the test for purity of the chocolate fat. The effect of additions of palm-kernel fat on the aniline point of cacao fat is recorded.

Matarese (*Ann. chim., Rome* 41, 264) reviews the chemical and physical characteristics of natural and synthetic oils with regard to their significance for indicating or detecting synthetic oils. Efforts to identify synthetic fatty acids, i.e., branched chain acids, on the basis of kinetics of esterification have not been very successful (Schulte—*Angew. Chem.* 62, 39; Schulte & Kirschmer—*Fette u. Seifen* 53, 456). In general the rate constant falls on introduction of an α - and still more on that of a β -group, but is unaffected by more distant methyl groups.

PHYSICAL CHARACTERISTICS. Measurements of velocity of ultrasonic waves in fatty acids show that a dispersion in palmitic acid appears at 80° and in stearic acid at 75° (Wada et al.—*Kagaku* 20, 187). These disappear at higher temperature. This is interpreted to indicate that fatty acids are associated as dimers in the liquid state just above the melting point and dissociate at higher temperature. The same phenomenon is observed with low molecular weight fatty acids (Sen—*Indian J. Phys.* 25, 237). Dielectric constant measurements have indicated that fatty acid esters of high molecular

weight alcohols below their freezing point have freedom for dipole orientation whereas there is absence of molecular freedom with ethyl and ethylene glycol esters of the fatty acids (Crowe & Smyth—*J. Am. Chem. Soc.* 73, 5401). Data on many esters are recorded.

Molecular films of fatty material are studied for information on the physical structure and size of the molecules. Vold (*J. Colloid Sci.* 7, 196) points out that many studies in this field fail to note the possible significance of the lack of cylindrical symmetry of the hydrocarbon chains. She suggests that in less compact films the molecules although elliptical in cross section, rotate freely, while in compact film such rotation is inhibited. Gilby & Heymanns' (*Australian J. Sci. Res.* A5, 160) measurements of the equilibrium spreading pressure of oleic acid on concentrated salt solutions indicates that the ions of stronger hydration are less adsorbed in the surface. In all cases the area of film collapse, about 30 sq. Å, is independent of the salt in the solution. A comparison of monolayer films of pure acids and binary mixtures has demonstrated that area of the mixed film is smaller than that of each component in each pressure region (Isemura & Hamguchi—*Mem. Inst. Sci. & Ind. Res. Osaka Univ.* 8, 131). A new apparatus for this type of work has been designed by Matsuura (*Mem. Faculty Sci. Kyusyu Univ. Ser. C Chem.* 1, No. 2, 47) and is used to determine pressure-area and area-composition curves of paraffin-fatty acid mixtures. The courses of the curves are discussed with regard to effect of solution formation, surface area, etc. Work on the same system by Inaba (*Ibid.* 63) is on relation between aggregative states in phase diagrams and wettability. The competition for adsorption of fatty acids and methyl orange on bovine serum albumin is investigated to determine the forces involved and the topography of the binding sites on the protein (Cogin & Davis—*J. Am. Chem. Soc.* 73, 3135). Competition for adsorption begins at high mole ratio of fatty acids and one fatty acid displaces more than one dye anion.

A new surface film balance has been designed and is used to determine the amount of hexane adsorbed on stearic acid monolayers (Dean & Hayes—*J. Am. Chem. Soc.* 73, 5583, 5584). The adsorption is described as following a type-III isotherm at low concentration of stearic acid and type-V at high acid concentration. Interfacial-tension data of fatty acids in a hexane-water system are used to determine the kinetics of adsorption at liquid-liquid interfaces (Ward & Tordai—*Rec. trav. chim.* 71, 482, 572). Equations are developed from the data to represent the kinetics of the reaction. Surface tensions, interfacial tensions against water, viscosity, and refractive indices at 75° are graphically recorded for saturated even-numbered normal fatty acids from C₂ through C₁₈ and for the corresponding methyl and ethyl esters (Gros & Feuge—*J. Am. Oil Chemists' Soc.* 29, 313). In this work the temperature effect is demonstrated with myristic acid. Mansfield (*Australian J. Sci. Res. A*, 5, 331) has recorded changes in interfacial tension accompanying transfer of oleic acid from paraffin to a surrounding alkaline solution. The transfer of oleic acid to the alkaline solution rather than a development of negative interfacial tension is associated with emulsification.

The solubilities of the C₁₀ to C₁₈ saturated even-carbon fatty acids and their methyl esters in benzene, cyclohexane, carbon-tetrachloride, chloroform, ethyl acetate, butyl acetate, methanol, 95% ethanol, *n*-butanol, acetone, and acetonitrile have been compared (Sedgwick *et al.*—*J. Org. Chem.* 17, 327). The esters in solution do not exhibit the tendency toward intermolecular association that is evidenced by the acids. The data in this work included solubility of other alkyl stearates in several of the solvents. The partition coefficients of homologous series of primary, secondary, and tertiary alcohols in fat and hydroxylated acid systems have been measured (Lindenberg—*J. Chim. phys.* 48, 350). The technique is recommended for determining the activity coefficient.

The Warburg apparatus has been applied to the determination of the solubility of cyclopropane gas in olive oil and in rat body fat (Blumberg *et al.*—*J. Pharmacol. Exptl. Therap.* 104, 325). The results are higher than previously reported by others. Similarly Davidson *et al.* (*Quart. J. Exptl. Physiol.* 37, 91) have described apparatus for the same purpose and have recorded solubility and diffusibility of hydrogen and oxygen in lard and olive oil, and carbon dioxide and nitrogen in ethyl stearate and palmitate. Nitrogen is not dissolved. The bearing of the results on movement of nitrogen in the body is discussed.

The applicability of the Bloom consistometer to shortening, butter, margarine, and other plastic products has been demonstrated (Clardy *et al.*—*J. Am. Oil Chemists' Soc.* 29, 591). Consistency is related to the force required to push a tapered ring into the plastic material. A consistency measuring instrument for grease is based on the same principle but in place of

a ring it has a disc with a number of tapered holes (Birdsall & Hotten—*Anal. Chem.* 24, 892).

The vapor pressures and boiling points of methyl esters of several fatty acids determined by Scott Jr. *et al.* (*Ind. Eng. Chem.* 44, 172) are shown to fit within $\pm 0.2^\circ$ of values calculated from the Antoine equation. This work also contains the heat of vaporization of the methyl esters of most of the common fatty acids. In similar work by Jantzen & Erdmann (*Fette u. Seifen* 54, 197) the vapor pressures of normal fatty acids are shown to agree with those calculated by use of the Dühring rule. This report contains a graph of the boiling point against pressure for fatty acids from C₁ to C₃₀. The physical constants of fatty alcohols are recorded with regard to separation by fractional distillation (Stage—*Ibid.* 53, 677). Usefulness of these data is demonstrated by analysis of the alcohol mixture from sperm oil.

The observations that the melting point of glycerides with randomly distributed acids is four degrees higher than the melting point of the mixed fatty acids, and that reduction of the amount of saturated triglyceride below that of random distribution lowers the melting point, are the basis for a new means for calculating the amount of saturated triglyceride in a fat (Karthä—*J. Sci. & Ind. Res., India* 11A, 354). Melting point curves of mixtures of dodecyl myristate and hexadecyl caprate have been determined to test the hypothesis of Oldham and Ubbelohde which suggests that melting points of ester mixtures are lowered due to lattice-flow formation (Bondi & Scott—*Nature* 167, 485). The mixtures behave like normal hydrocarbon mixtures; hence, the data do not agree with the hypothesis. Melting points and the solubilities in methanol of palmitic-stearic-oleic acid mixtures, and of palm oil, shea butter, and tallow fatty acids are developed as data fundamental to solvent separation of liquid and solid components of these (Schlenker—*J. Am. Oil Chemists' Soc.* 29, 94). The freezing point data of the ternary mixtures, capric-lauric-myristic acids and lauric-myristic-palmitic acids, show that eutectics exist respectively at 15.5 and 30.1° (Paquot *et al.*—*Bull. soc. chim. France* 1952, 139, 140). Compositions of the eutectic mixtures are also recorded. The titers of binary and tertiary mixtures of the most common fatty acids have been graphically recorded in 11 charts (Paquot—*Bull. mens. ITERG* 6, 174). These together with iodine value are intended to serve for determination of composition of fats. Similar data are recorded for stearic and palmitic acids and their methyl esters (Paquot—*J. recherches centre natl. recherche sci. Labs. Bellevue Paris No. 18*, 138). The melting dilation and coefficient of expansion of the solid and liquid state have been recorded for triglycerides of individual acids and mixed acids (Craig *et al.*—*J. Am. Oil Chemists' Soc.* 29, 128). The data concern the glycerides of the most common fatty acids. Melting point curves and heats of solidification for the three polymorphic forms of cacao butter have been determined (Vaeck—*Rev. intern. chocolaterie* 6, 350).

Singleton and coworkers (*J. Am. Oil Chemists' Soc.* 29, 149, 155, 452; *J. Phys. Chem.* 56, 696) have recorded various thermal properties of fats and oils. Their data show that melting dilations of fatty acids and their glycerides increase with each addition of two methylene groups to the acid, and the melting dilation of monoglycerides is half that of diglycerides and one-third that of triglycerides of the same fatty acid. The relations are expressed as equations. On α - and β -tung oils these authors record specific heat, heats of fusion, melting dilation, and entropy, and develop equations for the calculation of the specific heat. These data and x-ray diffraction spacings characterize the three polymorphic forms of β -tung oil. Their data on palmitic acid include melting dilation, specific volume, specific heat, heat of fusion, entropy, and equations for calculating specific heat at various temperatures for the liquid and solid forms respectively.

Time-temperature cooling and heating curves, and x-ray diffraction technique are used by Lutton and coworkers (*J. Am. Chem. Soc.* 73, 5593; 74, 4827) to characterize the polymorphic forms of C₁₆ and C₁₈ normal alcohols, and seven symmetrical diacid triglycerides whose fatty chains differ by 10-16 carbon atoms. The alcohols exist in three solid forms. The data from the glycerides is discussed with regard to relationship of the melting point to x-ray spacing. Like relationships have been studied by Fieldes & Hartman (*Nature* 168, 74) on binary mixtures of C₁₂ to C₁₈ fatty acids.

COMPOSITION OF FATS AND OILS. Many of the methods for segregating components of mixtures of fatty acids or their esters are useful for determining the composition of fats. Cannon *et al.* (*Anal. Chem.* 24, 1530) have recorded the countercurrent distribution of the methyl esters of 10 of the

CHARACTERISTICS OF FATS AND OILS

Oil or Fat Source	% Oil or Fat	Specific Gravity	Refr. Index	Acid No. or (% Free Fatty Acids)	Sapon No.	Iodine No.	SCN No.	Acetyl No. or (OH No.)	R.M. No.	Polenske No.	% Unsaponifiable	Melting Point	Hexabromide No.
<i>Abutilon indicum</i> seed ¹	5	0.9217 ²⁵	1.4670 ²²	16.5	181.8	114.7		14.8			1.77		
<i>Amni visnaga</i> seed ^{2, 3}	6.5	0.9377 ²²	1.4766 ²²	2.7	200.8	100.1		7.0	13.7	0.8	8.6		
<i>Annona reticulata</i> seed ⁴	42.0					87.6							
<i>Annona squamosa</i> seed ⁴	39.5					83.3							
Bean (white) ⁵		0.9384 ^{15/4}	1.4752 ²⁰	37.2	193.0	150.5	32.4				7.1		
<i>Pisostolus vulgaris</i>		0.8586 ²⁰	1.4619 ²⁰	33.2	177.8	119.1			0.57	0.66	6.1	43.6	
Buckwheat ⁶	3.1	0.9227 ^{15/4}	1.4571 ¹⁵	22.4	189.5	102.1		13.5	1.05	0.71			
Buckwheat ⁷	32.3	0.8903 ¹⁵	1.4678 ²²		190.0	103.0		25.0	5.8			9.11	
<i>Cardiopermum heticucubum</i> seed ¹⁰		0.9977 ²⁰	1.4988 ¹⁵	10.7		194.5					32.2		
<i>Chimacyparis obtusa</i> seed ¹¹													
Citron seed ¹²	19.3	0.9216 ^{25/25}	1.4748 ²²	(2.75)	192.2	127.8		16.05			0.86		
<i>Citrullus vulgaris</i>	63.6	0.9068 ¹⁵	1.4727 ¹⁵	(3.09)	167.5	79.0		18.6				35.0	10.55
<i>Curupira</i> chestnut kernel ¹³													
Fish	60.66				171.0	176.0					1.55		
Ray (<i>Raja clavata</i>) liver ¹⁷													
Genubok beans ¹⁸		0.9176 ^{15/15.5}	1.4624 ⁴⁰	0.8	187.8	86.9					0.6		
<i>Bauhinia esculenta</i>													
Jute seed	14.7		1.4861 ²⁵	(8.5)	186.3	104.6					5.4		
<i>Corchorus capularis</i> ²⁰	11.3		1.4724 ²²	(16.2)	188.3	119.2					5.0		
<i>Corchorus olitorius</i> ²⁰													
Okari nut kernel ²²	65.70	0.908 ²⁵	1.4645 ²⁵		198.4	61.1	47.5		0.15	0.3	1.7	32.0	0
<i>Terminalia kaerbachii</i>													
<i>Terminalia kaerbachii</i>	34.4	0.9273 ²⁰	1.4736 ²⁰	6.3	181.5	89.1		20.9			4.2		
<i>Pongamia glabra</i> seed ²³		0.9375 ^{15/4}	1.4787 ^{20/20}	1.12	198.4	162.4			0.47		0.61		
<i>Saprium japonicum</i> seed ²⁵													
Snake (moccasin) intestinal lobes		0.9268 ^{25/4}	1.4690 ²⁵		192.6	104.4	77.2	4.1	0.07	0.04	0.46		
<i>Aphistrodon piscivorus</i> ²⁶								(9.9)	0.42	0.27			39.2
<i>Spirea ulmaria</i> seed ²⁷	14.0	0.9331 ^{20/4}	1.4848 ^{15.5}	3.87	191.7	182.7							
<i>Strophanthus sarmientosus</i> seed ²⁸	29.35		1.4721 ¹⁷	(0.7.1.2)	189.192.1	91.4.93.4					1.4.2.4		
<i>Symphlocos crataegoides</i> seed ¹¹		0.9266 ¹⁵	1.4705 ²⁰	4.35	190.3	96.9					1.2		
<i>Symphlocos crataegoides</i> seed ²⁹		0.9172 ²⁵	1.4673 ²⁰	5.35	195.0	104.1			0.46	0.25	1.4		
<i>Trichosanthes japonica</i> seed ¹¹		0.9383 ¹⁵	1.5011 ¹⁵	2.16	189.6	158.7					3.2		
Uacu seed ¹³	28.4	0.9079 ^{25/4}	1.4656 ²⁵	2.78	192.194	60.4			1.65	0.48	0.6	22.7	
<i>Monopteryx uacu</i>													
Wood of <i>Dalbergia sissoo</i> ³⁰	5.35	0.9132 ²⁰	1.5311 ²⁰	0.65	192.5	31.3		3.94	0.79		2.56		
<i>Xanthium strumarium</i> seed ³¹		0.9286 ¹⁵	1.4771 ²⁰	1.54	193.9	136.0	79.7		1.7				

FATTY ACID COMPONENTS

Oil and Fat Source	Common Saturated Acids			Common Unsaturated Acids			Other Fatty Acids
	C ₁₄ Myristic	C ₁₆ Palmitic	C ₁₈ Stearic	C ₁₈ (-2H) Oleic	C ₁₈ (-4H) Linoleic	C ₁₈ (-6H) Linolenic	
<i>Ammi visnaga</i> seed ³	0.1	4.8	1.6	73.8	18.6	—	C ₂₀ 0.4, C ₂₂ 0.7
<i>Annona reticulata</i> seed ⁴	0.5	16.6	6.7	49.6	22.3	—	C ₁₆ (-2H) 4.3
<i>Annona squamosa</i> seed ⁴	0.3	12.5	8.9	54.2	20.0	—	C ₂₀ 1.8, C ₁₆ (-2H) 2.3
Buckwheat leaf meal ⁵	—	17.1	1.4	28.2	18.2	32.5	C ₂₀ 0.36, C ₂₂ 2.1, C ₂₄ 0.8
<i>Caesalpinia separia</i> seed ⁶	—	5.6	7.3	23.5	63.1	—	C ₂₄ 0.5
* <i>Cordiospermum helicacabum</i> seed ⁶	—	—	6.0	71.0	1.3	—	Volatile acids 0.75, C ₂₀₋₂₄ 11.0
Citron seed ¹²	—	—	—	—	—	—	C ₁₄ (-2H) 0.4, C ₁₆ (-2H) 0.8
<i>Ostruhtus vulgaris</i>	0.9	10.5	6.4	19.1	61.9	—	—
<i>Taigara Coco</i> seed ¹⁴	1.6	15.5	2.8	45.0	23.3	11.8	—
Fish	—	—	—	—	—	—	C ₁₄ (-2H) 0.2, C ₁₆ (-2.7H) 25.3, C ₂₀ (-5.7H) 7.5, C ₂₂ (-9H) 10.1, C ₂₄ (-9H) 0.2
* <i>Catla bichanani</i> body ¹⁵	2.9	29.0	6.5	—	17.9 (-2.5H)	—	C ₂₀ 1.4, C ₁₄ (-2H) 1.4, C ₁₆ (-2.7H) 10.0, C ₂₀ (-5.7H) 11.9, C ₂₂ (-9H) 2.1
* <i>Catla bichanani</i> viscera ¹⁵	2.8	25.3	7.9	—	37.2 (-2.5H)	—	C ₂₀ 3.1, C ₂₄ trace, C ₁₆ (-2H) 7, C ₂₀ (-4.8H) 26.5, C ₂₂ (-6.5H) 9.4, C ₂₄ (-8H) 2.6
<i>Catla bichanani</i> liver ¹⁵	0.6	19.0	6.4	—	25.4 (-2.7H)	—	C ₁₂ 0.2, C ₁₄ (-2H) 0.6, C ₁₆ (-2.6H) 15.1, C ₂₀ (-8H) 17.1, C ₂₂ (-9.2H) 10.3
Cod ¹⁶	10.0	13.8	4.5	—	28.4 (-3.0H)	—	—
<i>Nototheria rossi mamoratta</i>	1.5	14.2	4.0	—	32.6 (-2.4H)	—	C ₁₄ (-2H) 0.4, C ₁₆ (-2H) 8.4, C ₂₀ (-5.3H) 19.8, C ₂₂ (-8H) 19.1
<i>Wallago attu</i> liver ¹⁵	—	—	—	—	—	—	C ₁₆ (-2H) 4-8, others in minor amounts
Horse fatty tissue, muscle & liver ¹⁶	—	25-30	3-6	—	50-55	—	—
Jute seed	—	—	—	—	—	—	—
<i>Corchorus capsularis</i> ²⁰	—	12.0	4.6	28.7	41.3	4.7	C ₂₀ 2.2, C ₂₄ 0.9, C ₂₆ 1.2, C ₂₈ (-2H) 4.4
<i>Corchorus obtortus</i> ²⁰	—	16.9	3.7	9.1	62.5	0.9	C ₂₂ 1.8, C ₂₄ 1.1, C ₂₆ (-2H) 4.0
<i>Corchorus obtortus</i> ²¹	—	15.7	4.0	12.4	59.7	—	C ₂₂ 1.66, C ₂₄ 1.12, C ₂₆ (-2H) 2.4
Okari nut kernel ¹²	—	—	—	—	—	—	—
<i>Terminalia kaeribachi</i>	—	37.2	7.7	34.4	14.6	—	—
Rapeseed (Canadian) ²⁴	—	2.5	2.6	16.3	15.3	8.9	C ₁₆ (-2H) 0.2, C ₂₀ 0.8, C ₂₀ (-2H) 11.6, C ₂₂ 1.4, C ₂₂ (-2H) 39.7, C ₂₂ (-4H) 0.6
<i>Rosa rubiginosa</i> seed ²	0.4	1.6	1.5	6.6	73.6	16.3	—
<i>Sapitum japonicum</i> seed ²⁵	—	4.0	1.0	19.0	55.0	8.0	—
Snake intestinal lobes	—	—	—	—	—	—	—
<i>Aphistrodon piscivorus</i> ²⁶	1.77	15.93	8.37	35.25	16.00	—	C ₁₈ (-2H) 6.53, over C ₁₈ unsatd. 11.18
<i>Strophanthus sarmentosus</i> seed ²⁸	0.2	11.9	9.2	38.3	29.8	—	C ₂₀ 4.0, hydroxy C ₁₈ (-2H) 6.6
Toad adipose reserve ³⁰	—	—	—	—	—	—	C ₁₂ 0.5, C ₂₀ 0.5, C ₁₂ (-2H) 0.1, C ₁₄ (-2H) 1.1, C ₁₆ (-2H) 13.1, unsatd. C ₂₀ 1.4
<i>Bufo arenarum</i>	3.4	18.2	3.8	—	57.9	—	—
Tiger fatty tissue ³¹	1.0	22.5	24.6	38.9	4.1	—	C ₂₀ 1.2, C ₁₄ (-2H) 0.6, C ₁₆ (-2H) 7.1
<i>Felis tigris</i>	—	—	—	—	—	—	—
*Uacu seed ³²	0.7	11.0	5.3	67.8	10.8	—	C ₈ 0.5, C ₁₀ 0.2, C ₂₀ 4.6, C ₂₄ 4.8
<i>Monopertis uacu</i>	—	—	—	—	—	—	C ₂₀ 19.4
Wood of <i>Dalbergia sissoo</i> ³³	5.6	21.8	24.3	9.4	10.8	—	—

* Based on total fat.

CHART REFERENCES

- Gupta & Saharia. *J. Unit. Bombay* 19, Sect. A, Pt. 3, Sci. No. 28, 29.
- Cattaneo et al. *Anales No. 2 soc. quim. argentina* 39, 145.
- Cattaneo et al. *Rev. brasil quim.* 32, 386, 387.
- Naidu & Acharya. *J. Indian Chem. Soc. Ind. & News Ed.* 14, 53.
- Takahashi et al. *J. Agr. Chem. Soc. Japan* 22, 126.
- Franzke. *Deut. Lebensm-Rundschau* 48, 118.
- Obara & Kitamura. *J. Agr. Chem. Soc. Japan* 25, 426.
- Kreusson. *J. Am. Oil Chemists' Soc.* 29, 4.
- Mhaskar et al. *J. Unit. Bombay Sect. A*, 19, Pt. 5, 16.
- Covello. *Ann. Chim. Rome*, 41, 780.
- Tsuchiya & Kinomura. *Repts. Govt. Chem. Ind. Res. Inst. Tokyo* 45, 231.
- T-Sao & Potts. *J. Am. Oil Chemists' Soc.* 29, 444.
- Silva & Cavalcanti. *Rev. quim. ind., Rio de Janeiro* 20, No. 228, 20.
- Cattaneo et al. *Anales soc. cient., Argentina* 153, 95.
- Padhak & Agarwal. *Biochem. J.* 51, 264.
- Pedersen. *Fids. Kiemi, Bergesen Met.* 19, 83.
- Petrov. *Rybnoe Khoz.* 24, No. 6, 47.
- Coomber & Coomes. *Colonial Plant and Animal Products (Brit.)* 1, 122.
- Shorland et al. *Biochem. J.* No. 52, 400.
- Meara & Sen. *J. Sci. Food Agr.* 3, 237.
- Chakravarti & Sen. *J. Indian Chem. Soc.* 28, 390.
- Clark et al. *Australian J. Applied Sci.* 2, 378.
- Vidyarathi. *Indian Soap J.* 17, 54.
- Youngs et al. *Can. J. Chem.* 29, 871.
- Obara & Kitamura. *J. Agr. Chem. Soc. Japan* 25, 528.
- Pollard & McLaughlin, Jr. *J. Am. Oil Chemists' Soc.* 29, 631.
- Nordström & Nordström. *Finska Kemistisamfundets Medd.* 59, 11.
- Gunstone. *J. Sci. Food Agr.* 3, 185.
- Obara & Kitamura. *J. Agr. Chem. Soc. Japan* 26, 64.
- Cattaneo & de Saitton. *Rev. brasil quim.* 32, 388.
- Padhak & Agarwal. *J. Sci. Food Agr.* 3, 136.
- Pinto. *Bot. tec. inst. agron. norte. Brazil* 21, 51.
- Kathpalia & Dutt. *Indian Soap J.* 17, 235.
- Borozenets & Georgievskii. *Gigiena i. Sanit.* 1951, No. 7, 39.

common fatty acids using a 24-tube Craig apparatus and pentane-hexane hydrocarbon and 80% nitroethane-20% nitromethane mixture as the solvent. Ahren Jr. & Craig (*J. Biol. Chem.* 195, 299) similarly demonstrate separation of a mixture of C_{14} to C_{18} normal saturated even carbon acids and separation of mixtures of oleic, linoleic, and linolenic acids. The technique is used for segregating the fatty acids of pig mesenteric fat. Various chromatographic techniques are demonstrated for the separation of binary mixtures of saturated acids and binary mixtures of a saturated acid and an unsaturated acid (Tous & Pizarro—*Anales real soc. espan. fis y quim.* 46B, 375), separation of mixtures of stearic and oleic acids (Yamakita & Aids—*Bull. Inst. Chem. Res., Kyoto Univ.* 27, 72), segregation of a mixture of methyl esters of stearic, oleic, linoleic, and linolenic acids (Kurtz—*J. Am. Chem. Soc.* 74, 1902), and separation of mixtures of C_2 to C_{12} normal fatty acids (Vandenheuvel & Hayes—*Anal. Chem.* 24, 960). A chromatographic displacement technique previously used for isolation of fatty acid is demonstrated for the isolation of cholesterol, ergosterol, and other steroids (Hamilton & Holman—*Arch. Biochem. & Biophys.* 36, 456). Paper chromatography technique with fluorescent dyes as indicators has been used for separating and identifying linoleic, oleic, elaidic, erucic, stearic, caproic, caprylic, heptanoic, decanoic, octenoic, and undecylenic acids, and for detecting conjugated unsaturated acids and polymerized oils (Kaufmann *et al.*—*Fette u. Seifen* 54, 7, 10, 73, 348). Paper chromatographic technique described by Reid & Lederer (*Biochem. J.* 50, 60) for separation and estimation of lower fatty acids is done on the ammonium salts of the acids and from *n*-butanol-aqueous ammonia solution. The paper chromatographic technique schemes of Inoue *et al.* (*J. Agr. Chem. Soc. Japan* 23, 368; 24, 291, 295; 25, 161, 491, 496) involve use of solutions of hydroxamic acid derivatives of the fatty acids, potassium permanganate decomposition of certain acids, and analysis of oxidation products, and analysis of ozonide products. The techniques are demonstrated on many normal acids, their diacid oxidation products, butter, and coconut, linseed, rape, soybean, olive, and herring oils.

The ability of some fat constituents to form crystallizable complexes with urea is applied to analysis of the fats. With the unsaponifiable of wool fat the monohydric alcohols can be crystallized out of the mixture as the urea complexes (Rudloff—*Chemistry & Industry*, 1951, 338). A mixture of fatty acids of peanut oil and ricinoleic acid has been analyzed by separating the saturated acids using the usual lead-salt method, segregating unsaturated from hydroxy acids by precipitating the former as urea complex, fractional distillation of saturated and unsaturated components in the form of their methyl esters, and calculating composition from the weight, iodine value, and saponification equivalent of the fractions (Achaya & Saletore—*Analyst* 77, 375). The character of the urea complex formed served to determine the configuration of certain acids (Swern *et al.*—*J. Am. Chem. Soc.* 74, 1655). In this work the 9,10-dihydrostearic acid synthesized from elaidic acid is said to have -OH groups on opposite sides, and that from oleic acid on the same side. The urea complexes of 42 compounds, principally fatty acids, partial glycerides, fatty esters, isomers, and their oxidized products have been prepared and the temperature at which opacity occurs in each is determined (Knight *et al.*—*Anal. Chem.* 24, 1331). This character of each complex is suitable for identifying the various compounds.

New information pertinent to the spectroscopic analysis of fats has been recorded. The data of Sinclair *et al.* (*J. Am. Chem. Soc.* 74, 2570, 2575, 2578) contains the infrared absorption spectra of many saturated and unsaturated acids, their methyl esters, and the brominated derivatives of the unsaturated acids. Freeman (*Ibid.* 2523) records the same information on 27 branched, long-chain fatty acids. These data are discussed with regard to associating the absorption with structure and for use in analytical work. Such data are discussed with regard to analysis of sunflower oil and hydrogenated and nonhydrogenated cottonseed oils (Batishecheva *et al.*—*Izvest. Akad. Nauk S.S.S.R. Ser. Fiz.* 14, 458). Martens (*Farbe u. Lack* 58, 51) has reviewed the application of ultraviolet spectroscopy for the determination of such unsaturated acids as conjugated linoleic, α - and β -licanic, α - and β -eleostearic, punicic, and α - and β -parinaric acids. The American Oil Chemists' Society spectrophotometric method gives 2.4% higher results for linoleic acid in cottonseed oil than those calculated from iodine and thiocyanogen values (O'Connor *et al.*—*J. Am. Oil Chemists' Soc.* 29, 461). Use of a higher extinction coefficient for pure *cis*-linoleic acid results in good agreement between the two methods. Brices' and coworkers' (*Ibid.* 279) standardization recommendations for the method include modification in the procedure and changes in the extinction coefficient used.

O'Connell and coworkers (*Archives Biochem. & Biophys.* 36, 304) have designed spectroscopic procedures for determining the polyunsaturated acids in small amounts of blood. Modifications for improving the sensitivity of the spectrophotometric method for the analysis of acids more unsaturated than linoleic are made by Herb & Riemenschneider (*J. Am. Oil Chemists' Soc.* 29, 456). The procedure is applied to show that lard contains some pentaene acids. Desnuelle & Massoni (*Bull. mens. ITERG* 6, 204) demonstrate the use of the ultraviolet spectrophotograph for analysis of drying oils.

Many miscellaneous observations are recorded on the composition of various fats. The fact that tallows do undergo interesterification is pointed out as proof that the trisaturated glyceride content of tallows is less than expected on the basis of random distribution (Karthä—*J. Am. Oil Chemists' Soc.* 29, 109). Beef brisket fat differs from beef tallow composed from other portions of the carcass in that it has a higher iodine value, lower titer, lower saturated acid content and higher monethenoid fatty acid content (Dugan *et al. Ibid.* 298). Pig- and sheep-bone fats have less palmitic acid than corresponding body fats (Holmberg & Rosenqvist-Bergqvist—*Svensk Kem. Tid.* 63, 272). A comparison of the fatty acids of the phospholipides and the glycerides of egg yolk indicate that the phospholipides contain more C_{20-22} unsaturated acids and less hexadecenoic acid (Shorland—*New Zealand J. Sci. Technol.* 33B, 224). Similarly, the liver phospholipides of the horse contain more stearic and C_{20-22} unsaturated acids and less hexadecenoic acid than the liver glycerides (Shorland *et al.*—*Biochem. J.* 52, 400). In this work the fatty acid composition of glycerides of fatty tissues, muscle, and liver of the horse are shown to be generally similar. Cameline seed oil differs from other cruciferal oils by not containing erucic acid and by containing eicosenoic acid, some of its higher homologs, and also a hydroxy-acid (von Mikusch—*Farbe u. Lack* 58, 402). Determinations of the composition of linseed oils from Sweden, Uruguay, United States, Mexico, India, and Germany indicate that they differ less than commonly thought (von Mikusch—*Ibid.* 303). Among analyses of several tung oils, the oil of lowest (72%) eleostearic acid content contains 23% trieleostearin, 67% dieleostearic and 10% monooleostearic glycerides; whereas that of highest (82%) eleostearic acid contains 56% trieleostearins, 40% dieleostearic and 4% monooleostearic glycerides (Hilditch & Mendelowitz—*J. Sci. Food & Agr.* 2, 548). These data are discussed with regard to the drying properties of the oils.

Some communications on composition of fats are limited to specific fatty acids. Infrared spectrophotometric evidence is presented which indicates that beef fat contains 5-10% of trans acids (Swern *et al.*—*J. Am. Oil Chemists' Soc.* 29, 44). Raman analyses are used to confirm that erucic is a trans isomer and brassic acid has the *cis* form (Pigulevskii—*Doklady Akad. Nauk S.S.S.R.* 82, 413). Matsushima (*Folia Pharmacol. Japan* 48, No. 2, 109) has identified 8-oleic acid in the seed oil of Job's tears and suggested that it be named coixic acid. The amounts of mono-, di-, tri-, tetra-, and pentaene C_{20} and C_{22} acids in samples of butterfat are recorded (Shorland & Johannesson—*Nature* 163, 75). The Reichert-Meissl and Polenske values of the oil of neem fruits indicate a steam volatile acid content of 6.67% (Murai—*J. Pharm. Soc. Japan* 71, 1463). The main unsaturated fatty acids of herring oil from Hokkaido are $C_{22}H_{32}O_2$, $C_{20}H_{30}O_2$ and $C_{20}H_{30}O_2$, and minor components are $C_{24}H_{38}O_2$, $C_{24}H_{38}O_2$ and $C_{13}H_{26}O_2$ (Tsuchiya & Kato—*Repts. Govt. Chem. Ind. Res. Inst. Tokyo* 45, 191). An unsaturated hydroxy acid which forms 6.6% of the component acids of *Strophanthus sarmentosus* seed oil has been shown to be 9-hydroxyoctadec-12-enoic acid (Gunstone—*J. Chem. Soc.* 1952, 1274). In regard to branched chain fatty acids in normal fats a C_{20} saturated fraction containing at least three and possibly four branched methyl groups has been isolated from butterfat (Hansen & Shorland—*Biochem. J.* 50, 358), 14-methylhexadecanoic acid has been shown to occur as a minor constituent of mutton fat (Hansen *et al.*—*Ibid.* 203), a methyl branched isomer of *n*-heptadecanoic occurs in beef suet (*Ibid.* 581) and 26-methyloctacosanoic, 24-methylhexosanoic, and 28-methyltriacontanoic acids have been identified in wool fat (Tiedt & Truter—*Chemistry & Industry* 1952, 403). The uropygial gland of ducks and geese contains principally fatty acid esters of octadecanol, and the fatty acids comprise odd chain and side chain members in addition to normal acids (Weitzel—*Fette u. Seifen* 53, 667).

The distillation technique of Weitkamp has been used on the unsaponifiable portion of wool wax to isolate the following branched fatty alcohols: 14-methylhexadecanol, 16-methyloctadecanol, 18-methyleicosanol, 20-methyldocosanol, 22-methyltetracosanol, 24-methylhexacosanol, 18-methylnonadecanol, 20-methyl-

heicosanol, 22-methyltricosanol, and 24-methylpentacosanol (Murray & Schoenfeld—*J. Am. Oil Chemists' Soc.* 29, 416). A general discussion on the constituents of wool fat is written by Truter (*Quarterly Rev.* 5, 390).

A polyglycerol phosphatide has been isolated by chromatographic technique from the alcohol-insoluble phosphatides of dog liver (McKibbin & Taylor—*J. Biol. Chem.* 196, 427). Analysis of the bound and free sugars of soybean lecithin indicates that galactose, mannose, and arabinose are present (Scholfield *et al.*—*J. Am. Oil Chemists' Soc.* 29, 293). Kaufmann & Schmidt (*Fette u. Seifen* 54, 399) have related the phosphatide content of linseed oils to their bodying characteristics. The phospholipide, fatty acid, and cholesterol content of the blood of opossum, muskrat, and caribou, and the bile of opossum have been recorded (Wilber—*J. Mammalogy* 33, 105).

A new procedure for the determination of serum cholesterol is based on measuring the yellow component of the color developed by the Liebermann-Burchard reaction (Kenny—*Biochem. J.* 52, 611). The infrared adsorption data for cholesterol, ergosterol, and other sterols related to these as developed by Rosenkrantz *et al.* (*J. Biol. Chem.* 195, 503, 509) should aid in the determination and identification of these various sterols. A rapid assay method for cholesterol is based on the turbidity produced on precipitation with digitonin (Pollak & Wadler—*J. Lab. & Clinical Med.* 39, 791). In another rapid method, paper chromatography rather than digitonin precipitation is used for the actual separation of the cholesterol (Lata & Vestling—*Anal. Chem.* 24, 208). An investigation on skim sterols with modified Schoenheimer-Sperry reagents shows that cholesterol develops a blue-green color which reaches maximum intensity in 30-35 minutes and in one and a half minutes after this fades; the color, due to 7-dehydrocholesterol, reaches maximal intensity (Moore & Baumann—*J. Biol. Chem.* 195, 615). In this work the maximal color due to "fast acting" sterols is about four times as intense as that due to cholesterol. A major component of the "fast acting" sterol fraction from rat skin has been identified as 7-cholestene-3- β -ol (Idler & Baumann—*Ibid.* 623). The cholesterol contents of 68 foods common in the Norwegian dietary are recorded by Pihl (*Scand. J. Clin. & Lab. Invest.* 4, 115).

A new analytical scheme for determination of sesamol, sesamolol, and sesamin in sesamin concentrates and oil is based on solvent separation of free and bound sesamol and use of either spectrophotometric or photocolometric methods to determine each component (Suarez *et al.*—*Anal. Chem.* 24, 668).

In a series of studies on the unsaponifiable constituents of shea butter, the characteristics of this fraction are recorded, furfural is used to separate the terpenic alcohols from the rest of the unsaponifiable constituents, and the latex fraction is separated into a polyisoprene [$(C_5H_8)_n$ where $n \approx$ about 180], karitene B (a resinous hydrocarbon) and karitenes C and D ($C_{20}H_{32}O$, wherein $n = 8$ or 9) (Paquot *et al.*—*Oleagineux* 7, 195, 196, 198, 394). A new saturated hydrocarbon, $C_{24}H_{50}$, has been isolated from dolphin liver oil (Tsuchiya & Kato—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 53, 305). The sulfur content of Canadian erucic acid oils is found to be less than 0.001% (Lips—*Can. J. Technol.* 30, 61).

The charts in this section of the review contain analytical data from communications that are not cited in the text of this review.

Detergents

MANUFACTURE. Several patents on soap making concern continuous processes. A continuous method by Owen (*U. S.* 2,566,359) constitutes a short initial agitation of fat and saponifying agent to cause emulsification, a stage of self-saponification without agitation, and a final period of agitation to complete the saponification. Another invention pertains to adjusting operations so as to develop a soap phase that enters centrifuges at 180° and at a soap content of 38-62%; neat soap is separated from the mixture by the centrifuges (Lever Bros. & Unilever Ltd.—*Brit.* 662,648). Maintenance of fluids at a constant temperature so that proportion is not affected by volume change and of very good agitation to prevent curd formation are mentioned as outstanding characteristics of a continuous soapmaking apparatus patented by Ledgett (*U. S.* 2,594,461). Mills (*U. S.* 2,578,366) describes apparatus for continuous saponification of fatty acids in such manner that the soap produced contains 12-27% moisture and can be made into flakes, granules, or bars. The novelty of continuous apparatus patented by Jones (*U. S.* 2,599,331) concerns a multi-stage countercurrent saponifier equipment.

A kettle has been equipped with a special stirrer and circulating pump to produce kettle soap rapidly (Razis—*Brit.* 605,653). To separate neat soap from kettle-made soap the process is conditioned so that the soap entering the centrifuge from the kettle is homogeneous, contains 45-55% fatty acids and is at 190-200°F. (Bodman *et al.*—*U. S.* 2,572,102).

The patented features of a soap process designed by Akiyama & Tsuchiya (*Japan* 3631 ['50]) pertain to a method of heating which permits optimum separation of glycerol. The use of alcoholic solution of alkali as the saponifying solution is patented by Sumimoto (*Japan* 522 ['51]). A similar process described by Accinelli (*Olii minerali grassi e saponi, colori e vernici* 28, 24) includes also washing with saturated salt solution and ether. A soapmaking patent issued to Kao (*Brit.* 658,954) pertains to graining by introducing boiled soap in a fine stream into a soap batch at a predetermined graining strength. Smaller soap curds are produced which are quite free from lye. Anhydrous soap has been prepared by the action of sodium amalgam on stearic acid under anhydrous conditions (Stainsby—*Can. J. Chem.* 29, 838). The purpose of the work is to prepare pure soap for fundamental studies of its characteristics. The principle of a new soap-drying process is to spray the soap solution on predried soap particles and redry (Marshall—*U. S.* 2,579,944). A hard toilet soap prepared by van Loon (*Brit.* 664,484) is superfatated in a crutcher. The manufacture of paper coated on both sides with soap is patented by Amat (*Span.* 198,798).

Hydrogenation in aqueous solution with Raney nickel as the catalyst is developed for making hard soap from fish oil foots and sardine oil soap (Tsuchiya *et al.*—*Japan* 43 ['51]; *J. Oil Chem. Soc., Japan* 1, No. 1, 22).

The yields of soap from low grade fats have been investigated (Reutenauer & Dupin—*Bull. mens. I.T.E.R.G.* 5, 393, 514; Reutenauer—*Ibid.* 6, 225). The losses caused by the presence of various amounts of calcium soap, unsaponifiable, hydroxy acids, and polyunsaturated acids during the salting-out process from tallow, coconut oil, and peanut oil soaps are recorded. Methods of salting out soaps from poor stocks containing the above-mentioned impurities are developed. Webb (*Soap Sanit. Chemicals* 28, No. 8, 95; No. 9, 87; No. 10, 95) has recorded experimental soapmaking tests in which saponification, salting out, and washing techniques are studied with regard to glycerol recovery. Reintroducing spent lyes containing glycerol in the kettle process causes a loss of glycerol which can be recovered by using higher volume of wash liquor. Using spent lyes for making brine is recommended in place of using the lyes for preparation of new saponifying liquor. To avoid color and bad odor in the soap, brines made from the spent lyes should be used in the first change and avoided in the last change.

Two communications are on operation of ion-exchange glycerol purification plants. The Lever Bros. plant at Los Angeles with a capacity of 26,500 lbs. of crude glycerol per day is said to produce glycerol of up to 99% purity (Busby & Grosvenor—*J. Am. Oil Chemists' Soc.* 29, 318). In apparatus and method described by Rahles *et al.* (*Ibid.* 133) each passage of glycerol solution through the pair of exchange resins removes about 90% of the ionized solids. After repeated treatments the water is evaporated. In the example illustrated 95.0% glycerol is produced from 9.1% sweet water.

Homologous synthetic detergents of various types have been prepared and their surface tension, wetting, foaming, solubilities, and detergent properties examined. Disodium α -sulfolipmitate is found to be a good detergent; the lauric and myristic homologs are active but more soluble; and the stearate is less soluble (Stirton *et al.*—*J. Am. Oil Chemists' Soc.* 29, 198). Also in this report sodium 9-octadecenyl sulfate is found to have good solubility and detergent properties. Similar work is recorded on compounds of the type $ArCOCH_2CH_2CH(SO_3Na)COOR$ (Hedrick *et al.*—*Ind. Eng. Chem.* 44, 314). Maximum wetting power of these occurs when R, the alkyl group is a branched C_8 or C_{10} group with the substituent in Ar as isopropyl or *sec*-butyl, and when R is 2-ethylhexyl with Ar as EtC_6H_5 or $EtCH(Me)C_6H_5$. Maximum detergency is attained when R and its substituent in Ar together contain 12 to 14 carbon atoms. Similar data plus lime soap dispersibility, foam stability, and acid stability are recorded for the C_{10} to C_{18} alkyl-d-glyconamides (Mehlretter *et al.*—*J. Am. Oil Chemists' Soc.* 29, 202). In like work on fatty acid soaps of guanidine it is recorded that the aqueous solutions are quite alkaline and the C_1 to C_2 homologs are stable (Neuzil & Talpin—*Bull. soc. pharm. Bordeaux* 90, 123). Stüpel (*Mfg. Chemist.* 23, 99) experimented with 15 combinations of six synthetic detergents. Combinations of large amounts of weak with small amounts of highly active detergents seem most advantageous.

Many of the mixtures produce detergent power greater than the sum of the individual components.

Some experimental work is on the manufacture of various synthetic detergents. In experimental sulfonation of castor oil the reaction at the double bond at 30° increases with use of increased amounts of sulfuric acid (Burton & Byrne—*J. Soc. Leather Trades' Chemists* 36, 309). At 50°, sulfonate seems to be formed by reaction at the methylene group adjacent to the double bond. All sulfonation reactions with chlorosulfonic acid seem other than at double bonds because the iodine value is not lowered. Good procedures are worked out for manufacturing alkyl benzene sulfonates (Davidson—*Ind. Chemist* 28, 198), and for converting the fraction of Scottish shale oil boiling at 180 to 330° to sulfonated detergents (Stewart & McNeill—*Oil Shale Cannel Coal Conf.* 2, 758). Olefins of iodine value 130 to 150 prepared by dechlorination of chlorinated paraffins are proposed for use in making alkyl sulfate detergents (Girelli & Siniramed—*Riv. Combustibili* 5, 296). Alkylbis (dimethylbenzylammonium bromides), detergent compounds similar to "Zephirol," are prepared from the corresponding dibromides (Stanek & Letovsky—*Collection Czech. Chem. Commun.* 15, 406). Other literature on synthetic detergent manufacture is on newly patented products or manufacturing techniques. For convenience of presentation these are listed below with the assignee, or with the patentee:

- Allied Chem. & Dye Corp.
Sulfonated alcohols (*U. S.* 2,571,286).
- Amanoy, C.
Sulfonated naphthalenes (*Fr.* 971,988-90).
- Am. Cyanamid Co.
Guanidine sulfate (*U. S.* 2,567,676-7). Aliphatic amido propyl quaternary ammonium salts (*U. S.* 2,589,674). Reaction products of polyalkylene oxide polymers and dimerized fatty acids (*U. S.* 2,606,199). Reaction products of polyethylene glycols with sulfur dioxide addition product of a tertiary amine (*U. S.* 2,606,202). Alkylol-substituted aliphatic guanidinium *N*-alkylol aliphatic carbamates (*Brit.* 654,163).
- Anglo-Iranian Oil Co.
Reaction product of polymethylene sulfides (by-product of H₂SO₄ petroleum treatment) with alkyl halides (*Brit.* 649,135). Sulfated distillation cuts of shale oil (*Brit.* 657,598).
- Arkansas Co., Inc.
Fatty acid-alkoxy polyglycol aliphatic amine combinations (*U. S.* 2,593,413, 2,596,985).
- Armour & Co.
N-Aliphatic morpholines (*U. S.* 2,597,260).
- The Atlantic Refining Co.
Alkaryl sulfonates of low cloud point (*U. S.* 2,615,847). Addition of lecithin to above to reduce tack (*U. S.* 2,617,772).
- Atomix, Inc.
Combination of synthetic detergents and resins (*U. S.* 2,566,716).
- I. G. Farbenind. A.-G.
Sulfochlorinated products of hydrocarbons derived from petroleum, coal, bitumens, etc. (*Brit.* 676,857). Alkylated pyrrolidines (*Ger.* 805,521, Cl. 12 p.).
- Bauer, E.
Fatty acid esters of 4-ethanolmorpholine (*U. S.* 2,575,041).
- Bersworth, F. C.
Polyethylene polyamino acid compounds (*U. S.* 2,564,092).
- California Research Corp.
Esters of alkanephosphonic acids (*U. S.* 2,587,340). Addition of celluronic acid to alkaryl sulfonate to increase detergency (*U. S.* 2,589,190, 2,590,613). Neutralizing and spray drying solutions of organic sulfonic acid (*U. S.* 2,594,690, 2,594,875). Combinations of inorganic salts and synthetic detergents (*U. S.* 2,610,950).
- Ciba Ltd.
Improving synthetic detergents by additions of diimidazoles (*U. S.* 604,454) or amino-coumarins (*U. S.* 2,610,152). Reaction products of hydroxyalkyl derivatives of fatty acid amides with alkylamines (*Brit.* 657,422).
- Colgate-Palmolive-Peet Co.
High-molecular derivatives of piperazine (*U. S.* 2,574,407). Liquid anionic-dialkylolamide detergent (*U. S.* 2,607,740-1). Neutralizing sulfonated products (*Brit.* 666,206).
- Kelly, D. F.
Aconitic acid (intermediate in preparation of detergent) (*U. S.* 2,566,172).
- Creditanstalt-Bankverein
Sulfochlorination of mineral oil (*Austrian* 165,675).
- Detrex Corp.
Special mixtures of triethanolamine oleate and monoethanolamine (*U. S.* 2,576,419).
- Dow Corning Corp.
Silylphenoxy alcohols (*U. S.* 2,584,751). Trimethylsilylphenoxy esters (*U. S.* 2,584,752).
- Dugnami, A.
Mixtures of sulfuricinoleate with hydrocarbon and inorganic salts (*Ital.* 462,459).
- Durand & Huguenin A.-G.
Mixtures of alkylaryl sulfonic acid salts and trialkyl phosphate (*Swiss* 276,117).
- E. I. duPont de Nemours & Co.
Polyfluoroalkanic acids (intermediates for preparation of detergents) (*U. S.* 2,559,629). Polyfluorinated acyl peroxides (*U. S.* 2,559,630). Polyfluoroalkyl hydrogen sulfates (*U. S.* 2,559,751-2). Quaternary ammonium salts of high-molecular polymetaphosphoric acid (*U. S.* 2,592,273).
- Emulsol Corp.
Sodium salt of sulfate of fatty acid amide of isopropanolamine (a shampoo) (*U. S.* 2,588,197).
- Farbwerke Hoechst Meister Lucius & Brining
Reducing hydroscopicity of sulfonic acid products by addition of sodium sulfate (*Ger.* 840,543, Cl. 12a).
- Fujiwara, M. & Asano, T.
Mixture of fatty alcohol sulfonates, saponin, phenol, and incompletely saponified rosin (*Japan* 3735 ['50]).
- Garner, P. J. & Short, H. N.
Sulfonated olefin-containing hydrocarbons (*U. S.* 2,587,990).
- General Aniline & Film Corp.
2-(Alkylcarbamyloxy)-alkylamines (*U. S.* 2,556,146). Carbamate-quaternary ammonium compounds (*U. S.* 2,585,326). Mixture of thiourea and nonionic detergents (*U. S.* 2,601,329).
- General Electric Co.
Lithium salts of 3-thia-7,7-dimethyl-7-(trimethylsiloxy)-7-silafatty acid (*U. S.* 2,583,322).
- Hart Products Corp.
Polyoxyalkylene ethers (*U. S.* 2,588,771).
- Imperial Chem. Ind. Ltd.
Mixtures of anionic detergents and alkali metal carboxymethyl cellulose (*U. S.* 2,583,492, 2,603,605).
- Industrial and Commercial Detergents Ltd.
Special quaternary ammonium halides for bottle washing (*U. S.* 2,599,127).
- Ito, S.
Removing sodium sulfate from fatty alcohol sulfonates (*Japan* 173,079 ['46]).
- M. W. Kellogg Co.
Sulfation of olefins (*U. S.* 2,573,730).
- Ki, K.
Sulfonation of sperm oil (*Japan* 3635 ['50]).
- Kyodo Chem. Co.
Sulfonation of sperm oil (*Japan* 885 ['51]).
- Lech-Chemie Gersthofen
Sulfonated montan wax (*Ger.* 822,687, Cl. 12a).
- Lever Bros. & Unilever Ltd.
Sulfonation of alkyl aryl hydrocarbons (*Brit.* 669,899).
- LIAS Ölschiefer-Forschung-G.m.b.H.
Purifying sulfonic acids (*Ger.* 813,999, Cl. 12a).
- Lion Fats & Oils Co.
Continuous sulfonation (*Japan* 180,154 ['49]).
- Lubri-Zol Corp.
Sulfurized derivatives of alkyl diphenyl oxide sulfonic acids (*U. S.* 2,555,370).
- McCabe Jr., J. M. & Mannheimer, H. C.
Benzyl(acylaminoethyl)-morpholinium chlorides (*U. S.* 2,562,384).
- Mathieson Chemical Corp.
Compositions of urea and quaternary ammonium compounds (*U. S.* 2,584,056-7).
- Monsanto Chemical Co.
Sulfonation of organic compounds (*U. S.* 2,572,605) alkylene oxide condensation products of hydroxy, carboxyl, amino, and mercapto compounds (*U. S.* 2,586,767, 2,594,257-8, 2,594,421, 2,594,431, 2,594,453). Trichlorocyanuric acid in combination with alkaline salts (*U. S.* 2,607,738).

- Nateon Industries, Inc.
Acid shampoo of lauryl sulfate, ammonium chloride and sorbitolborate (*U. S.* 2,599,665).
- J. B. Niederl & Associates, Inc.
Unsymmetrical quaternary ammonium alkyl sulfates (*U. S.* 2,569,326).
- Nippon Mining Co.
Sulfonated spindle oil (*Japan* 3737 ['50]).
- N. V. Bataafsche Petroleum Maatschappij
Removal of free sulfuric acid from sulfonated alkenes (*Brit.* 652,161). Alkylated aromatic sulfonic acids (*Brit.* 661,383). Concentration of sulfonate detergents (*Brit.* 662,466, *Dutch* 68,571). Secondary sodium alkyl sulfates (*Dutch* 68,572).
- Petrolite Corp. Ltd.
Carboxyl-containing xylene-soluble resin derivatives (*U. S.* 2,571,120). Oxyethylated derivatives of esters of tricinolein (*U. S.* 2,576,285). Hydroxalkylated derivatives of allyl polymers (*U. S.* 2,593,276).
- Procter & Gamble Co.
Fatty ester-amide sulfonates (*U. S.* 2,584,701, 2,604,481).
- Process Chemicals Co.
Preparations from fatty acids, hydroxylalkylamines and polybasic acids (*U. S.* 2,599,391).
- Purex Corp. Ltd.
Deaeration and drying of sulfonated detergents (*U. S.* 2,606,156).
- Ritter, J.
N-Substituted amides (*U. S.* 2,573,673).
- Rohm & Haas Co.
Reaction products of polyoxyethylene glycol and alkyl aromatic halides (*U. S.* 2,596,091-3).
- Rosenfeld, M. & Pickett, C. F.
Mixture of diethylene triamine oleate and condensation product of diethylene triamine and diacetone alcohol (*U. S.* 2,616,856).
- Seifenfabrik Hoehdorf A.-G.
Improved alkylaryl sulfonates (*Swiss* 272,814). Improved fatty sulfonates (*Swiss* 273,375).
- Sharples Chemicals, Inc.
Reaction products of alkylphenols, tertiary amines, and epichlorohydrin (*U. S.* 2,547,965).
- Shell Development Co.
Stabilized aqueous solutions of sodium secondary alkyl sulfates (*U. S.* 2,603,606).
- Soc. anon d'innovations chim. dite: Sinnova on Sadie
Quaternary ammonium compounds from higher arylsulfonic acid esters (*Brit.* 673,842, 674,953; *Fr.* 965,159-60, 965,162-3). Sulfonated fatty acid condensates with pinene, abietic acid, or terebenthine (*Fr.* 973,288).
- Soc. carbochimique
Polyoxyethylene derivatives of naphthenic acid (*Brit.* 670,153).
- Soc. produits chimique L'Ariege
Mixture of sodium salt of sulfonated paraffin and polyethylene oxide (*Fr.* 961,581).
- Soc. produits chimiques industriels et vitrioles
Sulfonation of oils (*Fr.* 973,676).
- Sowa, F. J.
Special quaternary ammonium salts (*U. S.* 2,580,473).
- Stamford Chemical Co.
Combinations of sulfonated coconut fatty oil amide, aryl-alkyl sulfonate, sulfonated alcohol and sodium aryl sulfonate (*U. S.* 2,581,677).
- Standard Oil Co. of Indiana
Alkylation process (*U. S.* 2,564,072). Mixture of mahogany soap, rosin soap, and naphtha compounds (*U. S.* 2,607,741).
- Standard Oil Development Co.
Alkali salts of sulfonated propylene polymers (*U. S.* 2,600,415).
- Swift & Co.
Monofatty acid esters of alkylolamine (*U. S.* 2,586,496).
- Tomiyama, S. & Takao, S.
Sulfonated alkylated aromatic hydrocarbons (*Japan* 280 ['51]).
- Universal Oil Products Co.
Sulfonation of alkyl aromatic hydrocarbons (*Brit.* 664,577, 666,642-3; *U. S.* 2,573,675). Alkyltoluenes for conversion to sulfonated detergents (*Brit.* 669,657). Unsymmetrical diarylalkanes useful for conversion to detergents (*U. S.* 2,557,505).
- Vallermaud, J. P. A.
Alkylolamine esters of the fatty acids of murumuru butter alone or mixed with lauric acid (*Fr.* 971,322).
- Victor Chem. Works
Reaction product of lauric acid, phosphoric acid, and ethylene oxide (*U. S.* 2,586,397).
- Wyandotte Chemicals Corp.
Mixture of alkylaryl sulfonate and hydroxyethylcellulose (*U. S.* 2,602,781).

Normal soaps have been mixed with other detergents to improve their performance with salt and hard waters. Soap bars of this type developed for the armed services contain tallow soap, "Sorapon SF," "Nekal A," "Aerosol AY" and carboxymethylcellulose (Jelinek *et al.*—*Soap Sanit. Chemicals* 28, 42). In two patented processes for making such soaps, fatty acids (Sinnova Sadie—*Fr.* 969,622), and tall oil (Dobbelmann & van Loon—*U. S.* 2,571,639), respectively, are mixed with sulfonated hydrocarbons and the saponifiable materials are saponified. The innovation in preparation of a translucent plastic detergent for use with hard water deals with the choice of anionic synthetic detergent and the particular ratio of detergent, soap, and water used (Wood—*U. S.* 2,580,713). A gel-like detergent that may be used without water contains oleic acid, ammonium hydroxide, and a petroleum fraction boiling between 130 and 190° (Guastavino—*U. S.* 2,567,999). One in flake form comprises a mixture of soap, nonionic detergent, and borax (Safrin & Volz—*U. S.* 2,595,300).

Some communications on detergents pertain to inorganic material. Glassy alkali phosphates for detergent use made with 65-67% (Mackenzie—*U. S.* 2,574,047), and with 40-50% (Beiley & Razee—*U. S.* 2,568,110) P₂O₅ content, respectively, are patented. Means for preparing trisodium phosphate in glassy form patented by Guetierrez (*Span.* 194,253), pertain to the method of cooling the molten product. A special mixture of potassium metaphosphate and sodium pyrophosphate with low solubility is added to soap to serve as an abrasive (Munter—*U. S.* 2,581,278). Hizer (*U. S.* 2,622,068) in making a built soap adds slowly hydrating anhydrous sodium tripolyphosphate to an aqueous solution of the soap. A soap made by Dobbelmann & Bertram (*U. S.* 2,571,690) is coated with sodium fluoride, or sodium ferrous cyanide. These dissolve first to form nonionized compounds with cations of hard water thus preventing the formation of insoluble soaps. A sodium aluminum silicate obtained by treating certain clays with mineral acid is patented for use in soaps (Kuwada & Sugawara—*Japan* 1119 ['51]). A mixture of hollow beaded alkali tetraborates and nonionic polyglycol ethers is patented as a detergent composition (Sanders—*U. S.* 2,623,856).

Almost simultaneous reports from two laboratories reveal that magnesium salts may act like builders for synthetic detergents (Stüpel—*Fette u. Seifen* 54, 321; Jordan *et al.*—*Am. Dyestuff Repr.* 41, 413).

A study of the calcium sequestering action of several phosphate builders indicates that alkalies, containing calcium precipitating ions, reduce the effect of the builders (Dormuth—*Proc. Chem. Specialties Mfg. Assoc.* 1951, 114). Among trisodium phosphate, sodium carbonate, and sodium silicate, the trisodium phosphate exhibits the greatest adverse effect.

Water-insoluble ethyl cellulose is added to soap to retard ready solution of the soap (McDonald—*U. S.* 2,587,637, 2,588,264). The ethyl cellulose is dissolved in an organic solvent and mixed with aqueous solution of partial glycerol ester of a fatty acid to aid in incorporating it into the soap. The solubility of cellulose derivatives used as soap ingredients is increased greatly by incorporating them with aluminum polyborate (Funderburk—*U. S.* 2,579,381). Cellulose derived soap adjuncts are added to oily soapless detergents to cause gelling and permit drying (Pollok—*U. S.* 2,603,605). Jarrell & Trost (*Soap Sanit. Chemicals* 28, No. 7, 40; No. 8, 50) demonstrate the use of carboxymethylcellulose as a sizing for textiles. This sizing aids laundering and is superior to starch as a size. Cellulose, starch, or dextrin oxidized with nitrogen dioxide is said to be superior to carboxymethylcellulose as a soap ingredient (Nederlandsche Org. Toegepast-Natuurwetenschappelijk Onderzoek ten behoeve van Nijverheid Handel en Verkeer—*Dutch*—69,883).

Other materials are added to detergents for various purposes. Aluminum polyborates are added to powdered detergents (Funderburk—*U. S.* 2,579,380), and magnesium compounds to cleansing powders (Bradford & White—*U. S.* 2,589,330) to

inhibit caking. Soap is dedusted by addition of hygroscopic alkyl phosphate compounds (Bodman—*U. S. 2,592,535*). Various fluorescing dye-like compounds are patented as suitable optical bleach ingredients for detergents (Ciba Ltd.—*Swiss 272,256, U. S. 2,604,454*, Krahler—*U. S. 2,600,004*, J. R. Geigy A.G.—*Swiss 277,530-5, Swiss 278,451-5, Brit. 654,028*, Wallace—*U. S. 2,595,030*, Witte—*U. S. 2,581,059*, Wheelock—*U. S. 2,616,855*). Nieuwenhuis (*Wasindustrie 1*, No. 5, 12) reports that the fluorescent optical bleaches act as corrosion catalysts on copper and brass parts of washing machines. The corrosion is somewhat inhibited when carboxymethylcellulose is present. In other communications on corrosion by detergents, sodium silicate is recommended as the inhibitor. In these, data are presented on the corrosiveness of phosphate compounds on magnesium die casting alloy (Hazel—*J. Electrochem. Soc. 98*, 273), and on copper, zinc and brass (Bacon & Nutting, Jr.—*Ind. Eng. Chem. 44*, 146). Robinson (*Soap Sanit. Chemicals 28*, No. 1, 34) recommends soluble silicates with a 2:1 ratio of silicon dioxide: sodium oxide to retard corrosion of metals and vitreous enamels by alkali carbonates and polyphosphates in the detergent formulations. The presence of sodium metasilicate inhibits the tarnishing of silverware caused by polyphosphates of dishwashing detergents (Bacon & Nutting, Jr.—*Ind. Eng. Chem. 44*, 150). Beryllium oxide inhibits the corrosive action of polyphosphates on aluminum (Schaeffer—*U. S. 2,618,604*). Various high molecular weight organic amino compounds are used with detergents to inhibit corrosive action on copper or brass (Schaeffer—*U. S. 2,618,605-8*). Sodium beryllates, zincates, and aluminates are added to dishwashing detergents to inhibit deteriorative action on vitreous and ceramic surfaces (Bacon & Otrhalek—*U. S. 2,575,576*). The incorporation of small amounts of thiourea in a detergent mixture of nonionic polyglycol ether and alkali compounds stabilizes the color (Sanders & Maxey—*U. S. 2,601,329*). The yellowing of triethanolamine compounds is inhibited by the presence of a small amount of sodium sulfite (Wolff—*Fette u. Seifen 54*, 142). Zinc chloride is added to soap to improve solvation of resinous, albuminous, and glue-like substances (Lopez—*Span. 192,368*, Hashimoto—*Japan 597* ['51]). The communications on germicidal detergents pertain to the use of halogenated diphenylmethane (Hopf—*Fette u. Seifen 52*, 89; Depenning—*Indian 44,415*), a formaldehyde derivative (Hartge—*Alchimist 5*, 315), and iodine (Taub—*U. S. 2,599,140*), respectively, as the germicidal ingredient.

A newly patented skin soap contains about 50% formaldehyde-treated soybean meal as a partial substitute for the soap (McKinney & Cowan—*U. S. 2,610,153*). A shampoo of low soap content contains sodium alginate and specially treated clay as major ingredients (Sagawa—*Japan 2671* ['50]). Sodium alginate is said to improve sudsing and suds retention of soap (Watanabe—*J. Chem. Soc. Japan Ind. Chem. Sect. 52*, 308). Presence of rubber compounds in soap is also said to improve foam retention of its solutions (Grüner—*Ger. 807,423*). Other partial or complete substitutes for soap described in new patents or other literature are silk fibroin (Nomura—*Japan 3733* ['50]), alkali-treated shaved grass (Lai—*Austrian 171,736*), calcium salt of saponin (Kasai—*Japan 2390* ['50]), specially treated bentonite (Balbo—*Ital. 453,963*), and a volcanic tuff of high adsorptive capacity (Berecz—*Hung. 134,024*).

Some detergents are formulated for specific uses. A dishwashing detergent comprises a mixture of inorganic detergent with a minor portion of *N*-palmitoyl-*N*-cyclohexyl laurate (Sanders—*U. S. 2,617,607*). The formation on glassware of unsightly films due to hard water is inhibited by the presence of alkali gluconate in the washing detergent (Dvorkovitz & Hawley, Jr.—*U. S. 2,584,017, 2,615,846*). A detergent for floors and automobile driveways contains mahogany soap, rosin soap, and certain petroleum distillates (Arkis & Walker—*U. S. 2,607,741*). Two compositions for cleaning and rust-proofing metals contain petroleum hydrocarbon and triethanolamine soap, and, respectively, heavy metal soaps (Smith—*U. S. 2,587,777*) and pine oil (Campbell—*U. S. 2,583,165*). A general cleaning mixture is a solution containing ammonium hydroxide, ethanol, ether, and marseille soap (Spampatti—*Ital. 460,127*). A mixture for removing paint and oil stains from hard surfaces comprises vegetable oil, lye, benzene, mineral powder, and *p*-dichlorobenzene (Egawa—*Japan 686* ['50]). A mixture of silicone oil, volatile hydrocarbon and cationic detergent is intended for simultaneous cleaning and polishing (Baer & Conannon—*U. S. 2,584,413*). An acid cleaner for dissolving a film of coagulated milk protein from dairy equipment comprises organic acids, sodium bisulfate, and dodecylbenzene sodium sulfonate (Brissey & Young—*U. S. 2,593,259*). An adhesive liquid composition suitable for use in electrostatic dust pre-

cipitators is a mixture of nonionic detergents and oily hydrocarbons (Swiss & Hewitt—*U. S. 2,597,201*).

Many communications provide general economic, descriptive, promotional, or manufacturing information. For convenience of presentation these are tabulated under the subject treated:

Manufacture of soap:

Continuous processes (Habicht—*Fette u. Seifen 54*, 217; Boyle—*Soap, Sanit. Chemicals 28*, No. 4, 47). Kettle house operation (Boyle—*Ibid.* No. 5, 44). Soap plant insulation (Leaver & Lawrence—*Ibid.* No. 7, 79). Spray drying soap (Anon.—*Ibid.* No. 5, 67). Coconut oil liquid soap (Smith—*Am. Perfumer Essential Oil Rev. 58*, 457). Selection of soap stock (Mulani—*Proc. Oil Technol. Assoc. India*, 6, 66; Aggarwal—*Indian Soap J. 17*, 163). Recommendations for elimination of spot formation in soap bars. (Anon.—*Seifen-Öle-Fette-Wachse 77*, 591). Glycol ethers as soap additives (Rordorf—*Ibid.* 541).

Manufacture of synthetic detergents:

General reviews of products and manufacture (Verheggen—*Ing. Textile No. 382*, 19; Stüpel—*Soap Perfumery & Cosmetics 25*, 162, *Mitt. chem. Forsch. Inst. Ind. österr.* 5, 53, *Angew. Chem.* 63, 461, S.F.V. *Fachorgan Textilver.* 7, 154, 219, *Erdöl u. Kohle 4*, 687). Synthesis of alkylaryl sulfonates (von Segesser & Stüpel—*Chimia (Switz.) 6*, 84). Continuous production of synthetic washing agents (Stüpel—*Fette u. Seifen 54*, 455). Sulfochlorination of synthetic fatty acids (Manneck—*Seifen-Öle-Fette-Wachse 77*, 448). Synthesis and properties of alkanic acids (Seher—*Fette u. Seifen 54*, 544). Detergents from petroleum (Birch—*J. Inst. Petroleum 38*, 69). Sulfated oils and fats (Griffiths—*Paint, Oil and Color J. 121*, 755). Description of a sodium alkyl sulfate plant (Tiratsoo—*Petroleum Refiner 31*, No. 3, 142).

General information on synthetic detergents:

Classification and nomenclature (Metz—*Chem. Listy 46*, 57). Physical properties of detergents based on condensates from ethylene and propylene oxides (C. Vaughn *et al.*—*J. Am. Oil Chemists' Soc.* 29, 240; Kawamura & Minami—*J. Oil Chemists' Soc. Japan 1*, No. 1, 26). Synthetic detergents used in industrial laundries (Planeta—*Przemysl Chem. 31*, 29). Use of polyethylene glycols in the textile industry (Marcou—*Teintex 17*, 421). Microbiocidal properties of amine cation detergents (Dvorkovitz—*Soap, Sanit. Chemicals 28*, No. 5, 41).

General information on detergents:

Statistical and promotional information for soap usage (Peet—*Soap Sanit. Chemicals 28*, No. 8, 46). Colloid science aspects of detergency (Lawrence—*Chemistry & Industry 1952*, 183). Dissolving capacity of soap (Palit & Venkateswarlu—*Indian Soap J. 17*, 12). Condition of detergents in aqueous solution with regard to effect on the washing process (Kling—*Melliand Textilber.* 30, 412). The role of foam in detergent action (Stevenson—*J. Soc. Dyers Colourists 68*, 57). Requirements of cleansers for use in the food industry (Benk—*Seifen-Öle-Fette-Wachse 77*, 589). Public health regulations governing institutional dishwashing (Cain—*Can. J. Public Health 42*, 471). Nonionic emulsifiers in industrial cleaning (Pollack—*Metaloberfläche 46*, 79). Detergents in industry (Hagge—*Fette u. Seifen 51*, 12). Cleansers for automotive fleet cleaning (Weller—*Soap Sanit. Chemicals 28*, No. 11, 44).

Special soaps and detergents:

Medicated and medicinal soaps (Rao—*Indian Soap J. 17*, 155). Detergent-sanitizers (Lazarus—*Soap Sanit. Chemicals 28*, No. 2, 139). Review of germicidal soaps (Hopf—*Fette u. Seifen 54*, 89). Hand cleaners (Smith—*Am. Perfumer Essential Oil Rev. 59*, 213). New dentifrices (Lesser—*Soap Sanit. Chemicals 28*, No. 1, 38). Glass cleaners (Lesser—*Ibid.* No. 9, 46). Metal cleaners (Lesser—*Ibid.* No. 10, 42). Steam cleaners (*Ibid.* No. 4, 50). Solvent-detergents (Davidsohn—*Soap, Perfumery & Cosmetics 25*, 724).

Miscellaneous soap and cleaning chemicals:

Glassy phosphates (Mackenzie—*Soap Sanit. Chemicals 28*, No. 11, 42). Use of ethylenediamine tetracetic acid in detergents as a metal complexing agent (Zussman—*Ibid.* No. 11, 79). Reviews on use of optical whiteners or bleaches in detergents (Schlachter—*Fette u. Seifen 53*, 735; Uhl—*Ibid.* 53, 545; Widaly—*Seifen-Öle-Fette-Wachse 77*, 471). Soap perfume fixatives (Smith—*Am. Perfumer Essential*

Oil Rev. 59, 57). Dichloro-*sym-m*-xylenol as a bactericide in toilet soap (Gemell—*Mfg. Chemist* 23, 63). 2,2-Di-droxy-3,5,3',5'-tetrachloro-diphenylmethane as a bactericide in toilet soap (Maglio & Hannegan—*Soap Sanit. Chemicals* 28, No. 11, 38). Anti-irritant ingredients for soap (Carrie & Neuhaus—*Z. Haut- u. Geschlechtskrankh.* 7, 41). Laundry chemicals (Harwood & Wagg—*Rpts. on Prog. in Applied Chem.* 36, 211).

Analysis of detergents:

British standard methods for analysis of soaps (*Brit. Standard* 1715). Reviews on detergents analysis (Stüpel—*Chem. Ztg.* 76, 252, Resuggan—*Milk Ind.* 31, No. 1, 62; No. 2, 67). Infrared analysis for functional groups in surface-active compounds (Delsemme—*Mededel. Vlaam. Chem. Ver.* 13, 152).

Evaluation of detergents:

Technical problems of evaluation (Neu—*Seifen-Öle-Fette-Wachse* 75, 285). Cotton detergency testing (Lambert—*Proc. Chem. Specialties Mfrs. Assoc.* 1951, 103). Review of detergency test based on the use of radioisotopes (Armbruster & Ridenour—*Soap Sanit. Chemicals* 28, No. 6, 83). Use of field tests in evaluating detergents (Minkin—*Public Health Repts. U. S.* 67, 650). Measurement of wetting values (Guastalla *et al.*—*Bull. mens. ITERG* 6, 111). Review of fiber damage by detergents (Lindner—*Seifen-Öle-Fette-Wachse* 77, 612). In-vivo and in-vitro evaluation of antibacterial properties of antiseptic soaps (Gump & Cade—*Soap, Sanit. Chemicals* 28, No. 12, 52). Phenol coefficients of five quaternaries (Shields *et al.*—*Ibid.* No. 4, 153). Antibacterial properties of cationic and anionic detergents (Johnson *et al.*—*Am. J. Pub. Health* 42, 801). Determining efficiency of soaps containing hexachlorophene (Cade—*Am. Soc. Testing Materials, Papers on Evaluation of Soaps and Detergents Spec. Tech. Pub. No.* 115, 33).

Toxicity of soap and detergents:

Tests used in toxicological investigations on soaps (Barail—*Soap Sanit. Chemicals* 28, No. 12, 48). Toxicity testing and legal liability on shampoos (Shelanski—*Ibid.* 28, No. 1, 32). Detergents and the human skin (Nonaka—*J. Oil Chemists' Soc. Japan* 1, 67). Surface-active agents and the eye (Draize & Kelley—*Drug & Cosmetic Ind.* 71, 36).

Glycerol:

Production and uses for glycerol (Pattison—*Soap Sanit. Chemicals* 28, No. 2, 46, Freitag—*Seifen-Öle-Fette-Wachse* 77, 523).

CHEMICAL ANALYSES FOR DETERGENTS. A rapid method for estimating the amount of fatty acids in soap is based on the index of refraction of a bromonaphthalene solution of the fatty acids freed from the sample (Steinchen—*Seifen-Öle-Fette-Wachse* 77, 593). The fat content is estimated from the refractive indexes of the solution and of the fats with use of an equation designed for that purpose. Two methods for determining the amount of oleate soap in very dilute solutions are, respectively, based on using the solution for titrating a definite amount of aqueous cetyltrimethyl ammonium bromide, and on determination of spread on a continuous-recording surface balance containing 25% ammonium sulfate solution in 0.01N sulfuric acid (Glazer & Smith—*Nature* 169, 497). A method for determining rosin acids in fatty acids in soap analysis is based on the acid-catalyzed selective esterification of a large sample, removal of the acid catalyst, titration of the unesterified rosin acids, and use of an empirical correction factor (Herrlinger & Compeau—*J. Am. Oil Chemists' Soc.* 29, 342).

A new free alkali determination for soap depends on soap being insoluble in 14% salt solution (Accinelli—*Oleagineux* 7, 403).

Methods suggested for analysis of soaps for tetrasodium pyrophosphate content, described by Kaufmann & Neu (*Fette u. Seifen* 53, 690) include qualitative detection by color reactions with copper sulfate or hexamine cobalt chloride, and quantitative determination as zinc salt, and also by conversion to orthophosphate by boiling with nitric acid and determination of the latter by the German standard procedure. A method for differentiating poly- and metaphosphates is based on metaphosphates precipitated by quaternary ammonium compounds being insoluble in excess of precipitating agent whereas the precipitates of polyphosphates dissolve in excess of the precipitating reagent (Neu—*Fette u. Seifen* 54, 397). A modification of this method for detection of hexametaphosphate makes use of *m*-phenyldiamine-HCl, 1,2,4-diaminophenol-HCl, or *o*-toli-

dine in place of the quaternary ammonium compounds as precipitants (Dewald & Schmidt—*Z. Anal. Chem.* 136, 420).

The methods for determination of sodium carboxymethylcellulose in household detergents are based on the green color formed by reaction of anthrone with carbohydrate materials in sulfuric acid solution (Black—*Anal. Chem.* 23, 1792, Samsel & DeLap—*Ibid.* 1795). The color intensity is measured with a spectrophotometer.

An analysis of needle-like crystals which separated on the surface of commercial laundry soaps has indicated that they are composed of oleic acid containing small amounts of oxy-acids and saturated lower fatty acids (Tsuchiya & Ohkubo—*J. Nippon Oil Technol. Soc.* 4, 1). A series of analyses during natural drying of soap containing some salt and sodium carbonate has shown that the sodium carbonate wanders to the surface of the samples and salt to the center; during forced artificial drying the sodium carbonate concentrates intermediately between surface and center (Musso—*Olii minerali, grassi e saponi, colori e vernici* 28, 62).

A method of quantitative determination of relative wear of soap bars is based upon the measurement of thickness of samples before and after subjecting them to wear by a sponge and warm water (Masters—*J. Am. Oil Chemists' Soc.* 29, 412).

A scheme for detecting the various substances in washing compounds comprises extraction with methanol, testing solutions of the extract with aluminum acetate which precipitates anionic substances; with silicotungstic acid which reacts with nonionic substances; observation under ultraviolet light after reaction with strong inorganic acid for detection of "Nekals" alkylnaphthols, and alkylnaphthalenes; and reaction with permanganate, which detects phenylmepasinsulfonate in the presence of Mersols (Wurzschmitt—*Angew. Chem.* 62, 40). An analytic method for sulfate esters is based on determination of sulfate after hydrolysis and determination of average molecular weight (Gauthier & Mazau—*Ann. pharm. franc.* 9, 678). A modification of the *p*-toluidin technique for determination of alkylaryl sulfonates pertains to separation of the precipitated complex converting it to free sulfonic acids by cation exchange, and then titrating (Wickbold—*Fette u. Seifen* 54, 394). Two methods developed for extraction of commercial sodium dodecylbenzenesulfonate from food contaminated with the cleaning preparation are based on extractions, respectively, with alcohol and with 7N sodium hydroxide (Harris & Short—*Food Technol.* 6, 275). The detergent is determined by forming complexes with bromophenol blue and cetyltrimethyl ammonium bromide, or with methylene blue. A procedure for determination of cetyl sulfate in solution is based on forming a complex with methylene blue, separation of this by absorption on quartz, elution, and measurement colorimetrically (Edwards *et al.*—*Analyst* 77, 205).

A method for testing whether the quaternary ammonium compounds present in dishwater are at concentrations adequate for bactericidal efficiency is patented (Conklin—*J. Milk Food Technol.* 15, 27, U. S. 2,599,697). The procedure depends on appearance of violet color on reaction with bromophenol reagent. A gravimetric method for quaternary ammonium compound is based on precipitation with ammonium reineckate (Wilson—*J. Assoc. Offic. Agr. Chemists'* 35, 455). The method for titrating alkaline earth ions with ethylenediaminetetraacetic acid in the presence of Eriochromschwartz T as the indicator is reversed to determine ethylenediaminetetraacetic acid or Trilon B in detergent compositions (Kerkow—*Z. Anal. Chem.* 133, 281).

"Leonil-O" detergent can be qualitatively and quantitatively determined in dilutions as low as one in one hundred thousand by a reddish-brown precipitate formed with a reagent prepared by condensing resorcinol with glucose in the presence of sulfuric acid (Haakh *et al.*—*Melliand Textilber.* 32, 699). Leonil-O is a condensation product of one mole of sperm oil alcohol and about 30 moles of ethylene oxide.

PHYSICAL CHARACTERISTICS. Vold *et al.* (*J. Phys. Chem.* 56, 128) has developed x-ray spectrometer patterns of a series of the saturated sodium soaps that permit identification of the crystal modifications of the soaps. The existence of a large number of modifications is confirmed. In this work, water up to 3% is involved in the structure, probably as a solid solution. X-ray technique also has been used to determine the unit-cell dimensions of potassium soaps at 25 and 75° (Lomer—*Acta Cryst.* 5, 11). The data indicate three distinct crystalline phases. Transition temperatures and unit-cell dimensions are recorded for all the phases. Sorption-desorption isotherms at 12 and 2° have been obtained for the three forms of sodium- and potassium palmitates, using water vapor as the adsorbate (Milligan & Draper—*J. Phys. Chem.* 56, 123).

Various aspects of foaming or sudsing of detergent solutions have been studied. Vallee (*Textex* 17, 235) demonstrates that good foam-producing detergents are not necessarily good detergents. Peters (*Angew. Chem.* 64, 586) has designed apparatus which permits simultaneous comparative determination of the dynamic and static foaming power of 30 tests. The foams are produced by gas bubbles. Of three new methods for determining consistency of foam of detergents two are based on the torque required to cause slow rotation of a cylinder or paddles in the foam and the other depends on resistance to a plunger passing through the foam (Scott & Thompson—*J. Am. Oil Chemists' Soc.* 29, 386). Levaldi (*Compt. rend.* 234, 1287) has studied foaming of soap solution with regard to effect on the solution. His data show that foaming reduces concentration and modifies the chemical composition of the soap solution, but the pH remains constant.

Long chain alcohols increase the foam volume obtained from dilute sodium dodecylsulfate solutions and also make the stability of a film of the solution equal to that of sodium oleate solution (Matalon—*J. Soc. Cosmetic Chemists'* 2, 122). This is interpreted to indicate that alkyl sulfate solutions can be brought to the same level of surface activity as normal soap. Addition of sodium ricinoleate to dilute sodium oleate solutions lowers foam volume whereas sodium abietate has no effect on foaming capacity of sodium oleate solutions (Shkodin & Tikhomirova—*Kolloid Zhur.* 14, 279). Wide differences obtained for the foaming capacity of nonionic detergents at various temperatures are explained on the basis of altering the solubility (Fineman *et al.*—*J. Phys. Chem.* 56, 963).

Viscosity tests on alcohol-water solutions of soaps reveal that additions of alcohols to aqueous solutions cause the viscosity to increase to a maximum and then decrease (Bose—*J. Indian Chem. Soc.* 29, 43). It is assumed that alcohols arrange themselves between oleate ions and water. Specific conductance-temperature curves of the alcohol-water soap solutions are straight lines at the lower alcohol concentrations (*Ibid.* 135). A maximum rise in viscosity is also observed on addition of benzene to aqueous solutions of a polysoap, derived from poly-2-vinylpyridine and *n*-dodecyl bromide (Layton *et al.*—*J. Polymer Sci.* 9, 295, 509). The results are interpreted to mean that the polysoap molecules act as independent solubilizing units, but that their structure is changed by solubilizing the benzene in such a way as to affect their mutual interaction.

Syneresis of sodium oleate gels in pinene or xylene increases with decreasing temperature or decreasing concentration of the soap (Prasad & Sundaram—*Proc. Indian Acad. Sci.* 33A, 295, 305, 333, 339, 344). In case of xylene-toluene mixtures, syneresis seems to be additive, whereas with xylene-pinene there is a maximum of syneresis at 80% xylene-20% pinene. In tests on solubilizing water in xylene by C₁ to C₁₆ primary amines and oleyl amines, the dodecylamine *n*-butyrate, and the octadecylamine propionate dissolved most water, reaching 29 moles of water per mole of detergent (Palit & Venkateswarlu—*Proc. Roy. Soc., London*, A208, 542). Viscosity and freezing point data are reported on some of these systems.

Data on molecular weights determined in various solvents, viscosities of solutions, dielectric properties, changes of absorption spectra with concentration, effect of dyes on the absorption spectra, and density are recorded for polyoxyethylene alkyl ethers (Goto *et al.*—*Bull. Inst. Chem. Res. Kyoto Univ.* 25, 63; 26, 81, 82, 83; 28, 64, 65, 66). These data are discussed with regard to formation of solutions and development of micelles.

Powell and Alexander (*Can. J. Chem.* 30, 1044) have measured the electrophoretic mobility of oil droplets, the interfacial tension in the systems, and the gegen-ion adsorption in soap solutions. The data are discussed with regard to the electrokinetic theory and an estimate is made of the fraction of the gegen-ions which are bound to the droplet. This latter value is similar to that found by others for the spherical soap micelle. In similar work, Kling & Lange (*Kolloid-Z.* 127, 19) record electrophoretic behavior of pigment particles in detergent solutions. The ζ -potentials of lampblack and ferric oxide are raised considerably by anion-active detergents. Nonionics tend to lower mobility and eventually discharge particles.

Tests have shown that adsorption of either soap or detergent on cotton is almost entirely physical in nature, whereas adsorption on wool is both physical and chemical (Meader, Jr. & Fries—*Ind. Eng. Chem.* 44, 1636). Data from this work is discussed with regard to rinsing of soap and detergents.

A hydrolytic adsorption at the free surface of aqueous sodium lauryl sulfate solutions is demonstrated by pH measurements correlated with composition of the foam and by means of curves plotting surface tension versus pH at constant con-

centration and ionic strength (Cook & Talbot—*J. Phys. Chem.* 56, 412). Observations on adsorption of sodium ions from solutions of Aerosol OTN containing salt have indicated that the adsorbed species is undissociated sodium di-*n*-octyl sulfosuccinate (Judson *et al.*—*J. Chem. Phys.* 20, 519). The film characteristics, spreading pressures, of Nekal BX on salt solutions have been determined (Schäfer—*Kolloid-Z.* 124, 15).

Published data on soap micelles are interpreted with regard to a three-region concept in soap-water-electrolyte systems, monodispersity in micellar size, shape, and order, hydration, solubilization, and interaction in micellar soap systems (Phillipoff—*Discussions Faraday Soc. No. 11*, 96, 147). Magnesium C₈-C₁₂ sulfonates have been prepared and their critical concentrations for micelle formation are determined from conductance data (Lelong *et al.*—*J. Am. Chem. Soc.* 73, 5411). The data are similar to those of corresponding sodium salts. A method has been described for determination of dissociation of micelles of 1-dodecanesulfonic acid by use of the acid-catalyzed reaction between iodine and acetone (Kolthoff & Johnson—*Ibid.* 4563). The critical concentration for micelle formation of tall oil soaps increases and the degree of hydrolysis decreases with the number of double bonds in the soap molecules (Harva—*Acta Acad. Aboensis, Math. et Phys.* 17, No. 4, 130 pp.). In this work the properties of soaps of tall oil and rosin are compared with those of fatty soap. In mixtures of rosin soap and fatty soaps, those with critical concentrations of the same magnitude undergo mixed micelle formation, whereas where critical concentrations differ each component behaves independently of the other. The molecular weights of micelles of alkylbenzenesulfonic acid derivatives in aqueous solutions have been determined from light scattering data (Yurzhenko & Kucher—*Kolloid Zhur.* 14, 219). The weight and size data are discussed with regard to a steric hindrance that may hinder packing and agglomeration. The effect of acid or alkali is explained on the basis of altering solubility, and that of ethanol on a dehydrating effect. Change in streaming potential of soap sols is discussed with respect to change in form of the micelle (Thiele—*Kolloid-Z.* 125, 31). The change is reversible and is accomplished by changes in viscosity, turbidity, spinnability, and frothing capacity. Difference in orientation of C₁₄ and C₁₆ alkyltrimethylammonium bromides is explained on the basis of difference in size of the rod-like micelles formed (Backus & Scheraga—*J. Colloid Sci.* 6, 508). The C₁₄ micelles are considered too small to be orientated. A Fourier analysis of the x-ray diffraction of the micelles in sodium dodecyl sulfate solutions indicates that they are spherical (Brady—*J. Chem. Phys.* 19, 1547). Similar work on long chain hydrocarbon polyethylene oxide systems shows much disorder, but it is postulated that there is a transition of lamellae to cylinders to spheres when warm and lamellae to cylinders when cold (Schulman *et al.*—*Discussions Faraday Soc. No. 11*, 117).

Action of organic compounds on soap and phosphatide coacervates has been measured and the results explained on the basis of the distribution of the organic compounds between three sites: in the aqueous phase, parallel to the carbon chains in the soap micelle, and between the methyl end groups in the micelle (Booij & Mullen—*Proc. Koninkl. Nederland Akad. Wetenschap.* 54B, 273; de Jong & Weijzen—*Ibid.* 81; Booij—*Kolloid Z.* 125, 21; *Rec. trav. chim.* 71, 101). The effect of inorganic salts on alignment of the organic chains between parallel soap molecules is also discussed, and it is suggested that the biological activity of many substances can be understood from a distribution of these substances in the various possible places in a lipide system. The effects of inorganic salts and organic compounds on elastic-viscous soap systems have been recorded by de Jong *et al.* (*Proc. Koninkl. Nederland. Akad. Wetenschap.* 54B, 240, 291, 303, 317, 399). An equation is developed for representing the effects of concentration of salt, concentration of organic compounds, and temperature.

PERFORMANCE TESTS. A new experimental washing device for testing detergents is based on having soiled test cloths stretched on frames which act as fins of a stirrer, use of beakers to contain the wash solution, and means of regulating temperature (Peukert—*Fette u. Seifen* 54, 453). Harris (*J. Am. Oil Chemists' Soc.* 29, 110) has recommended adjustments in wash tests using the Terg-O-Tometer and Launderometer wash test methods so that they should produce comparable soil-removal data. New artificial soil mixtures for cloths used in evaluating detergents by washing tests have been proposed by Wagg (*J. Textile Inst.* 43, T515), Stüpel (*Fette u. Seifen* 54, 143) and Ringeissen (*Oleagineux* 6, 345; *Ind. Textile* 68, 38). In these reports reasons for choosing each ingredient comparison with other soils, and correlations with laundry trials on naturally soiled articles are included. A study to determine the

possibility of establishing "national standards" for soil removal as judged by soiled test cloths has indicated that this is not practical, because a single, soiled test piece does not adequately measure soil removal under all operating conditions (Mitchell—*Am. Soc. Testing Materials, Papers on Evaluation of Soaps, Detergents Spec. Tech. Pub. No. 115*, 3). Tests to compare artificially soiled nylon and cotton fabrics indicate that soil removal is much easier from the former (Segesser & Stüpel—*Textil-Rundschau* 7, 93). Work on standardizing or comparing different instruments for evaluating whiteness or cleanliness of washed test cloths is reported by Neu (*Fette u. Seifen* 54, 636) and Machemer (*Ibid.* 324).

Knowles, Jr. (*J. Am. Oil Chemists' Soc.* 29, 158) has used the Tergotometer wash test in investigations to evaluate the efficiency of washing agents for preventing deposition of lime soaps from hard water onto cotton fabrics. The tests did not give a realistic index of the extent to which synthetic detergents prevent firm deposition of the lime soap. An empirical method designed to classify detergents according to their power of preventing precipitation of lime soaps by hard water is based on the amount of detergent necessary to clarify a standard turbid solution of freshly precipitated magnesium oleate (Dupin & Reutenauer—*Bull. mens ITERG* 5, 519).

The new comparisons of methods for the evaluation of wetting of textiles have indicated that the hydrometer method is most desirable because it measures the rate of wetting (Reutenauer et al.—*Am. Dyestuff Repr.* 41, P25; Shapiro—*Ibid.* P16. In these reports equipment and method for modifications of the hydrometer wetting test are described. The wetting tests have been investigated on greige cotton as to effect of temperature and relation between water pickup and wetting rate (Wolfrom & Nuessle—*Textile Res. J.* 22, 246). A peak in wetting time occurs as temperature of test approaches 85° which is the melting point of cotton wax. Moisture pickup of absorbent fabric is not improved by a wetting agent, whereas with nonabsorbent fabrics moisture pickup increases with increasing amount of wetting agent.

Some investigators have recorded wash tests with detergents or combinations of detergents. In investigations on soap-phosphate combinations, soap containing sodium tetrapolyphosphate and potassium polyphosphate gave better results than soaps in combination with sodium tetrapolyphosphate, sodium tripolyphosphate or sodium hexametaphosphate (Stüpel—*Textile-Praxis* 7, 231). In comparisons of soap with 1:1 mixtures of soap plus various synthetic detergents, best cleaning is obtained with soap (Stüpel—*Fette u. Seifen* 54, 553). Among many synthetic detergents and compounds tested for ability to prevent deposition of soiling matter on unsoiled fabric, soap has been most effective even when carboxymethylcellulose and sodium carbonate have been used to aid the synthetic detergents tested (Wagg—*J. Textile Inst.* 43, T325). In continuing this work on nonaqueous cleaning systems it is found that trichloroethylene alone is most effective; and that the effect of detergent additives varied with the cleaning solvent (*Ibid.* T331). A series of tests on washing wool as influenced by pH have indicated that nonionic soap is most effective at the isoelectric zone of wool; anionic soaps wash well at pH 6.5-8; and the one cationic soap tested washes best at pH 2.0 (Aida & Kasai—*J. Soc. Textile Cellulose Ind., Japan* 7, 165, 170). In this work alkylphenathalenesulfonates with short chain alkyl groups are good detergents only at relatively high concentrations, whereas fatty alcohol sulfonates and polyoxyglycol anionics wash well at relatively low concentration. An investigation relative to detergency and adsorption of anionic compounds by wool indicates that some leave wool darker than it was before washing because of redeposition (Fessler—*Am. Soc. Testing Materials, Papers on Evaluation of Soaps Spec. Tech. Pub. No. 115*, 9). This difficulty is surmounted by increasing the amount of detergent used. In evaluation tests of polyoxyethylated alkylphenols the mole ratio of ethylene oxide in the detergent does affect the wetting rate, but surface tension, foam stability, and detergency of cotton and wool are relatively unaffected by mole ratio distribution (Mayhew & Hyatt—*J. Am. Oil Chemists' Soc.* 29, 357).

The new laboratory evaluation tests for wool-scouring detergents described by Leonard (*Am. Soc. Testing Materials, Papers on Evaluation of Soaps Spec. Tech. Pub. No. 115*, 13) and van Overbeke et al. (*Bull. inst. textile France* No. 21, 59) are based on treating wool samples successively in a standard series of detergent baths and determining residual grease on the sample. The latter's tests on various detergents show that an ethylene oxide condensate with lauric acid is most desirable.

Some evaluation tests and data on detergents pertain to action in limited specific applications. Wells, Jr. (*Soap Sanit.*

Chemicals 28, No. 6, 42) recorded the effect of 15 different detergent material solutions on battleship linoleum, rubber tile, asphalt tile, and plastic tile. Maglio & Pollnow, Jr. (*Ibid.* No. 8, 149) have rated materials for their wax polish removing ability. In a search for a detergent for cleaning milking machines, the efficiency of several materials on removal of fat from rubber and their effects on rubber are determined (Whitlstone—*J. Soc. Dairy Technol.* 5, 177). A detergent developed in this work contains various inorganic cleaning agents and an anionic detergent. Tests have been developed for evaluation of detergents for economical use in mine dust abatement (Walker et al.—*Ind. Eng. Chem.* 44, 2389). The data developed indicate the concentration necessary, and are interpreted to explain inconsistent results in use of detergent sprays for dust abatement.

Detergents have also been tested for precipitation of carboxyhemoglobin and oxyhemoglobin (Stary & Tekman—*Bull. Faculte med. Istanbul* 14, No. 1, 18), for the influence of pH on their denaturation of various proteins (Jirgensons—*Arch. Biochem. Biophys.* 39, 261), for the deformation they cause on denaturing proteins (Chernyak & Pasynskii—*Kolloid Zhur.* 14, 204), for their spreading on proteins (Gorter & Boter—*Proc. Koninkl. Nederland. Akad. Wetenschap.* 55C, 113), and for possible detergent-protein interactions (Goddard & Pethica—*J. Chem. Soc.* 1951, 2659).

Irritation of the skin and toxicity of some detergents is reported. Synthetic detergents, as compared to soap, lower the ability of the skin to regenerate lipides and thus leave the skin less resistant to secondary irritants (Neuhaus—*Fette u. Seifen* 53, 552). Greither & Kleinschmitt (*Fette u. Seifen* 54, 272) have tested 200 subjects for sensitivity to various detergents. All tests with fatty acid condensates are found negative, some soap-perfuming compounds give positive tests, and the remainder of the data in this work are for various trade-named detergents. Rabbit eye irritation studies are reported on various shampoo materials (Cain & Markland—*Soap Sanit. Chemicals* 23, No. 7, 36). The shampoos generally cause more eye irritation than 10% soap solution but no more severely than 40% liquid potassium soap. Similar tests on many detergents line-up eye irritation effect in the following decreasing order: cationic, anionic, and nonionic detergents (Draize & Kelley—*Proc. Sci. Sect. Toilet Goods Assoc.* 17, 1). There is no dependable correlation of eye irritation with physical properties, such as surface tension, wetting power, foam height, and protein precipitation (Hazelton—*Ibid.* 5; *Drug & Cosmetic Ind.* 71, 184). Certain invert soaps, Zephirol, Hydramon and others, have an antiacetylcholine action similar to curare when tested on the rectus muscle of frogs (Hohensee—*Z. ges. inn. Med.* 6, 219). The first reported case of fatal human poisoning from ingestion of cationic detergent pertains to taking less than one ounce of "Synth-San," a 10% solution of methyl-dodecylbenzyltrimethylammonium chloride (Adelson & Sunshine—*Am. J. Clin. Pathol.* 22, 656). The lethal effect is probably due to combined inhibition of cholinesterase and intracellular oxidative enzymes.

The antibacterial properties of several detergents are evaluated. *In-vivo* tests, performed by incorporating detergents in blood of laboratory animals infected with virulent organisms, gave no conclusive evidence to prove or disprove reduction in infectivity of surviving organisms (Johnson et al.—*Am. J. Public Health* 42, 801). Tests on the efficiency of various soaps for preventing growth of tubercle bacillus indicate that maximum effectiveness is with the C₁₄ soap (Luzzati—*Ann. inst. Pasteur* 32, 774). In two reports on bacterial properties of quaternary ammonium salts, those with C₁₂-C₁₆ (Smith et al.—*J. Am. Chem. Soc.* 73, 2964), and C₁₆-C₁₈ (Cella et al.—*Ibid.* 74, 2061) alkyl chains, respectively, are reported as most effective. 2-Alkyl-1-methyl-pyridinium iodides are not effective at C₁₄ alkyl chain length (Birchenough—*J. Chem. Soc.* 1951, 1263). Twin chain quaternary ammonium compounds have less bactericidal power than a normal chain compound of the same number of carbon atoms (Resuggan—*J. Applied Chem.* 1, S86). Tests on effect of pH on antibacterial properties of quaternary ammonium compounds show that different organisms show resistance at different pHs and some may show peak resistance at two quite separate pHs (Soike et al.—*J. Dairy Sci.* 35, 764). A comparison of alkaline materials, quaternary ammonium derivatives, and active chlorine compounds as disinfectants has indicated that the compounds without active chlorine are ineffective as dairy sanitizers (Gisske—*Milchwissenschaft* 7, 75). Escherichia coli bacterial colonies remaining alive after treatment of heavy inoculum with cationic detergent are quite resistant to higher concentrations of the detergent (Benigno & Berti—*Atti ist. veneto, Classe sci. mat. e nat.* 109, 233). A technique developed

for determining bacteria on plates in testing bacterial removal by dishwashing detergents is based on transferring agar from a petri dish to the plate, incubation, and observing bacterial growth (Flett & Guiteras—*Soap, Sanit. Chemicals* 28, No. 10, 48).

Sewage processing engineers are concerned with the increase in use of synthetic detergents because they may affect conventional sewage processing. In Germany, considerable foaming in aeration basins due to household and textile-industry usage of the synthetic is encountered in recent years (Imhoff—*Gas-u. Wasserfach* 93, 512). Spraying the surface with clarified effluent has aided in the control of this foaming. In England sewage processing difficulties have arisen from use of synthetic detergents for scouring wool (various authors—*Inst.*

Sewage Purif. J. and Proc. 1948, Pt. 1, 100, 102, 105, 109, 113; 1950, 276). Manganelli's (*Sewage and Ind. Wastes* 24, 1057) work on the problem indicates that anionic and nonionic detergents do not interfere with oxidation of sewage; cationic types retard oxidation; anionics and nonionic types may interfere with coagulation; cationic compounds aid coagulation; all three types improve dewatering of sewage sludge, and that any surface-active compound may impair aeration in activated sludge units. Some investigators found no evidence that household detergents, even in concentrations above those expected, cause adverse effects during treatment of the sewage (Wells & Seherer—*Sewage & Ind. Wastes* 24, 670; Fuller—*Ibid.* 844).

ERRATUM: U. S. Patent No. 2,598,469 listed on page 202 of the first part of this Review should have read No. 2,598,468.

Iodine Values of Acidulated Coconut Oil Soapstock

S. R. KUBER and WALES H. NEWBY, Opelousas Oil Refinery, Division of Cotton Products Company Inc., Opelousas, Louisiana

SOAPSTOCK is the by-product of the alkali refining of glyceride oils. It consists largely of soap, formed by reaction of the refining alkali with the free fatty acids present in all crude oils, and moisture, together with lesser quantities of entrained neutral oil, unsaponifiable material, and extraneous foreign matter. Soapstock can be used directly in the manufacture of soap, and formerly this was the major method of utilization. Today, however, most of the soapstock produced is eventually treated with sulfuric acid to hydrolyze the soap present and dissolve out as much non-fatty material as possible; it is then known as acidulated soapstock. Black grease or black acids are analogous terms sometimes applied to acidulated soapstock. The commercial value of this acidulated soapstock lies in its content of fatty acids which are normally purified by distillation. Each type of soapstock is designated by the name of the parent crude oil source, as acidulated coconut soapstock, acidulated cottonseed soapstock, etc.

Although the total production of various soapstocks is quite large (1) and they have been produced and utilized for many years, very little has been published regarding their composition or characteristics. A few references can be found (1, 2, 3, 4, 5), but they deal only with processing methods or determination of total fatty acid content, moisture, etc. No comprehensive study of fatty acid composition or iodine value of authentic samples can be found in any U. S. publication. In the absence of any published information to the contrary, it might be assumed that soapstocks have the same iodine value as the parent oil, but it will be shown that such an assumption is not warranted.

Prior to about 1940 the dearth of information on soapstock characteristics was of little importance because the end-users of distilled fatty acids were not too critical. In recent years however the increased use of fatty acids as raw materials for the synthetic chemical industry has called for more exacting specifications. This is especially true in the case of acidulated coconut oil soapstock, for coconut oil contains a high proportion of valuable acids not found in any other common oil. Accordingly in an effort to obtain pure coconut oil soapstocks, some processors have set up maximum iodine value specifications on the assumption that anything above some arbitrary value

indicates contamination. In the absence of any extensive list of iodine values of authentic acidulated coconut oil soapstock samples it was difficult to say what the maximum iodine value of an authentic pure product should be.

Accordingly samples have been taken from a number of regular tank car receipts of crude coconut oil, received from three separate producers over a period of two years. These samples have been laboratory-refined and the resultant soapstocks acidulated. Iodine values were then determined on both the refined oils and the corresponding acidulated soapstock. Iodine values have also been determined on laboratory acidulated samples of commercially produced coconut oil soapstocks for comparison to the laboratory refining results. And some data concerning the role of entrained neutral oil was obtained by a study of neutral oil free soapstocks. Similar studies on soapstocks from other oils are under way, and although they were not sufficiently advanced to include in this report, they will be referred to wherever necessary to prevent misunderstanding.

The data accumulated disclosed some interesting relations, which it is felt may be of general interest, not only to producers and processors of coconut soapstock, but also to fat-splitters or students of fatty acid behavior.

Analytical Methods

All the laboratory refinings were made by Method Ca9a41 from the Official Methods of Analysis of the American Oil Chemists' Society, and the resulting soapstocks were acidulated with sulfuric acid. After acidulation the samples were allowed to stand in tall thin cylinders at 90°C. for some time to remove excess moisture. They were then stirred with a little dry sodium chloride to remove the remaining moisture and filtered through qualitative filter paper. Iodine values were determined by the standard Wijs method, using a 30-minute reaction time.

In some cases the soapstocks are referred to as having been freed of neutral oil before acidulation. This was accomplished by dissolving a 10-g. sample in 50% ethyl alcohol and extracting repeatedly with Skellysolve F. The alcohol was then evaporated, the soap solution acidified with hydrochloric acid, and the fatty acids extracted with Skellysolve F. Obviously, this method extracted the unsaponifiable matter pres-