

# Review of Literature On Fats, Oils and Soap for 1941\* —Part 2†

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## Biochemical and Physiological Studies

The 1940 developments in the field of fat metabolism were thoroughly reviewed by Eckstein (*Ann. Rev. Biochem.* 10, 181).

The relative nutritive values of various fats have not been clearly established. Investigators at the University of Wisconsin have published data indicating that butterfat has growth-promoting properties superior to vegetable oils. In their latest announcement (Boutwell *et al.*—*J. Dairy Sci.* 24, 1027) it was suggested that this superiority was probably due to a long chain saturated fat acid or acids. The unsaturated portion of butter was converted to the active compound by hydrogenation. Certain vegetable oils such as corn, coconut, cottonseed and soybean did not contain the unsaturated form of the compound, for their nutritive value did not improve on hydrogenation. The results of work by Federal Government investigators (*U. S. Dept. Agr. B. A. I. Rept.* 1941, 12-13) were not in full agreement with the above. Growth experiments with young rats on diets containing 5% fat indicated that soybean oil and corn oil were superior to other fats. At a 15% fat level, butterfat and soybean, corn and linseed oils were superior in growth-promoting properties to other fats. Butterfat, oleo stock, mutton tallow, soybean oil, corn oil, linseed oil, coconut oil and cocoa butter were the fats studied. In digestion studies with diets containing 5% fat, soybean, corn and coconut oils had digestion coefficients of 98 to 99%, butterfat 88, oleo stock 74, mutton tallow 74, and cocoa butter 63. With diets containing 15% fat the soybean, coconut and linseed oils had digestion coefficients of 97-99%, butterfat 91, oleo stock 87, mutton tallow 85 and cocoa butter 82. Work similar to the above, but with very young calves, by Gullickson *et al.* (*J. Dairy Sci.* 24, A315) indicated that butterfat excelled, followed closely by lard and tallow; corn, cottonseed and soybean oils were least satisfactory. A review on the subject was prepared by Munin (*Fette u. Seifen* 48, 88). His evidence claiming the superior nutritive value of butterfat was taken from work by the Wisconsin investigators and tests on very young calves reported in the Swedish, Danish and Norwegian literature.

Hoagland and Snider (*J. Nutr.* 22, 65) fed young rats lard and hydrogenated cottonseed oil at levels of 5, 15, 30 and 54%. The growth properties of the fats were the same at the 5% level, but lard was superior at higher feeding levels. Maximum growth with both fats occurred on the diets containing 30%

and minimum growth when 5% fat was present in the diet. Lard was superior in digestibility to hydrogenated cottonseed oil at each level of fat intake. Braun and Shrewsbury (*Oil & Soap* 18, 249) found monostearin, monolinolien and lard practically equal for the growth of rats. The fat acids fed as monoglycerides appeared in the depot fat as triglycerides. Murlin *et al.* (*J. Nutr.* 22, 589) demonstrated that indigestible residues did not interfere with the digestion and absorption of fats. Their work was on the comparative digestibility of constituents of white and whole grain breads.

Digestion and growth could be influenced by the basal diet. Wasteneys, Crocker and Hamilton (*Am. J. Physiol.* 135, 6) recorded that digestion of protein was increased in the presence of fat. In the work of MacKay *et al.* (*ibid.* 139) rats on high protein diets had less depot fat.

A few publications dealt with the absorption of various fat acids. In the work of Deuel *et al.* (*J. Nutr.* 21, 373) butyric, caproic and caprylic acids were absorbed most rapidly. Propionic, valeric and heptonic acids disappeared from rat intestines more slowly; while nonylic was intermediate. Appel *et al.* (*Z. physiol. Chem.* 266, 158) found no difference in nutritive value

of "even" and "uneven" cocoa fat. The "uneven" cocoa fat was prepared from cocoa fat acids by reducing to the alcohols, converting to bromides then to nitriles, hydrolyzing to fat acids and re-synthesizing to "uneven" fat. In tests on rats at 5, 10 and 20% fat levels no significant differences in body weight, deposition of fat, residual fat after starvation, etc. were observed. The absorption of the fats was practically equal in man. Work by Emmrich and Nebe (*ibid.* 174) confirmed the equality of the "uneven" and "even" cocoa fats by evidence that similar compounds were excreted by men or dogs fed these fats. Emmrich and co-workers (*ibid.* 183) also reported that dicarboxylic acids such as sebacic, decanedioic, tetradecanedioic and hexadecanedioic fed as sodium salts were utilized by dogs and the last 3 were utilized by men.

Because of the the slowness of entry of fat acids into mucosa phospholipids and because of the minute amounts present at the time of the maximum rate of absorption, Burr *et al.* (*J. Biol. Chem.* 140, 233) believed that phosphorylation was not an essential part of fat transport. The study was made by spectroscopically distinguishing the methyl esters of conjugated fat acids of corn oil during absorption and transport. Winter and Crandall (*ibid.* 97) found that

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† CORRECTION TO PART I, *Oil & Soap* 19, 45:  
The 1941 import figure of 1,364 should have been marked for the first 9 months only.

the portal-arterial fat acid content during fat absorption was no greater than that found in the fasting state. The data demonstrated that there was no quantitative evidence for the belief that fat acids were absorbed into the portal system. Little and Robinson (*Am. J. Physiol.* 134, 773) recorded that the lipids of the left thoracic duct lymph during and immediately after absorption of fats varied from 4 to 17%. There was no definite increase of neutral fat in the circulation during absorption.

In *in-vitro* studies, thin sections of rat and rabbit organs did not form unsaturated acids from caproic, caprylic, nonylic, capric or myristic acids; nor were volatile acids formed from myristic or lauric acids (Glaser—*Z. physiol. Chem.* 266, 123). Stearic and palmitic esters were acted upon by fat acid dehydrogenase, but dicarboxylic acids were not. Cruickshank and Kosterlitz (*J. Physiol.* 99, 208) demonstrated that heart muscle utilized the fat acids of the heart and blood. This utilization depended on the degree of depletion of the carbohydrates in the blood and heart muscle. Fishler *et al.* (*J. Biol. Chem.* 141, 809) pointed out that the synthesis and breakdown of liver phospholipids *in-vitro* could be studied with radioactive phosphorus as an indicator. Koch and Sister Duellman (*Oil & Soap* 18, 86) developed a method for *in-vitro* measurement of digestibility of fats with enzymes.

Several investigators collected data on deposition of fats. Söderlind (*Kgl. Lantbruksakad. Tidskr.* 79, 18) recorded that kidney fat of hogs was more saturated than back fat. The food fats affected the kidney fat the and inner layer of back fat more than the outer layer. Fat was generally softer in winter than in summer. Slow growth was believed to result in the production of soft fat. Waelsch *et al.* (*J. Biol. Chem.* 140, 885) in work using deuterium as an indicator found that deposition and regeneration of fats in the brain were highest during the period immediately following birth, when the demand for new depot fats was also greatest. Hilditch and Maddison (*Biochem. J.* 35, 24) recorded more analytical data to confirm earlier findings that the component fat acids of milk phosphatides were different from milk fat acids. The milk phosphatide fat acids were similar to those of the phosphatides of ox liver. MacLachlan's (*Proc. Soc. Exptl. Biol. & Med.* 48, 411) data showed that blood phospholipids and fat increased in mice during fasting. The same author with Hodge, Bloor and other investigators (*J. Biol. Chem.* 139, 897) traced the mobilization of lipids in fasting mice. The utilizable carcass lipids were mobilized and disappeared in 2 days. There was no evidence of a selective utilization of the more unsaturated fat acids. The liver lost half of its weight in 2 days after which there was no further loss. The body lost 20% of its weight in 2 days and thereafter lost an additional 10%.

The relationship of cholesterol to fat metabolism was studied. The feeding of 1% cholesterol from weaning throughout the life span of rats did not affect growth, health and time of survival (Okey—*Proc. Soc. Exptl. Biol. & Med.* 46, 466). Under stress of increased metabolic rate due to dinitrophenol injection, liver phospholipids and cholesterol were decreased (Chalecki *et al.*—*ibid.* 48, 302). This was interpreted to be consistent with the belief that part of the phospholipids and cholesterol in the liver was

important in fat metabolism. Treadwell and Eckstein (*J. Biol. Chem.* 140, 35) recorded that the amount of fat in the diet did not influence the free and total cholesterol content of the whole blood and serum or the neutral fat, phospholipid and cholesterol content of the livers of fasting rats.

New information on the influence of certain glands on fat metabolism appeared. After pancreatectomy rats ate more fat and little or no carbohydrate (Richter and Schmidt—*Endocrinology* 28, 179). Adrenalectomy inhibited fat absorption in rats (Bavetta, Deuel *et al.*—*Am. J. Physiol.* 134, 619). A higher than normal accumulation of fat acids in the intestine also occurred after adrenalectomy. Restoration to normal took place after administration of cortin. Barnes, Miller and Burr (*J. Biol. Chem.* 140, 241, 247) found that the restriction of fat transport in adrenalectomized animals was limited to the neutral fat fraction of the liver lipids. They believed that adrenal secretion was not necessary for the normal rate of fat absorption or the normal rate of incorporation of absorbed fat acids into intestinal mucosal lipids. Knouff *et al.* (*Anat. Rec.* 79, 17) recorded that excessive exercise to the point of fatigue reduced the cholesterol esters in the adrenals, but the effect was not accompanied by a decrease in the total lipids. Fasting caused no change in weight of the right adrenal (Oleson and Bloor—*J. Biol. Chem.* 141, 349). MacKay and Sherrill (*Endocrinology* 28, 518) recorded the losses in weights of adult rats for 10 months after thyroidectomy. Friedlander *et al.* (*Am. J. Physiol.* 132, 24) reported that denervation of a muscle was followed by an increase in its capacity to deposit labeled phospholipids.

Choline was demonstrated to be a significant dietary factor for the transport of fat. The literature on this subject was well reviewed by Griffith (*J. Nutr.* 22, 239). A brief resumé was prepared by Best (*Science* 94, 523). Hegsted, Mills, Elvehjem and Hart (*J. Biol. Chem.* 138, 459) showed that choline was essential for growth and prevention of perosis in chicks. This factor was synthesized by rats (Jacobi *et al.*—*J. Biol. Chem.* 138, 571). Choline administration prevented liver cirrhosis in rats on high fat-low protein diets (Blumberg and McCollum—*Science* 93, 598). This was attributed to the lipotropic activity of choline. Cystine, betaine, methionine sulfoxide and dithiodiglycolic acid also exhibited lipotropic activity when added to a low protein-high fat diet (Singal and Eckstein—*J. Biol. Chem.* 140, 27). Cysteine lost its effect on liver fat when alkylated with the lower alcohols. Griffith and Mulford (*J. Am. Chem. Soc.* 63, 929) attributed the effectiveness of betaine in dietary choline deficiency to the utilization of one of its methyl groups. Creatine did not contribute a labile methyl group but exerted a sparing action on labile methyl groups. Diffused nodular cirrhosis of liver in rats was produced on stock diets supplemented by large amounts of wheat germ oil or corn oil (Blumberg and Grady—*J. Biol. Chem.* 140, *Proc.* 35, 15).

Extensive studies were made on the effect of the pancreatic (lipocaic) factor on the distribution of lipids in the animal body. Chaikoff *et al.* (*J. Biol. Chem.* 138, 477; *Am. J. Physiol.* 133, P391) reported that the anti-fatty liver factor of the pancreas was heat-labile. This factor was also present in pancreatic juice for it could replace the raw glandular tissue

in the prevention of fatty livers in depancreatized dogs kept alive with insulin. Shapiro and Wertheimer (*Arch. Intern. Pharmacodynamie* 64, 265) demonstrated that the anti-liver fat pancreatic factor was heat-labile and they also reported that this factor was more active than choline in preventing fatty livers. Lombroso (*Ann. physiol. physicochim. biol.* 16, 298) believed that the pancreas acted as an endocrine gland for the absorption of fat. Dragstedt, Allen, Julian and Stinger (*Am. J. Physiol.* 135, 135) reported that removal of fat from liver by lipocaic was not accompanied by an increase in blood ketones nor did lipocaic prevent or cure the ketonemia of insulin deficiency. Isabolinskaya (*Bull. biol. med. exptl. U.R.S.S.* 9, 107, 112) reported that lipocaic did not inhibit fat infiltration of livers of phosphorus poisoned rats. He believed that this suggested that the preventive action of lipocaic in fat infiltration was not due to the inhibition of fat mobilization. Rodnyanskii (*Problemy Endokrinol. U.R.S.S.* 5, No. 4, 57) recorded that lipocaic increased the cholesterol content of blood while liver extract had no effect on blood cholesterol.

Clinical investigation with lipocaic treatment of psoriasis in which the lipid content of the blood was affected by lipocaic supported the belief that psoriasis was a manifestation of disturbed lipid metabolism (Walsh *et al.*—*J. Investigative Dermatol.* 4, 59). Other work studying fat tolerance in psoriasis led to the conclusion that psoriasis was not due to a disturbance in lipid metabolism (Le Winn and Zuger—*Am. J. Med. Sci.* 201, 703).

The administration of thiamine, riboflavin, pyridoxine, nicotinic acid and calcium pantothenate to rats on a fat free-high carbohydrate diet led to the production of fatty livers containing a high concentration of cholesterol (Forbes—*J. Nutr.* 22, 359). Absence of nicotinic acid in the diet reduced the cholesterol content of the fatty livers. Choline exerted a definite lipotropic effect when added to the diet. Gyorgy and Goldblatt (*Proc. Soc. Exptl. Biol. & Med.* 46, 492) also described the liver injuries resulting from deficient diets, which could be prevented by addition of yeast extract to the diet. McHenry and Gavin (*J. Biol. Chem.* 138, 471) showed that while administration of thiamine alone would cause synthesis of fat from carbohydrates, it would not do so from proteins unless pyridoxine was present. The same investigators (*ibid.* 141, 619) found that biotin given to rats in conjunction with thiamine, riboflavin, pyridoxine and pantothenic acid caused fatty livers. The effect was prevented by simultaneously feeding egg white, lipocaic or inositol. It was concluded that the fatty liver effect of a beef liver fraction owed its activity to its content of biotin. Leites *et al.* (*Bull. biol. med. exptl. U. R. S. S.* 9, 100) recorded data on the effect of liver extracts on ketonemia, lipemia and glycemia in rabbits. Low fat livers in rats caused by diets containing carotene, vitamin D, thiamine, riboflavin, pyridoxine, corn oil and choline were increased 100% in fat in 3 weeks by the addition of calcium pantothenate to the diet (Engel—*J. Biol. Chem.* 140, *Proc.* 35, 37). Vitamin B<sub>6</sub> injected into corn oil fed rats having symptoms of egg white acrodynia caused its disappearance (MacKay and Barnes—*Proc. Soc. Exptl. Biol. & Med.* 46, 353). Longenecker, Gavin and McHenry (*J. Biol. Chem.* 139, 611) recorded that the liver fat acids syn-

thesized when thiamine, riboflavin, pyridoxine and choline were given, were largely C<sub>16</sub> and C<sub>18</sub>, the C<sub>16</sub> acids being 54% of the total. Further supplementing the diet with liver fraction caused a greater increase of the C<sub>18</sub> acids than the C<sub>16</sub> acids and also augmented the quantity of unsaturated acids.

Mannering *et al.* (*Proc. Soc. Exptl. Biol. & Med.* 46, 100) demonstrated that an increase in the fat level in a riboflavin-low ration had a deleterious effect on the growth of young rats. Mrs. Emerson (*ibid.* 47, 445) was unable to detect a sparing action of essential fats on pyridoxine. Barnes, Miller and Burr (*J. Biol. Chem.* 140, 773) recorded that essential fat acid-deficient rats absorbed less fat than animals cured of the deficiency. It was suggested that this effect might have been due to poor physical condition. Haurowitz, Schwerin and Yenson (*ibid.* 353) suggested that the indispensability of the essential fat acids in nutrition might be connected with their capacity to destroy hemin and hemoglobin. At 38° linoleic and linolenic acids destroyed hemin and hemoglobin.

Several communications contained advice on increasing fat in farm animal and poultry feeds. Maynard *et al.* (*Proc. Am. Soc. Animal Production* 1940, 340) and Sandelin (*Maataloustieteellinen Aikakauskirja* 11, 86) advised increasing the fat content of dairy cow diets to obtain higher yields. Wennerström (*Biedermanns Zentr. B. Tiernähr.* 12, 207), Schubert and Wells (*Mich. Sta. Quart. Bull.* 23, 72) reported that there was no advantage in increasing the fat in normal dairy cow rations. The addition of cottonseed oil to a satisfactory poultry ration markedly reduced the hatchability of the eggs produced (Ringrose *et al.*—*Poultry Sci.* 20, 57). Chicks fed fat free rations grew somewhat more slowly than chicks receiving fat; however, the slight difference was overcome by the time pullets reached maturity (Davis and Upp—*ibid.* 459). There was some correlation between egg production and the fat in the diets of hens. The seborrhea producing property of bottlenose-whale oil in rats was found to run parallel with the iodine value of the oil.

Quigley *et al.* (*Am. J. Physiol.* 134, 132, 804) and Card (*Am. J. Dig. Diseases* 8, 47) recorded data on the inhibiting action of fats on the motor activity of the pyloric sphincter region and on the process of gastric evacuation. Fat products decreased the activity in the order soaps, fat acids and natural fats.

Deatherage, McConnell and Mattill (*Proc. Soc. Exptl. Biol. & Med.* 46, 399) demonstrated that it was not possible to interfere with the process of reproduction in female rats on an adequate diet by administering oxidation products of fats. Mortality of the young was great.

Mattill (*Ann. Rev. Biochem.* 10, 395) reviewed the 1940 progress in the chemistry and metabolism of the fat-soluble vitamins. A review by Hordh (*Anales assoc. quim. Argentina* 28, 147) dealt only with fish oils. Vitamin analytic records covered Australian fish oils (Wood and Kuchel—*J. Council Sci. Ind. Research* 14, 69), vitamin A in fish oils (Correa—*Anales assoc. quim. farm. Uruguay* 43, No. 1, 17), vitamin A in seal oil (Lojander—*Suomen Kemistilehti* 13B, 22); vitamin D in Bengal fish oils (Basu and Gupta—*Indian J. Med. Research* 27, 865), relation between oil content of fish liver and vitamin A content of liver oil (Higasi—*J. Agr. Chem. Soc. Japan* 16,

1141), vitamin A in dairy butters (Neal, Haurand and Luckmann—*Ind. Eng. Chem. Anal. Ed.* 13, 150), provitamin A in palm oil (Cardoso and Villela—*Mem. inst. Oswaldo Cruz* 35, 771), isolation of palm oil carotenoids (Hunter and Scott—*Biochem. J.* 35, 31), vitamin A content of palm kernel oils (Fehlmann and Poe—*Colo. U. Studies Ser. D. Phys. & Biol. Sci.* 1940, 29) and effect of treatment on the vitamin A potency of fats (Dyme *et al.*—*Iowa State Coll. J. Sci.* 15, 189).

Sherman (*Proc. Soc. Exptl. Biol. & Med.* 47, 199; *J. Nutr.* 22, 153) discovered that inefficient utilization of carotene occurred in rats when methyl linolate or linolenate was fed. A deficiency of  $\alpha$ -tocopherol intensified the symptoms of lack of carotene. Soybean oil yielded good growth in the vitamin A-deficient diets. Mackenzie, Mackenzie and McCollum (*Science* 94, 216) reported that vitamin E,  $\alpha$ -tocopherol, prevented the production of lesions in skeletal muscles of rabbits receiving cod-liver oil.

#### Deterioration

General communications and resumés relating to this portion of the review presented information on the mechanism of autoxidation (Mattill—*Oil & Soap* 18, 73), cause and prevention of spoilage (Singer—*Seifensieder-Ztg.* 66, 829, 840, 849, 859, 869, 879), stabilization of fats against rancidity (Henk—*Fette u. Seifen* 48, 90; *Zellwolle, Kunstseide, Seide* 46, 17; Belani—*Seifensieder-Ztg.* 67, 515, 526), measurement of rate and extent of oxidation of fats (Vibrans—*Oil & Soap* 18, 109) and a brief review on rancidity (Dean—*Soap Perfumery Cosmetics* 14, 307).

Methods for detecting rancidity and evaluating the stability of fats were investigated. Schweigart and Hencke (*Vorratspflege u. Lebensmittelforsch.* 2, 189) and Kiermeier (*Fette u. Seifen* 48, 11) agreed in the selection of petroleum ether as the best solvent for extraction of samples on which the peroxide value was to be determined. If ether is used it should be acetone free. Evaporation of the solvent under carbon dioxide or in a vacuum was of no special benefit. White (*Can. J. Research* 19D, 278) developed a procedure for the preparation of bacon fat for investigating its rancidity. The peroxide value and the Kreis test were considered to be most suitable for estimating the rancidity. Dastur and Lea (*Analyst* 66, 90) discussed the usefulness of tests based on the determination of active oxygen and ketones and issued suitable recommendations for the active oxygen procedure. Sabalitschka (*Ber.* 74B, 1040) prepared data on the influence of reaction time and the presence of water on the true active oxygen value. He believed that the true value was not obtained because some of the iodine disappeared. However, the results were considered suitable for comparing oils or evaluating the protective action of antioxidants. Stansby (*Ind. Eng. Chem. Anal. Ed.* 13, 627) investigated several procedures for determining peroxide compounds. Data on the effect of reaction time, acidity, sample size, the reagents used, etc., were tabulated. To make the reaction more nearly quantitative and less dependent upon experimental conditions, he recommended increasing the acidity of the reaction mixture by the addition of strong mineral acids. Johnston and Frey (*ibid.* 479) recommended the use of the Barcroft-Warburg apparatus for measuring oxidation of oils. Data on the rates of oxygen absorption of sesame, corn and cottonseed

oils were tabulated. Clark and Rugg (*ibid.* 243) preferred the measurement of the spreading pressure of a drop of oil placed on a monomolecular film on a hydrophilic balance to the determination of peroxide value for evaluating the oxidation of vegetable oils. Miss Shaner (*Univ. Microfilms, U. of Mich. No.* 279, 139 pp.) tabulated the effect of various factors and changes in fat constants with the volume of oxygen absorbed by fats. Hubata (*Oil & Soap* 18, 37) reported that pH indicators may be used to replace the organoleptic test and peroxide titration for ascertaining the end of the induction period in tests on lards with the Swift fat-stability test. Room temperature holding tests were useful and fairly accurate for determining the keeping quality of butter (Jacobsen *et al.*—*J. Dairy Sci.* 24, 883). Högl, Flam and Shanger (*Mitt. Lebensm. Hyg.* 31, 130) preferred measurement of the amount of potassium permanganate necessary to oxidize the steam volatile compounds for evaluating the degree of spoilage of butter. Knaysi (*J. Bact.* 42, 587) reviewed the methods of demonstrating hydrolysis of fats with the use of basic dyes.

The chlorophyll value, a new method of evaluating rancidity, was discussed by the originator (Coe—*Oil & Soap* 18, 227). The method seemed to indicate the degree of autoxidation. Rancidity appeared as the chlorophyll value increased. It was considered superior because it measured the unoxidized portion.

The results of investigations indicated that rancidity was a form of oxidation which was not necessarily correlated with the production of active oxygen, fat acids and aldehydes. Since the chlorophyll value was believed to indicate the keeping quality of an oil, it was considered feasible for the producers to adopt a certain chlorophyll value as a control factor in the refining of their oils.

Gray and Robinson (*Poultry Sci.* 20, 36) reported that a high free fat acid content of the fat in animal protein concentrates was not a true index for evaluating the nutritive value of the products in a well-balanced ration for poultry feeding. High rancidity in the animal protein concentrate did not greatly affect the nutritive value of such products when used at a 10 to 15% level in poultry feeds.

A rapid and convenient method of estimating antioxidant potency was based on ultra-violet irradiation of a mixture of halibut liver oil and the antioxidant in chloroform solution and estimating the vitamin A difference by means of the antimony trichloride reaction (Parker *et al.*—*Can. J. Research* 19B, 17). McKinney and Bailey (*Oil & Soap* 18, 147) tested 6 fats for their stability in baked goods, both under normal and accelerated conditions. The accelerated tests did not yield a true indication of stability. Data on development of acidity, aldehydes and active oxygen in peanut, coconut, rape, palm, whale and linseed oils at temperatures between  $-24$  and  $35^{\circ}$  were tabulated by Kiermeier (*Fette u. Seifen* 48, 326). In general the decomposition was rapidly accelerated between  $10$  and  $35^{\circ}$ , while in storage tests between  $-35$  and  $10^{\circ}$ , the rate of spoilage increased only slightly. Myers, Kass and Burr (*Oil & Soap* 18, 107) found that free fat acids had induction periods, thus indicating the autocatalytic nature of the spoilage reactions. Storage tests on cottonseed oils indicated that it was more desirable to store them in the refined state than as crude oil (King—*ibid.* 16). The crude oil was more stable but refining losses and free fat acids

increased and bleachability decreased. Rushkovskii (*Biokhimiya* 5, 502) recorded that linseed oil from ground seeds oxidized or dried faster than oil pressed from whole seeds. The storage of hydroxylated fish oils in the form of insoluble soaps was patented (Licata—*U. S. 2,211,139*).

Several storage investigations were on animal fatty tissue. To store bacon for as long as 48 weeks, the temperatures should be below  $-18^{\circ}$  (Cook and White—*Can. J. Research* 19D, 53, 85, 96). At  $-8^{\circ}$  bacon could not be kept for over 3 months without impairment of its taste (Nakonechnyi—*Kholodil'naya Prom.* 1939, No. 3, 27). To increase the stability of animal fat tissue at  $-8^{\circ}$ , Ciani (*Olii minerati, grassi e saponi* 20, 88) recommended adding boric acid and compressing.

Tabulated data by Glimm and Ellert (*Fette u. Seifen* 48, 60) gave the relative stability of triolein, lard and butter when exposed to the sun. The presence of calcium or magnesium carbonates did not influence the decomposition.

Carlin and Lannerud (*Oil & Soap* 18, 60) developed information on factors that influenced the stability and quality of potato chips and baked goods. Variation in potatoes, types of equipment, methods of production and packaging materials were shown to affect the products. Elder (*ibid.* 38) recorded that the stability of wheat germ oil in flaked cereal was markedly lowered by cooking or by shaking with dilute salt brine. It also appeared that the colloidal and physical aspects of flake surfaces had a greater influence on stability than chemical consideration of oxidation as influenced by antioxidants.

Coe (*Oil & Soap* 18, 241), Greenbank and Holm (*Ind. Eng. Chem.* 33, 1058) recorded that light of wave lengths 5400 to 7500 angstrom units had the least accelerating effect in promoting oxidation of fats and oils. Greenbank and Holm recorded tabularly and graphically the effect of various wave lengths of light on butter oil, lard, cottonseed oil and corn oil. Coe's data was on cottonseed oil.

Vitamin A dissolved in cod liver oil or olive oil was almost completely destroyed when air was bubbled through the oil at  $28^{\circ}$  for 90 hours (Basu and Gupta—*Current Sci.* 10, 288). With peanut oil, over half the original potency of added vitamin A was retained after 160 hours' aeration. According to Bolam and Sim (*J. Soc. Chem. Ind.* 60, 50) the rate of oxidation of fat was greater in acetic acid solution than in hydrocarbons or in the absence of solvents. With chlorine substituted acetic acids the oxidation was still further increased. The rate of oxygen absorption was not increased in alcohol solution.

Golumbic (*J. Am. Chem. Soc.* 63, 1142, 1163) investigated the antioxidant properties of tocopherols, hydroxychromans, hydroxycoumarans, several antihemorrhagic compounds and other related compounds. Thirteen hydroxychromans and hydroxycoumarans effectively stabilized lard. The hydroxycoumarins, dihydrocoumarins and methoxycoumarins were ineffective as antioxidants and the desoxy forms, with one exception, were also ineffective. Methylation progressively destroyed antioxygenic capacity. With dimethyltolcol and dimethylhydroquinones, the stabilizing effect varied with the position of the methyl groups. In tests with naphthols, quinones and other similar compounds, no relationship existed between antihemorrhagic and antioxygenic activity. The same

author with Mattill (*ibid.* 1279) recorded that ascorbic acid enhanced the antioxygenic activity of the above-mentioned antioxidants. Olcott (*Oil & Soap* 18, 77) also expressed this view. Nakamura and Tomita (*J. Soc. Chem. Ind. Japan* 43B, 245, 271, 272) found the unsaponifiable fraction of soybean oil acted as an antioxidant even after irradiation with ultra-violet light for 25 hours at  $30^{\circ}$ . The irradiated sterols were inactive. It was also suggested that the inhibitol concentrate was not the only natural antioxidant present. Bull (*Food Ind.* 13, No. 4, 48) fostered the rendering of lard in the presence of sugar to obtain a more stable product. The process imparted a slightly dark color and caramel-like odor and flavor to the product. The use of parchment paper containing oat flour for wrapping butter was recommended by Combs *et al.* (*J. Dairy Sci.* 24, 117). Dahle and Nelson (*ibid.* 29) reported that oat flour extracts had greater protective power in butter fat than the corresponding extract of soybean flour.

The antioxidants patented during the year were: the first distillate collected from vegetable oils during high-vacuum short-path distillation (Distillation Products, Inc.—*Brit.* 527,381), monobasic sugar acids and lactic acid (Grettie—*U. S.* 2,236,569, 2,251,485), esters of gallic acid (Sabalitschka and Bohn—*U. S.* 2,255,191, *Hung.* 124,996, special tertiary amine compounds (Sabalitschka and Bohn—*Ger.* 700,385 *Cl.* 23a), special phosphorus compounds such as organic monophosphonic acids and dihydroxyphosphines (Bolton—*U. S.* 2,230,371), neutral phosphates of polyhydric phenols (Martin—*U. S.* 2,247,280), diphenyl amines (Martin—*U. S.* 2,247,281), hydrogenated crude tocopherols (Taylor and Jakobsen—*U. S.* 2,267,224), water soluble compounds derived from the wash water employed in refining petroleum distillates (Trinidad Leaseholds Ltd.—*Brit.* 513,105), hydrocarbons produced by the pyrolysis of benzene (Jenkins—*U. S.* 2,240,073), special nitrogen substituted aminophenols (Clarkson—*U. S.* 2,220,065), heating the oil with a combination of sugar and other antioxidants (Musher—*Fr.* 848,523, *Brit.* 514,241) and liquid soybean or oat oil (Musher—*Brit.* 515,481). Cummings (*U. S.* 2,262,270) patented a package provided with a translucent sheet of transparent cellulose coated with blushed film. The sheet allowed inspection of package contents while protecting them from rancidity. Package materials patented by Musher (*U. S.* 2,233,141-3) were coated with antioxidant material and wax. Development of rancidity in the fish from which oil was to be extracted was prevented by treatment with sodium carbonate and formaldehyde, phenol, resorcinol or cresol.

A few publications on "fishiness" and flavor reversion of fats were presented. Bickford (*Oil & Soap* 18, 95), Glimm and Nowack (*Allgem. Oel- u. Fett-Ztg.* 37, 211) showed that generally autooxidation promoters favored the tendency towards reversion. Davies (*J. Indian Chem. Soc. News Ed.* 4, 1) reported that feeding betaine-containing sugar beet by-products to cattle accelerated the "fishiness" tendency of the butter produced. Tests by Broge (*Fette u. Seifen* 48, 183) on herring oil indicated that "fishiness" developed in the presence of highly unsaturated fat acids.

Only a small amount of activity occurred in the enzyme and bacteriological fields on fats. Olcott and Fontaine (*Oil & Soap* 18, 123) reported that no lipase

could be detected in either deteriorating cottonseed or meals from the seeds. Therefore, the mechanism of fat acid development in wet seeds during storage was considered obscure. The same authors (*J. Am. Chem. Soc.* 63, 825) recorded the properties of lipase in germinating cottonseeds; conditions for optimum activity, development and stability were investigated. Similar information, with a review, on soybean lipase was presented by Yorbach (*Fette u. Seifen* 48, 308). Strain (*J. Am. Chem. Soc.* 63, 3542) detected fat oxidase in soybeans, alfalfa seeds, scarlet runner beans, white clover seeds, garden peas and purple vetch seeds. Some reactions of these products with antioxidants were described. Castell and Garrard (*Can. J. Research* 19C, 106) recorded the lipolytic and oxidase properties of several pure cultures of bacteria on triolein; Schiff reaction, Kreis test and effect on Eh indicators were used as criteria. According to Thaler and Eisenlohr (*Fette u. Seifen* 48, 316) ketoneformation by *Penicillium glaucum* from saturated fat acids was practically equal in acid and neutral but weak in alkaline solution.

### Composition and Characteristics

The tables appended to this section of the review give data on the characteristics and composition of oils from those communications which could be thus best represented. In some cases uses for the oils analyzed were given. To some publications references only were available to the writer. These were on the following subjects:

Sunflower seeds of 8 widely separated localities of Canada. Anderson—*Dept. Trade & Commerce Can. Grain Research Lab. Winnipeg Ann. Rpt.* 13, 44.

Variations in characteristics of Western Canada flaxseed. Lehberg and Anderson—*Sci. Agr.* 21, 727.

Studies on 118 varieties of rape seed. Nagosi—*J. Imp. Agr. Expt. Sta. Japan*, 3, 421.

California olive varieties for oil. Condit—*Western Canner & Packer* 32, No. 7, 34.

Analysis of 304 samples of olive oils from different origins in Europe and Africa. Mathiesen and Tangen—*Tids. Hermetikind.* 26, 140, 209.

Bacteriological—chemical examination of 100 Netherland butter samples. Kruisheer *et al.*—*Dept. Landbouw Visscherij Directie Landbouw, Rijkszuivelsta* 1940, 51 pp.

The fat content of 168 brislings caught off the Norwegian coast in 1940. Mathiesen *et al.*—*Tids. Hermetikind.* 27, 117.

Oil of bati (*Ouratea parviflora*). Sta. Rosa—*Rev. chim. ind., Rio de Janeiro*, 8, No. 92, 11.

Seed oil of *Lonchocarpus discolor*. Machado—*Rev. soc. brasil quim.* 9, 65.

Some investigations were on factors that affect the metabolism of the oil-bearing bodies and the characteristics of the subsequent oil. Work on flax, poppy and rape plants by Schmalfuss (*Congr. intern. tech. chim. ind. agr. compt. rend. VI congr. Budapest* 2, 581) indicated that low water content in the plant and its organs during maturing of the seeds resulted in a low iodine value of the oil; a high yield per acre lowered the iodine value and fertilization favoring the water balance such as with potassium and chloride ions increased the iodine value. Meloy (*U.S.D.A. Agr. Marketing Service Apr.* 21) pointed out that soil moisture directly affected synthesis of oil in cotton-

seed. A good combination of soil moisture and sunshine favored production of cottonseeds with both a high oil and a high protein content. Large variations in the composition and characteristics that may be due to climate and variety of seed planted was well illustrated in the work on linseed oils by Rose and Jamieson (*Oil & Soap* 18, 173), from which minimum and maximum figures are presented in the tables. Dalle-Rose (*Ricerca sci.* 12, 707) also presented like data illustrating the effect of climate and fertilizers on linseed oil. Data on castor seed composition and characteristics of the oil during various stages of ripening were recorded by Bauer and Frasoldati (*Fette u. Seifen* 48, 292). According to Clarke and Mazur (*J. Biol. Chem.* 141, 283) lipids from freshly gathered marine diatoms contained a very high percentage (59-82) of free fat acids; on standing in suspension these fell markedly.

A method with curves and tables for calculation was devised for determining moisture of tung fruit from its electrical resistance (McKinney—*Oil & Soap* 18, 188). Beckel and Earle (*Ind. Eng. Chem. Anal. Ed.* 13, 40) plotted the release of moisture from various types of soybeans under analytical moisture determination conditions.

Kharshat and Korobkov (*Lab. Prakt. U.R.S.S.* 16, No. 2, 23) fostered the use of trichloroethylene as the solvent in the soxhlet oil determination. The results closely checked those obtained with ether as the solvent. Refractometric oil and iodine value determination methods were recommended for soybean oil by Zeleny and Neustadt (*U. S. Dept. Agr. Circ.* 748, 22 pp). A rapid method for determining the oil in tung fruit comprised extracting the ground fruit under a specific procedure with ethylene tetrabromide and determining the density of the solution (McKinney and Rose—*Oil & Soap*, 18, 25). A chart was used for calculating the percentage of oil in the solution. Drying grape seed at 100° prevented the extraction of oil with petroleum ether (Solina and Guzzardi—*Olii minerali, grassi, e saponi* 20, 126). For accurate results it was necessary to dry seeds over sulfuric acid. The oil of heat treated seeds was not released by treatment with acid. Drying sewage also prevented quantitative extraction of the grease or oil (Pomeroy and Wakeman—*Ind. Eng. Chem. Anal. Ed.* 13, 795). The authors described procedures for extraction without preliminary drying. Details of a modification of the usual method for grease analysis in sewage were described by Gehm and Trubnick (*Sewage Works J.* 13, 467). According to Mohlman *et al.* (*ibid.* 485) the standard methods for sewage gave low results. Wet extraction of sludge was inaccurate but was satisfactory for sewage containing a low concentration of total solids. In some biological work there is an objection to drying because some volatile ether soluble constituents may volatilize. This led to the development of new apparatus for extraction from wet material (Kaye *et al.*—*J. Biol. Chem.* 138, 643; Holmes—*Ind. Eng. Chem. Anal. Ed.* 13, 918; Crampton and Purdy—*Can. J. Research* 19B, 116). A method for determining fat in cheese by Bogner (*Fette u. Seifen* 48, 332) depended on hydrolysis of the casein with hydrochloric acid and extraction of the released fat with solvents. Special extraction flasks were designed for this procedure. According to Starr and Herrington (*J. Dairy Sci.* 24, 165) only about 24% of the free fat acids were recovered in the Mojonnier butter fat test on samples

containing free fat acids. The Gerber method for determining butter fat in butter serum and sweet cream buttermilk yielded fat readings 0.2 to 0.3% lower than those determined by the Gottlieb-Roese method (Mohr and Baur—*Fette u. Seifen* 48, 8). This error was reduced to 0.1-0.2% by the new ratios of sample to reagents suggested.

A rapid method for determining moisture in lard according to Galle (*Allgem. Oel-u. Fette-Ztg.* 37, 171) comprised heating the sample until clear and observing the temperature at which turbidity appeared on cooling. Turbidity temperatures of 95.5, 90.8, 85.0, 75.2, 64.5, 53.5, and 40.5 corresponded with moisture contents of 0.45, 0.4, 0.35, 0.30, 0.25, 0.20, and 0.15% respectively. A method for determining soap in refined oil comprised adding a small amount of 0.05*N* ammonia, then concentrated hydrochloric acid followed by water; the water layer was treated with sulfuric acid and evaporated to 1 cc. (Boekenooen—*Oil & Soap* 18, 8). The sodium was determined by precipitation with Kahane's reagent, a mixture of magnesium acetate, uranyl acetate and acetic acid in alcohol solution.

A symposium on the molecular structure of fats and oils was prepared in the form of a collection of papers by leaders in this field of chemistry (*Chem. Rev.* 29, 199). The collected papers form a very good monograph on the subject. The following were presented:

Introduction. King.

Composition and structural characteristics of glycerides in relation to classification and environment. Longenecker.

Structural peculiarities of acid fast bacterial lipids. Anderson.

The structure of phospholipids. Working.

Constituents of fats and oils affecting the development of rancidity. Olcott and Mattill.

Synthetic fat acid glycerides of known constitution. Daubert and King.

Preparation and properties of optically active derivatives of glycerol. Fischer and Baer.

The separation of natural components of fats and oils by molecular distillation. Embree.

Low-temperature crystallization of the fat acids and glycerides. Brown.

The polymorphic forms or phases of triglyceride fats. Ferguson and Lutton.

Surface films of fat acids, alcohols and esters. Harkins.

Ultra-violet absorption spectra of fat acids and their application to chemical problems. Burr and Miller.

Hilditch (*Chem. Products* 3, 78) prepared a brief discussion on the separation of fat acids. The process comprised the lead salt method of separation into saturated and unsaturated acids followed by distillation of the methylated fractions. Weitkamp and Brunstrum (*Oil & Soap* 18, 47) suggested a method for approximating the composition of fats from distillation curves. For example, a distillation curve of hydrogenated sardine fat acids showed that sharp separations were obtainable between adjacent homologous fat acid esters. With the use of their still they showed the degree of separation obtainable from a mixture of methyl oleate and methyl stearate even though the difference in boiling point did not exceed 2-3°. The acid composition of sperm oil determined

by their method was presented. Kaufmann and Wolf (*Fette u. Seifen* 48, 51) recorded the characteristics of "molecularly distilled" fractions of commercial triolein, commercial trimyristin, palm kernel fat, palm oil, butter fat, linseed oil and soybean oil.

Hilditch and Maddison (*J. Soc. Chem. Ind.* 60, 258) crystallized Palestine and Italian olive oils into 5 or 6 fractions from acetone at various temperatures down to -30° and determined the component acids of each fraction. The data showed that the minor components, palmitic and linoleic acids, were present chiefly as monopalmito- or monolinoleo-dioleins. The Palestine oil contained about 30% triolein, the Italian less than 5%. About 25% of the Palestine and 45% of the Italian oils were glycerides which contained a linoleic radical. An investigation by Zehnpfennig and Schuette (*Oil & Soap* 18, 189) on the quantitative recovery of the saturated acids from elm seed oil showed that the separations by the lead salt-amylenes or by the *p*-nitrosodimethylaniline methods were unsuccessful. Schuette and Vogel (*ibid.*, 246) pointed out the value of solidification points for identifying saturated fat acids. Ravich *et al.* (*Acta Physicochim. U.R.S.S.* 14, 403) recommended wider use of crystallization curves as criteria of purity for fat acids. Stewart and Wheeler's (*Oil & Soap* 18, 69) work on binary mixtures of fat acids demonstrated that the oleic-linoleic acid system had eutectics for the  $\alpha$ - and  $\beta$ - forms of oleic acid of 75.2 and 76.3 per mole of linoleic acid at -10 and -9.8° respectively. Linoleic and linolenic acid mixtures had melting points intermediate between the pure acids. The oleic-linolenic acid system had eutectics for the  $\alpha$ - and  $\beta$ - forms of oleic of 82.7 and 85.5 mole per cent linolenic acid at -15.7 and -15.1° respectively.

A rapid means of separating high- and low-titer fat acids comprised separating the fraction that precipitated on cooling with dry ice to -50° (De Gray and De Moise—*Ind. Eng. Chem. Anal. Ed.* 13, 22). The method could be applied to fats to give a distribution of fat acids in the glyceride molecule. Brown *et al.* (*J. Am. Chem. Soc.* 63, 1064, 1483) prepared pure linoleic acid by bromination-debromination and by crystallization at low temperature. About 12% isomers occurred in the products. Linolenic acid prepared by the first procedure also contained isomers.

Nobori (*J. Soc. Chem. Ind. Japan* 43B, 340) reported that fish and whale oils contained small amounts of lauric, capric and caprylic acids. Isanic acid, C<sub>18</sub>H<sub>28</sub>O<sub>2</sub>, a newly discovered fat acid containing two double bonds and one vinyl group, was found to be the main component of isano oil (Steger and van Loon—*Rec. trav. chim.* 59, 1156; 60, 342). The oil was obtained from the seeds of *Onguekoa gore*.

Batyl alcohol and cholesterol were isolated from the yellow marrow of cattle bones (Holmes *et al.*—*J. Am. Chem. Soc.* 63, 2607). Cholesterol constituted 50% of the unsaponifiable fraction of halibut-liver oil (Swain—*Fisheries Research Board Can. Prog. Rpts. Pac. Sta. No.* 46, 12) and was the only sterol isolated from pituitary gland extracts (Marker and Wittbecker—*J. Am. Chem. Soc.* 63, 1031). Täufel and Heimann (*Biochem. Z.* 306, 123) definitely identified highly unsaturated hydrocarbons, the squalenes (C<sub>30</sub>H<sub>50</sub>) in 9 of 23 fats. Nakamiya and Koizumi (*Bull. Inst. Phys. Chem. Research Tokyo* 20, 141)

recorded that squalene had no special selective absorption maximum but impurities, such as pristane, caused special absorption bands. Several pigments containing 40 carbon atoms were isolated from the unsaponifiable of soy bean oil (Nakamura and Tomita—*J. Soc. Chem. Ind. Japan* 43B, 246).

Among the nonlipoids of rape seed oil reducing and nonreducing sugars and sulfur were found (Lishkevich—*Masloboino Zhir. Prom.* 16, No. 5/6, 12). These were probably partly in the form of thioglucosides. They were removed during refining. Heddle and Brawn (*Can. J. Research* 18B, 386) found the concentration of phosphorus in fish oils too low to exert an antioxidant effect. The fish oils were a good source for dietary iodine.

Paranjpe and Deshpande (*J. Univ. Bombay* 9, pt. 3, 24) recorded the dielectric polarization and refraction of fat acids dissolved in benzene. The values were the same as those of dimeric molecules, suggesting that the carboxyl groups of pairs of molecules were drawn together in some manner. Dielectric constant measurements were found useful for identifying mixtures of tung and oiticica oils (Caldwell and Payne—*Ind. Eng. Chem.* 33, 954). This characteristic could also be used as a control in the bodying of oils.

Seelich (*Fette u. Seifen* 48, 15) fostered the use of interfacial tension technic for control of refining and characterizing oils and fat acids. Poch (*Rev. facultad cienc. quim. U. La Plata* 15, 267) recorded that the interfacial tension of fat acids in benzene solution against very dilute caustic solutions did not differ enough to enable identification of fat acids by this method.

Kofler and Opfer-Schawn (*Fette u. Seifen* 48, 49) recorded the optical refraction of the unsaponifiables from most of the common oils of commerce. The data indicated that olive oil could be distinguished from other oils by this means.

Ultra-violet absorption curves on boiled and blown linseed oil were recorded by Mitchell and Kraybill (*Ind. Eng. Chem. Anal. Ed.* 13, 765). The absorption coefficient of the blown oil increased with the viscosity until a 4.5 poise viscosity was attained; after this the viscosity increased but the specific absorption at 2700 Å remained the same. With heat bodied oil there was a strong absorption band with a maximum at 2320 Å that was attributed to the formation of conjugated compounds. The data could be used to distinguish between heat polymerized and oxidized linseed oils or to determine the amount of oxidized oils in oxidized-raw linseed oil mixtures. Norris *et al.* (*J. Biol. Chem.* 139, 199) recommended the use of absorption spectra data in isolation and structure work with unsaturated fat acids. Infra-red and Raman spectroscopic examinations were used in identifying the isomers of the C<sub>18</sub> acids (McCutcheon *et al.*—*Oil & Soap* 18, 9). The naturally occurring acids were believed to contain *cis*-double bonds; whereas artificial elaidic and linelaidic contained only the *trans*-linkages. Pestemer (*Fette u. Seifen* 48, 178) recorded the ultra-violet absorption spectra of trimethyl, ethylene, heptene, allyl alcohol, acetone, acetic acid, several fat acids, elaidinized fat acids, cholesterol, ergosterol and other natural constituents of fats and oils.

A rapid method for determining hardness of fats, especially recommended for margarin fats, comprised

a means of measuring resistance to a wire of a slab of the fat hardened on ice (Chufarovskaya—*Masloboino Zhir. Delo* 16, No. 3, 18). A patented means for measuring the plasticity of fats comprised a standard procedure for pressing a block of fat and measuring its deformation (Roller—*U. S.* 2,259,491).

The literature and data on melting point, melting curves and consistency of fats were reviewed by Erlandsen (*Fette u. Seifen* 47, 510). Williams (*Analyst* 66, 3) standardized a procedure for determining the melting range of fats and devised apparatus for dilatometric measurements. The latter comprised a glass bell in which weighing could be done under water during melting. It was suggested that the rate of volume or density change during melting could be used as a characteristic of the fat. Hofgaard (*Ingenioren* 48K, 1) pointed out that the polymorphism of triglycerides and the difficulty in obtaining thermodynamic equilibrium markedly affected the results obtained from dilatometric measurements. He recorded dilatometric data on several animal and vegetable fats in an attempt to offer a basis for determining the amount of the solid phase and the consistency of the fat.

According to Al'perin (*Masloboino Zhir. Delo* 16, No. 3, 17) a higher free fat acid content of fresh than of dried sunflower seeds was obtained after solvent extraction. This was probably due to the volatilization of some acids during storing and drying.

By employing iodine bromide solutions of up to twice the concentration used in the Hanus iodine method, Mikusch and Frazier (*Ind. Eng. Chem. Anal. Ed.* 13, 782) developed a procedure for determining the unsaturation of both conjugated and nonconjugated oils. Their figures on conjugated and nonconjugated tung oil agreed; and theoretical iodine values for 9,11-linoleic acid were obtained. A method by Uhrig and Levin (*ibid.*, 90) comprised direct titration of samples dissolved in chloroform with standard solutions of bromine in glacial acetic acid, using the bromine color as the indicator.

The work on the thiocyanogen value determination was principally on standardization. Norris, Kass and Burr (*Oil & Soap* 18, 29) could not obtain theoretical values for pure fat acids by the Kaufmann and modified methods. They suggested that further work was necessary before acceptance of the empirical values. Average thiocyanogen values of 96.6 for linoleic acid and 166.3 for linolenic were obtained by Matthews and co-workers (*ibid.* 182). These values were used with excellent results in equations for the analysis of 5 mixtures of known composition. Riemenschneider and co-workers (*ibid.* 203) in like work suggested that the Fat Analysis Committee of the American Oil Chemists' Society consider tentatively adopting the values 89.4 for oleic, 93.9 for linoleic and 162.0 for linolenic acid when 0.1 N thiocyanogen solution was used and values 89.4, 96.8 and 167.5 with 0.2 N solution. Mulder (*Verlag. Landb. Onderzolk No.* 46, C 439) recorded thiocyanogen and iodine values of 62 Netherland dairy butters. The figures showed a high degree of correlation.

Current micromethods in the fat field were reviewed by Gorbach (*Fette u. Seifen* 47, 499). Semi-micro modifications for the determination of Reichert-Meissl, Polenske and Kirschner values of butter fat were developed by Dyer and co-workers (*Analyst* 66, 355; *Chem. & Industry* 60, 403).



A miscellaneous group of fat and oil procedures included a method of estimating carotene in butter by color intensity (Gallup and Kuhlman—*Oil & Soap* 18, 71), a modification of Emmerie's iron-dipyridyl method for determining tocopherol content of oils (Parker and McFarlane—*Can. J. Research* 18B, 405) and 2 methods for determining gossypol in cottonseed products (Halverson and Smith—*Ind. Eng. Chem. Anal. Ed.* 13, 46; Podol'skaya—*Masloboino Zhir. Prom.* 16, No. 5/6 48). Adams *et al.* (*J. Am. Chem. Soc.* 63, 528, 535, 2439) contributed new data on the structure of gossypol.

The collaborative work of the International Commission for the Studies on Fats during 1938-9 was reported by Kaufmann (*Fette u. Seifen* 48, 114, 190). Determination of fat in oil seeds and oil cake and of the Reichert-Meissl and Polenske values were the methods investigated. The American Oil Chemists' Society Refining Committee (*Oil & Soap* 18, 208) studied the refining method recommended by the U. S. Regional Soybean Laboratory. The Soybean Analysis Committee of the American Oil Chemists' Society (*ibid.* 132) recommended as a tentative procedure the U. S. Regional Soybean Laboratory method of obtaining moisture of soybean products by drying at 130° for 2 hours. Standard specifications were published on dehydrated castor oil (Colbeth—*A.S.T.M. Bull. No.* 110, 29; *Paint Oil Chem. Rev.* 103, No. 14, 7), copra (Tompkins—*Oil & Soap*, 18, 103) and soybeans (U. S. Dept. Agr., Agr. Marketing Ser.—*Fed. Register* 6, 2675).

Olive oil was most often the subject of investigations on adulteration. The American Oil Chemists' Society Olive Oil Committee (*Oil & Soap* 18, 187) slightly modified the Fitelson test for olive oils. Dickhart (*Am. J. Pharm.* 112, 371) also suggested modification of the procedure. The Bellier reaction was recommended for detecting mastic-tree seed oil in olive oil (Macciotta—*Ann. chim. applicata* 31, 83). Wallace (*Am. J. Pharm.* 112, 131) recorded that virgin olive oil gave a pea or emerald green color with antimony trichloride, refined oil gave a blue color and unsaponified matter of the oils gave a red color with the reagent. Kifler and Opfer-Schawn (*Fette u. Seifen* 48, 49) found the optical refraction of the unsaponifiable fraction of olive oil sufficiently below that of other common oils to be used as a means of identification.

The Bomer value as modified by Kerr was recommended by Sutton *et al.* (*Analyst* 65, 623) for examination of lard. A value of 70 indicated the presence of 5-15% beef fat and a value of 65 indicated 15-40%. Their tests for hydrogenated fats depended on the iso-oleic acid determination. The lecithin content was used as a criterion for detection of adulteration of lard with pig bone fat (Karoly—*Kutatasok* 14, 179). A slight modification was made in the procedure for detecting sesame oil by the Bishop reaction (Pavolini—*Olii minerali grassii e saponi* 20, 79). The same investigator (*ibid.* 21, 149) reported that the Bishop, Bellier, and Villavecchia and Fabris reactions were less distinct after refining, whereas the Halphen reaction for cotton-seed oil became more distinct. Broge (*Fette u. Seifen* 48, 333) described the standard procedure for determining the Bellier value of oils and discussed its application for analytical problems.

Sorges (*Chim. e. ind. Italy* 22, 267) tabulated the color reactions of (1) arsenic chloride and (2) antimony trichloride, added to solutions of oil in chloroform, (3) 10% tin chloride in 38% hydrochloric acid added to oils, (4) the addition of oils to 2 cc. of a 1:1 mixture of ether and chloroform containing one drop of concentrated sulfuric acid, (5) the addition of silver nitrate in absolute alcohol to oils and (6) addition of concentrated sodium hydroxide or potassium hydroxide to oils. As low as 0.5% croton oil in olive oil was detected by test 4 in the above list. In similar work David (*Ber. ungar. pharm. Ges.* 17, 130) placed a few drops or crystals of (1) acetone, (2) benzidine, (3) *p*-dimethylamidobenzaldehyde, (4) formaldehyde, (5) orcinol, (6) resorcinol, (7) dextrose or (8) vanillin in dry test tubes, added 2 cc. of concentrated hydrochloric acid, shook the mixtures with 15 drops of various oil samples and after 30 minutes observed the colors. The data were tabulated.

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CHARACTERISTICS REPORTED ON FATS DURING THE YEAR (Continued)

Oil or Fat Source	% Oil or fat	Density	Refr. Index	Acid No. (% Free Fat Acid <sup>2</sup> )	Sapon. No.	Iodine No.	R-M No.	Polenksé No.	Acetyl No.	% Unsap.	(SCN) No.	m.p.	Solifi- cation p.
Prickly pear seed <sup>1</sup> <i>Opuntia ficus indica</i>	6.34	0.9216	1.4744	5.26	194.10	125.20			24.5	1.73			-10
Rape seed of Japan <sup>2</sup>		0.9147	1.4719	171.3	171.3	99.4							
<i>Brassica campestris</i>		-0.9196 <sup>15</sup>	-1.4734 <sup>20</sup>	-177.0	-177.0	-103.6							
Red root pig weed seed <sup>3</sup> <i>Amaranthus retroflexus</i>	7	0.9233 <sup>34</sup>	1.4751 <sup>35</sup>	3.9	187.4	89.9			14.4	7.6			
Rice <sup>4</sup>		0.9121	1.4670	16.25	180.7	99.1				4.32			
<i>Azadirachta indica</i>		-0.9171 <sup>36</sup>	-1.4703 <sup>30</sup>	-67.61	-185.6	-107.2				-5.21			
Royal palm nut <sup>5</sup>		0.917	1.4560 <sup>38</sup>	5.8	249.6	5.8	5.8	5.7					
<i>Attalea gomphococca</i>		-0.922	-1.4768 <sup>36</sup>	181.2	-255.2	-7.4	7.3	-6.4					
Shaddock seeds <sup>6</sup>	39	0.9200 <sup>30</sup>	1.4763 <sup>31</sup>	15.37 <sup>*</sup>	189.7	145.7	0.26			0.52	82.2	23.5	-15.0
<i>Sida acuta</i>	44	0.9088 <sup>32</sup>	1.4643 <sup>31</sup>	2.5 <sup>*</sup>	189.7	92.7				0.48			
Sterculia foetida kernels <sup>8</sup>		0.9222 <sup>32</sup>	1.4760 <sup>30</sup>	1.31 <sup>*</sup>	189.7	70.0				<1			
Tallow tree seed <sup>9</sup> <i>Trichilia emetica</i>	58.3	0.857 <sup>00</sup>	1.4636 <sup>30</sup>	4.9	198	43.9						36	28
Tiger claw shrub seed <sup>10</sup> <i>Martynia diandra</i>	-61.8	0.9173 <sup>35</sup>	1.4636 <sup>30</sup>	4.9	198.4	118			31.4			-39	-32
Tiger claw shrub seed <sup>10</sup> <i>Martynia diandra</i>	30	0.9232	1.4390	0.5	193	118			0.4		84.0		
Tobacco seed of Bulgaria <sup>41</sup>	-40	-0.9262 <sup>15</sup>	-1.4770 <sup>15</sup>	-13	-198	-142	0.3	0.3	-3.0		-84.7		
Turtle (sea) <sup>42</sup>		0.9222 <sup>32</sup>	1.4664 <sup>34</sup>	0.07	198.5	82.2				2.46			6.03
<i>Dermochelys schlegelii</i>													
Turname seeds <sup>43</sup>	7	0.9291 <sup>15</sup>	1.475 <sup>30</sup>	3	193	149				2.4	75.2		
<i>Glycyne ussuriensis</i>		0.9250	1.4758	0.77		123.0			4.6				-30 to
Walnut <sup>44</sup>		-0.9288 <sup>15</sup>	-1.4809 <sup>30</sup>	-8.96		-166.0			-7.2				-27
Wheat bran <sup>45</sup>		0.9299 <sup>15</sup>	1.4805 <sup>32</sup>	54.25	188	118				4.20			

COMPOSITION OF FAT ACIDS

Fat Source	Common Saturated Acids			Common Unsaturated Acids			Other Acids Some designated by No. of C and double bonds (=—2H)
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Ava bran							
<i>Setaria itarica</i> <sup>4</sup>	16.5	10.6	5.5	8.7	80.7		
Babassu <sup>5</sup>	0.4	5.8	12.3	11.9	2.8		
Beef blood <sup>7</sup>		24.5		17.4	36.5	4.2	Caproic 0.0, Caprylic 4.1, Capric 7.6, Lauric 45.1, Arachidic 0.7
Caper seeds <sup>9</sup>		6.5-9.2		42.4-45.9	44.9-51.1		Arachidic 0.8, Palmitoleic 2.6, Arachidonic 1.3
<i>Capparis spinosa</i>							
Cardo seed <sup>11</sup>		11.9		22.6	63.5	1.5	
<i>Cynara cardunculus</i>				32	51		
China tree fruit <sup>12</sup>		2.6					
<i>Melia azederach</i> <sup>*</sup>							
Cocunut of South Sea Islands <sup>13</sup>	15.86	9.58	3.16	6.28	1.53		Caproic 0.3, Caprylic 9.17, Capric 9.67, Lauric 44.05, Arachidic trace.
Corn starch (released by hydrolysis) <sup>16</sup>		21.2	7.8	37.7	31.1	1.2	Undetd. saturated acids 1.0
<i>Dacryodes rostrata</i> <sup>18</sup>	1.0	12.7	30.9	49.5	2.8		Arachidic 3.1
Fish <sup>20</sup>	8.3	14.9	4.7		31.1		C <sub>12</sub> unsaturated trace, C <sub>14</sub> unsatd. 23.4, C <sub>20</sub> unsatd. 8.4, C <sub>22</sub> unsatd. 3.4
Menhaden							Arachidic 2.5
Kokum butter seeds <sup>18</sup> <i>Garcinia morella</i>		0.7	46.4	49.5	0.9		
Kokum butter seeds <sup>18</sup> <i>Garcinia indica</i>	1.4	2.5	56.4	39.4	1.7		
<i>Hydrophila spinosa</i> <sup>21</sup>		5.4	11.9	9.8	71.5		
Linseed (7 samples expressed oil) <sup>25</sup>	1.2	3.84-6.87	2.17-4.84	14.92-34.45	9.20-23.31	28.13-60.92	Arachidic 0.22-0.86 Lignoceric 0.0-0.36
Olives of Palestine <sup>47</sup>	3.7	11.8	1.8	76.4	6.3		Arachidic 0.3 C <sub>14</sub> (-2M) 0.3, C <sub>18</sub> (-2H) 0.3, C <sub>14</sub> (-2H) 1.5, C <sub>18</sub> (-2H) 2.1.
Olives of Tuscany, Italy <sup>47</sup>		4.4		66.8	21.5		
Po-Yoak <sup>20</sup> <i>Parinarium spherocense</i> <sup>*</sup>		12			8		Coupeic 41, Volatile acids 1.8, Eleostearic 31
Red-root pig weed <sup>33</sup> <i>Amaranthus retroflexus</i> <sup>*</sup>		16.9	1.7	46	25		
Shaddock seed of India <sup>37</sup>		20.7	15.3	55.46	8.07	0.48	
Tiger claw shrub seed <sup>40</sup> <i>Martynia diandra</i> <sup>*</sup>		8.08	11.25	35.84	32.37		Arachidic 1.34

\* Based on total oil.

### Detergents

New physical chemical data on pure anhydrous soaps were recorded (Miss Vold—*J. Am. Chem. Soc.* 63, 160, 168; Marton, McBain and Vold—*ibid.* 1990; Vold—*ibid.* 2915). Data for transition temperatures of sodium soaps and for volume changes of sodium oleate and potassium stearate were presented. The transition temperatures for all phases in soaps from  $C_6$  to  $C_{22}$  of even members of the homologous series of fat acids were determined by 3 different experimental methods. The following phases could occur between crystalline and true liquid soap: subwaxy, waxy, superwaxy, subneat, neat and ordinary liquid. Certain forms were absent in a few of the soaps. An electron-microscope study of the curd fibers of sodium laurate showed that the curd consisted of a mass of fibers which were thin ribbons whose widths tended to be integral multiples of approximately twice the length of the sodium laurate molecules. Differences in heats of transition of the phases suggested that low temperature transitions were probably due to changes in the arrangement of the hydrocarbon chains, while the high temperature transitions were due to the rearrangement of the polar heads of the molecules. The heat effect was large at the transition of the curd fiber phase to waxy soap and from subwaxy soap to waxy soap. At the higher temperature transitions the heat effects were small.

Phase studies were also recorded on soap with water (McBain *et al.*—*J. Am. Chem. Soc.* 63, 875, 1000, 1049, 1293; Miss Vold—*ibid.* 1427). The activity of water in soap curds was determined by 2 independent methods: namely, measurement of vapor pressure at constant temperature, and of the amount of ice formed at various temperatures, both as a function of the total composition. Sodium soaps of palmitic and oleic acids could contain up to nearly one mole of combined water per mole of soap. Crystallized fibers contained more water. Solubilities of various pure and commercial soaps were characterized by a value  $T_s$ , the temperature of ready solubility which was defined by reference to the lower temperature boundary of moderately concentrated isotropic solution. For palm oil  $T_s$  was  $52^\circ$ ; above this temperature as much as 30 grams of soap dissolved in 70 grams of water. Only  $2^\circ$  below  $T_s$ , this solubility fell to 5 grams in 95 grams of water. The effect of the chain length of the soap molecule on the phase diagram involved at least 2 opposing factors; the longer-chain soaps were less soluble at low temperatures and at low concentrations of soap, while at high temperatures and high concentrations the shorter-chain soaps were less soluble. Dodecanesulfonic acid did not exhibit liquid-crystal formations but interacted with water in such a manner as to make them possible. The lithium, sodium and potassium dodecanesulfonates each had a transition from liquid-crystal resembling subneat soap, and gave phase rule diagrams with water similar to those of soaps. The above phase data on both anhydrous and wet soap should be valuable aids for the investigation and improvement of soap manufacturing procedures and equipment.

Marine oil soap stock was improved by converting it into fat acids and distilling under conditions that separated the  $C_{18}$  acid fraction with less than 3% of the  $C_{20}$  and  $C_{22}$  fat acids in the distillate (Potts and

McKee—*U. S.* 2,224,985). This fraction was hydrogenated before use in soap manufacture. A special toilet soap patented by Mangeot (*Brit.* 513,696) was made from stock containing only oleic and myristic acids. The fat acid soap stock obtained as a by-product of the pulp industry could be freed from lignin by extracting the soap stock with dilute solutions containing sodium hydroxide, sodium carbonate and sodium sulfide (Francisco—*U. S.* 2,248,978). According to Ruemele (*Seifensieder-Ztg.* 68, 182) distillation of tall oil, a pulp industry by-product, improved its use as soap stock. Use of more than 25% of this product in the processing gave soft soaps. Hydrogenated fat and distilled or raw tall oil soap cleansed better than those made only from the fats.

The use of rosin in soap was fostered by Pohle (*Oil & Soap* 18, 244, 247). Calcium soaps of rosin acids were found to be more soluble than those of saturated fat acids. In foaming properties the soaps made from rosins, modified rosins and rosin acids were more like sodium laurate than the other individual fat acid soaps. The preparation of soap stock from oxidized petroleum products was the subject of several patents (Beller—*U. S.* 2,230,582; I. G. Farbenind. A.-G.—*Ger.* 694,141, 695,602, 695,647 *Cl.* 12e; Vereinigte Oelfabriken Hubbe & Farenhaltz—*Brit.* 515,720). New equipment and means of removing nonsaponifiable material were described.

New information on soaps containing silica included soap manufactured by saponification with alkali silicates (Mukai—*Japan* 134,217; Hustinx—*Dutch* 49,635; Bergell—*Ger.* 700,226 *Cl.* 23e), use of aergel (Curtis—*U. S.* 2,257,545), bentonite in soap (Anon.—*Soap* 17, No. 3, 63) and use of mixtures of silicates, alkali phosphates and other alkaline reacting salts in detergents (Liddiard—*Brit.* 528,964; Kalle & Co. A.-G.—*Ger.* 693,088 *Cl.* 8i). The use of the sodium subsilicate which contained 2 moles of sodium oxide to one of silicon dioxide was fostered as a soap builder by Davies and Hall (*Oil & Soap* 18, 125). The advantages were listed as follows: it was a good solvent and neutralizer for the acid substances that otherwise use soap; its buffering action was in the ideal pH range; it had detergent properties; it rinsed readily from clothes; and it was compatible with soap. Thomas (*Can. J. Research* 19B, 153) advised adding 25% sodium metasilicate to dish washing detergents in order to protect aluminum utensils. This silicate protected the metal more efficiently than sodium pyrophosphate or trisodium phosphate. Clouding in liquid soaps was prevented (Roschen *U. S.* 2,255 629) by separating the calcium and magnesium compounds from the soap solution and adding 1-2% water-soluble alkali metal hexametaphosphate.

Several references concerned the addition of some miscellaneous materials to soaps. Soluble soybean proteins and the colloidal mucilage in soybean waste liquor were used as emulsifying agents for soap stock to hasten the saponification process (Nakamura and Tanizaki—*Japan* 131,867). Proteins digested with papain at pH 5 were used as a soap stock ingredients (Hagiwara and Noro—*Japan* 133,273). One granular soap contained aliphatic alcohols and alkali perborates (Bergell—*Ger.* 693,026 *Cl.* 23e). The addition of 0.01-1% tri-*o*-tolyl phosphite or di-*p*-tolyl phosphorous acid monochloride was a new means of preserving soap (Martin—*U. S.* 2,234,379). The use of

$\alpha$ -stannic acid as a soap preservative was also patented (Maxwell—*U. S. 2,258,619*). Water insoluble dyes were recommended for dyeing soap because they did not stain the wash (Franke—*Ger. 695,750 Cl. 23e*).

Several improvements were made in the continuous soap manufacturing method of Refining Inc. (*U. S. 2,235,628, 2,242,187, 2,245,536, 2,249,675-6, 2,254,996*). A quick high temperature saponification zone, means of saponifying with anhydrous alkali, equipment to portion the soap in batches and purify it, a device for removing molten soap from the vacuum chamber without breaking the vacuum and a continuous cooling means for the withdrawn soap were patented. A continuous system patented by Lorenz (*U. S. 2,232,544*) contained a means of spraying the anhydrous soap countercurrently against steam to remove the glycerol.

Soap made from certain wood resins (Hereules Powder Co.—*U. S. 2,242,289, 2,242,529; Brit. 527,479*) or from fat acids, tall oil and resins (Plauson—*Ger. 693,241, 696,733 Cl. 23e*) could be conveniently saponified cold if the stock was emulsified with water before addition of the caustic. A special soap for use in the textile industry was saponified to the extent of 60-80% with potassium hydroxide in the presence of butyl or amyl alcohol (Matuda—*Japan 133,345*). A novel high temperature saponification method was described by Jacobs (*Chem. Industry 49, 484*). The fat was dissolved in kerosene, solid lye was added, the mixture was heated to high temperatures and the hot mass of soap and kerosene was sprayed in a vacuum chamber where the kerosene and glycerol were vaporized off leaving a dry granular soap.

Improvements in spray drying equipment and methods for soaps were patented by N. V. de Bataafsche Petroleum Maatschappij (*Dutch 50,032; Brit. 531,359*), Jones (*U. S. 2,249,960*) and Hagopian (*U. S. 2,238,588*). A soap product patented by Rowe (*U. S. 2,226,075*) was a water soluble hydrophilic polymerized vinyl compound containing soap in the form of a flexible sheet. According to Kubota (*Japan 132,158*) bar soap could be kept in its original condition until stamped by moistening with dilute glycerol by spraying and then drying. A soap wrapper patented by Shearer and Householder (*U. S. 2,267,310*) was coated with a moisture- and alkali-resistant coating of vinyl resin. A new cake of soap was provided with corrugations or bumps to massage the surface to be cleaned (Wallace—*U. S. 2,250,318*).

Several new cleaning agents were described. A waterless cleaner comprised a gelled 3% soap chip-water solution (Tyler—*Soap 17, No. 9, 30*). The new patented cleansers were a sodium silicate product coated with at least 5% soap (Vail—*U. S. 2,243,054*); a paste containing potassium soft soap, pumice and a small amount of oil of lemon grass (Goymour—*Brit. 512,642*); a mixture of soap, powdered stone, chalk, alkalies, alcohol and water (Badstuber-Eiehler—*Swiss 205,101*); a mixture of condensation product of lysalbinic acid with palmitic acid and equal amounts of anhydrous sodium pyrophosphate, sulfuric acid to adjust the pH to 6 and a mixture of cellulose ethers to yield a kneadable mass (Nassau—*U. S. 2,260,123*). A dry-cleaning soap contained diatomaceous earth, hydrogenated fish oil soap and mineral oil (Olsen—*Can. 393,953*). A general household cleanser comprised a mixture of petroleum sol-

vent, sulfonated oil and oleic acid (Manierre—*U. S. 2,209,785*). A carpet cleaning solution contained calcium oxychloride, sodium carbonate and sodium lauryl sulfate (Mathieson Alkali Works—*Brit. 526,647*). A cleaning agent for jewelry was a mixture of methylcellulose, soap flakes, potassium cyanide and water (Miss Anders and Mrs. Berg—*Ger. 700,384 Cl. 22g*). A review on the use of enzymes for cleaning textiles was prepared by Henk (*Seifensieder-Ztg. 68, 143*). New condensation products of albumins with fat acids were patented for use in the textile industry (Meyer—*Ger. 697,324 Cl. 80; Sommer—Ger. 688,633 Cl. 80; Weigand—Ger. 702,242 Cl. 12s*).

Numerous graphs and tables on the absorption of moisture (sweating) of soaps were prepared by Goswami, Choudhury and Basak (*Indian Soap J. 7, 9*). The presence of coconut oil in tallow soap increased moisture absorption. In the case of 80% tallow and 20% coconut oil as the soap stock, with 10% talc filler or peanut oil soap added to the soap, there was a loss in weight at humidities 0-78% and a gain in weight at 85-100% humidities. The transition humidity points, *i.e.*, the point at which sweating began, were between 79 and 84% humidity. Starch and casein fillers increased sweating.

Several communications tabulated germicidal data on soaps. Information on the potassium soaps was by Klarman and Shternov (*Soap 17, No. 1, 23*). The antibacterial properties of the commercial products tested were not sufficient to entitle the soap to be called disinfectant, antiseptic or germicidal, although rosin soap had unusual efficacy against staphylococci and hemolytic streptococci. Pohle and Stuart (*ibid. No. 2, 34; No. 3, 34; Oil & Soap 18, 2*) fostered the use of rosin in soap to improve germicidal activity. Regular use of the soaps led to a great reduction of the transient and resident flora of the hands. In tabulated data the efficiency of various soaps against *Staphylococcus aureus*, *Escherichia coli* and *Eberthello typhosa* was evaluated. Ordal, Wilson and Borg's (*J. Bact. 42, 117*) data concerned the effect of the pH and wetting agents on the germicidal action of phenolic compounds. The germicidal action of solutions of phenol, buffer and wetting agent decreased with increased alkalinity from pH 9-11, although the germicidal action of solutions without wetting agents increased in the same range. Jones and Miss Lorenz (*J. Investigative Dermatol. 4, 69*) found that incorporation of avirulent strains of staphylococci into calcium soap-oil mixtures increased the ability of the organisms to enter follicles and sebaceous glands and produce infection. The prevention of calcium soap formation in wash water and its deposition on the skin, hair or clothing was suggested as an active prophylactic measure. The data by Kuhn and co-workers (*Ber. 73B, 1080, 1092, 1095, 1100, 1105, 1109*) were obtained to study the bactericidal action of invert soap. "Zephirol," a commercial invert soap, was a mixture of alkyldimethylbenzylammonium chlorides. Many other invert soaps were synthesized and their physical and germicidal properties were recorded. The germicidal value of soaps containing phenols was improved by removing the unsaponifiable matter and preparing the soap free from saturated acids only (Hartung—*U. S. 2,251,934-5*). A germicidal detergent prepared from phenolic compounds and sulfonated alcohol or its salt was more effective than one made with ordinary soap

(Rawlins—*Brit. 515,386*). Another patented germicidal detergent contained calcium oxychloride, sodium carbonate and ammonium salts of sulfonated fat alcohols (Mathieson Alkali Works—*Brit. 526,646*).

Ekwall *et al.* (*Kolloid-Z. 92, 141; 94, 42*) recorded graphical data on the hydrolysis of sodium laurate in support of the theory on hydrolysis of soap which holds that the ions of fat acids associate stepwise and the association products then hydrolyze directly, the hydrolysis proceeding more readily at higher stages of association.

The electrical conductivity of oleate soap was 5-10 times as great as equimolar solutions of stearate soap owing to the difference in degree of dispersion (Angelescu and Woinarosky—*Kolloid-Z. 92, 355*). Cresol compounds caused increase in the soap dispersion and conductivity. The extent of the effect with various cresols was plotted. McBain and co-workers (*J. Am. Chem. Soc. 63, 670, 875*) recorded the increases in solubility of water-insoluble dyes and hydrocarbon vapors in water caused by the presence of soap and discussed the phenomenon from the viewpoint of detergent action.

A test soil for determining washing action was prepared by mixing one part of the mixture oil 30, lanolin 5, egg yolk 1 and egg albumin 1 gram, with 9 parts of a boiled mixture of milk 250, cocoa 20, soot 2, starch 4, sugar 10 and water 250 grams (Gehm—*Seifensieder-Ztg. 68, 159, 170, 181*). Special test cloths and an experimental washing were also described. The whiteness of the washed cloth was measured with the Pulfrich-photometer. Treffler's (*Soap 17, No. 5, 28*) detergent tests showed that high-titer soaps of saturated acids and the low-titer soaps of unsaturated acids used without alkalies gave better results at 21 and at 71° than the soaps of lower fat acids. It was suggested that at high temperatures the solubilities of low-titer soaps of the saturated acids were so much increased that they lost the properties of colloids and their detergency was low. The addition of bentonite to laundry soaps improved cleaning of greasy fabrics, but more soap was required. The washing tests by Vaughn *et al.* (*Ind. Eng. Chem. 33, 1011*), revealed that with soap solutions containing modified soda, soil removal increased to a maximum and then decreased as the amount of soda was increased. Palmer (*J. Soc. Chem. Ind. 60, 56, 60*) recorded that the presence of salt increased the capacity of sulfonated alcohol for removing olive oil from wool. This improvement rose to a maximum and then began to decrease as the salt concentration was raised. Magnesium, calcium and barium salts were needed at much lower concentrations than sodium salts to effect the same increase in detergency. Studies on cleansing eating utensils showed that detergents in which wetting and emulsifying properties predominated removed oils and fats but had limited action on protein particles for which deflocculating and dispersing properties were essential.

A method for comparing the foaming properties of soaps was described by Ross and Miles (*Oil & Soap 18, 99*). Kliewe and Peukert (*Z. Hyg. Infektionskrankh. 122, 560*) demonstrated that there was no correlation between foaming and germicidal power of soaps. Smith (*Am. Perfumer 43, No. 1, 55*) reviewed the information on the lathering properties of various soaps.

Two studies were on the effect of detergents on the skin. Fachini (*Rev. ital. essenze profumi 23, 273*) believed that soaps containing pectin substances and sulfonated products were less injurious to the skin because the skin pH increased the least after washing with these. This was not substantiated with patch tests by Parkhurst (*Arch. Dermatol. Syphilol. 43, 299*). He described a good technic for washing a sensitive skin.

A survey of pH measurements on soap solutions by Bacon *et al.* (*Ind. Eng. Chem. 33, 723*) disclosed wide errors particularly with colorimetric methods. Data on pH obtained by 2 electrical and 2 colorimetric methods on soap solutions containing various modified soda concentrations were presented. Vishnyakov and Rodicheva (*J. Applied Chem. U.R.S.S. 13, 1517*) recommended preparing titration curves to secure proximate analysis. Four maxima in the titration curves represented neutralization of the base formed on hydrolysis of soap, change of neutral soap to acidic soap, decomposition of acidic soap and finally decomposition of sodium carbonate and bicarbonate.

Grossfeld's (*Rev. trav. chim. 59, 534; Z. Untersuch. Lebensm. 81, 1*) procedure for determining fat acids in soaps was to shake a standard amount of organic solvent with the acidified soap and calculate the fat acid content from the weight in an aliquot of the solvent. Modifications and precautions were given for using the method on soaps containing various fillers, hydroxy acids or low molecular weight acids. In a similar method Muntoni (*Ann. chim. applicata 31, 131*) recommended using a centrifuge to reduce the effect of emulsions. Another means (Coatti—*Rev. ital. essenze profumi 22, 472*) for preventing emulsions in the test on soaps containing "tergine," bentonite or other emulsifiers comprised extracting the acidified soap from a 70% alcohol solution. Charts for applying refractometric methods for determining fat acids in soaps were prepared by Steinchen (*Seifensieder-Ztg. 68, 81*). The American Oil Chemists' Society Soap Analysis Committee (*Oil & Soap 18, 256*), recommended that the McNicoll method for rosin in soap be substituted for the Wolff method and that the volumetric method using the glass electrode be tentatively adopted for pyrophosphates in soap. Kerosene was recommended as the solvent for determining unsaponified fat in soap (Semenov and Zaliopo—*Masloboino Zhir. Prom. 16, No. 5/6, 70*).

A new method for free alkali in soap comprised dissolving the soap in neutral alcohol, centrifuging and decanting until the solution was clear, then titrating (Biffen—*Oil & Soap 18, 14*). Hitchcock and Divine (*ibid. 80*) improved apparatus for determining carbon dioxide in soap. A colorimetric method for determining small amounts of titanium oxide in soap was described by Parsons and Vaughan (*ibid. 64*). Methods for determining "tergine" in soaps were devised by Italian investigators (Costa—*Ann. chim. applicata 31, 160*; Stefano and Muntoni—*ibid. 30, 467*; Spallino and Fetonti—*ibid. 31, 263*). "Tergine" is made by hydrolyzing the residues from the manufacture of citric acid from lemons; its determination in soap was based on the cellulose content.

A scheme for qualitatively differentiating wetting agents and detergents was prepared by Linsenmeyer (*Melliand Textilber 21, 468*). The substances were divided into 8 classes: soaps, sulfonated oil (Mono-

pole), highly sulfonated oils (Avirol), naphthalene sulfo acids (Nekal), fat alcohol sulfates (Gardinol), fat acid condensation products (Igepon), protein fat acid condensation products (Lamepon), ethylene oxide condensation products (Igepal). The reagents used in the analysis were 5% hydrochloric acid, water of 20° hardness and concentrated hydrochloric acid. Analytical methods for petroleum oil-soluble sulfonic acid soaps were described by Archibald and Baldeschwieler (*Ind. Eng. Chem. Anal. Ed.* 13, 608). The unsaponifiable matter method for sulfated oils and alcohols was improved (Burton and Robertshaw—*J. Intern. Soc. Leather Trades' Chem.* 24, 293).

Several other publications on non-soap detergents merit discussion. Van Antwerpen (*Ind. Eng. Chem.* 33, 16) tabulated the name, type, use and manufacturer of the surface-active agents made in the United States. Data on the structure and wetting power of 36 sulfosuccinic esters were tabulated (Caryl—*ibid.* 731). Selective sulfonation of tall oil yielded a means of separating rosin and obtaining a wetting agent (Vilbrandt *et al.*—*ibid.* 197). Quaternary ammonium salts of long-chain phenol derivatives and quaternary morpholinium salts, the so-called invert soaps, were prepared and some of their properties recorded (Niederl *et al.*—*J. Am. Chem. Soc.* 63, 1475, 1476). A detergent powder, consisting of saponin and certain gums was prepared by roasting and pulverizing the pericarp of the soap-nut fruit (Sarin and Uppal—*Ind. Eng. Chem.* 33, 666). Wash tests showed that under optimum conditions the product had a higher detergent value than soap under its own optimum conditions. The saponin detergents were reviewed by Sandermann (*Seifensieder-Ztg.* 68, 102, 126, 138, 147, 160). Schmittmann (*Ger. 696,126 Cl. 8i*) improved saponin detergents by adding cellulose esters. A shampoo contained the ammonium or monoethanolamine salt of the sulfonic esters of monoethanolamine of coconut fat acid as the active ingredient. Forster (*J. Soc. Dyers Colourists* 56, 497) evaluated the sapamines, *i. e.*, fat acid alkylolamines, for use in various textile processes. Davis *et al.* (*Ind. Eng. Chem.* 33, 1546) evaluated the various wetting agents for improving electrodeposition of nickel. McGovern and Chidester (*Paper Trade J.* 111, No. 24, 35) compared several commercial products for improving penetration of bisulfite in sulfite pulping. Wetting agents cut time required for chemical peeling of peaches (Olsen—*Food Ind.* 13, No. 4, 51).

The following general communications are most conveniently incorporated in this review by reference:

Reviews on detergents and wetting agents. Anon.—*Fette u. Seifen* 48, 138, 212; Snell—*Food Ind.* 10, No. 10, 48; Bartell—*Ind. Eng. Chem.* 33, 737; *Chem. & Industry* 60, 475; Lenher—*ibid.* 497; Vallance—*Soap Perfumery Cosmetics* 13, 848; Duemling—*Arch. Dermatol. Syphilol.* 43, 264.

Soybean oil in soap manufacture. Anon.—*Soap* 17, No. 11, 21.

Continuous soap making. Wigner—*Soap Perfumery Cosmetics* 14, 169.

Modern soap factory. Löffl—*Seifensieder-Ztg.* 68, 13, 26.

Cold process coconut oil soap. Ghose—*Indian Soap J.* 7, 224.

Liquid toilet soap. Tyler—*Soap* 17, No. 1, 27, No. 2, 31.

Washing powders. Schremmer—*Seifensieder-Ztg.* 68, 69; Thomssen—*Soap* 17, No. 12, 27.

Processing soap scrap. Kemp—*Soap* 17, No. 5, 21. Rancidity and darkening of soap. Zafcev—*Seifensieder-Ztg.* 67, 142, 152.

Free alkali in soap. Ruemele—*Seifensieder-Ztg.* 68, 101.

Tylose HBR for soap powders. Hermada—*Seifensieder-Ztg.* 68, 114.

Pectin as soap filler. Wittka—*Seifensieder-Ztg.* 68, 48.

Water glass as soap filler. Foulon—*Seifensieder-Ztg.* 68, 169.

Tetrasodium pyrophosphate. Treffler—*Soap* 17, No. 11, 29.

Alkalies in cleaning. Liddiard—*Chem. & Industry* 60, 480, 684, 713.

Glassy condition of soap. Tyutyunnikov *et al.*—*Seifensieder-Ztg.* 68, 193, 205, 215, 227, 237.

Essential oils for the soap industry. Young—*Oil & Soap* 18, 63; Foulon—*Wein. Pharm. Wochschr.* 74, 97.

Specialized soaps. Rayner—*Soap Perfumery Cosmetics* 13, 437.

Disinfectant and therapeutic soaps. Ruemele—*Seifensieder-Ztg.* 68, 8, 19; Glenn—*Soap Perfumery Cosmetics* 14, 48.

Cleaning aluminum. Akers and Mears—*Soap* 17, No. 4, 25.

Paint cleaners. Tyler—*Soap* 17, No. 5, 24.

Health hazards in soap manufacture. Wagner—*Seifensieder-Ztg.* 67, 421.

Plastics in the soap industry. Smith—*Soap* 17, No. 10, 34.

Production of mineral oil sulfonic acids. Hetzer—*Chem.-Ztg.* 64, 160.

Manufacture of sulfonated oils. Singer—*Seifensieder-Ztg.* 67, 147, 157, 167, 177, 187, 197, 208, 218, 237, 248, 267, 279, 290, 299, 308.

Soap standards, specifications or definitions. Trevithick—*Proc. Am. Soc. Testing Materials* 40, 398, 401, 403; *Soap* 17, No. 7, 21; *Chem. Industries* 48, 200; Anon.—*Soap* 17, No. 4, 47, No. 2, 109.

Glycerol—recovery, refining, etc. McCutcheon—*Soap* 17, No. 11, 24, No. 12, 24.

Synthetic glycerol. Williams—*Chem. & Met. Eng.* 48, 87; Kelly—*Fuel* 20, 43.

Glycerol derivatives—properties and uses. Dupuis, Lenth and Segur—*Oil & Soap* 18, 31.

Pharmaceutical uses of glycerol. Lesser—*Am. Professional Pharmacist* 6, 634.

Glycerol as a viscosity standard. Tukamoto and Kuriyama—*J. Soc. Chem. Ind. Japan* 44B, 24.

Substitutes for glycerol in cosmetics. Sedgwick—*Soap Perfumery Cosmetics* 14, 42.

Instructions with a theoretical discussion on purifying spent soap lyes were issued by Zaliopo (*Masloboino Zhir. Prom.* 16, No. 5/6, 28). A sludge obtained in recovering nickel catalyst from hydrogenated fats was said to be superior to aluminum oxide for purifying spent soap lyes.

Tyutyunnikov (*Seifensieder-Ztg.* 68, 57, 70, 82, 103) investigated the composition and source of

esters in glycerol distilled from a van Reymbeke still. He suggested that the esters found had been formed in the vapor state. Fat acids and the sulfonaphthenic acids from "Kontakt reagent" were carried over by steam if excess alkali was absent. At 280°, with excess caustic, glycerol yielded propylene glycol, methanol and acetic and formic acids. In the absence of excess alkali, lactic acid was formed. The above compounds participated in ester formation. Salts of higher and lower fat acids of lactic acid and lactids, when present in distilled glycerol were due to entrainment. The decrease in ester content of distilled glycerol by the introduction of excess alkali into the crude raw material was attributed to lessening of alcoholysis of soaps and the condensation of aldehydes into non-volatile compounds. Equations suggesting the manner of ester formation were presented. Crystallization of glycerol from aliphatic alcohols was a new method for its purification (Hass—*U. S. 2,233,606*; *Ind. Eng. Chem.* 33, 615). Several patents dealt with the recovery of glycerol from distillery residues (Baudot—*Brit. 518,616*; Walmesley—*U. S. 2,235,056-7*). A method of purifying glycerol prepared from hydrocarbons utilized a special still (Evans *et al.*—*U. S. 2,234,400*). Glycerol still residues were neutralized, adsorbed on silica, sawdust or like material, and extracted with organic solvents to recover di- and poly-glycerol (Henkel & Cie.—*Ger. 696,822 Cl. 23e*). A process for the manufacture of glycerol monochlorohydrin employed a solvent miscible with glycerol and the product was used to dissolve the reaction components (Dow Chemical Co.—*U. S. 2,257,899*).

A modified Bertram-Rutgers procedure for glycerol determination in low-grade process materials was prepared by the American Oil Chemists' Society Glycerol Analysis Committee (*Oil & Soap* 18, 14). A refractometric method for glycerol in spent soap lyes was described by Matumoto (*Repts. Chem. Research Prefectural Inst. Advancement Ind. Tokyo No. 3, 1*).

The patents on non-soap type detergents, which include manufacture, uses, etc. will only be listed as in the past reviews of this series. Those that dealt with sulfonated fats, fat alcohols, hydrocarbons or esters were:

- Alrose Chem. Co.—*U. S. 2,237,066*.
- Am. Cyanamid Co.—*U. S. 2,234,140, 2,241,605*.
- Am. Hyalsol Corp.—*U. S. 2,264,737*.
- Armour & Co.—*U. S. 2,229,307*.
- Böhme Fettchemie-G. m. b. H.—*Ger. 687,462 Cl. 12a, 690,628 Cl. 8i, 696,904 Cl. 12s*.
- Brand—*Hung. 125,390*.
- Colgate-Palmolive-Peet Co.—*Brit. 516,735*; *U. S. 2,227,999, 2,235,098, 2,235,534, 2,236,828, 2,242,979, 2,244,512, 2,250,092*.
- E. I. du Pont de Nemours Co.—*Ger. 694,481 Cl. 12o*; *U. S. 2,240,920*.
- Deutsche Hydrierwerke A.-G.—*Brit. 516,188, 516,879, 516,978, 517,339*; *U. S. 2,263,948, 2,246,374*.
- Emulsol Corp.—*Brit. 514,721*; *U. S. 2,251,932, 2,251,940*.
- General Aniline & Film Corp.—*U. S. 2,220,099, 2,229,649, 2,230,587, 2,257,183*.
- Harris—*U. S. 2,255,285, 2,255,316*.
- Hercules Powder Co.—*U. S. 2,245,643*.

- Hotta—*Japan 129,439*.
  - Imp. Chem. Ind. Ltd.—*Brit. 531,194*.
  - I. G. Farbenind. A.-G.—*Brit. 513,076*; *Fr. 847,549, 849,564*; *Ger. 694,945 Cl. 12o*.
  - Inoue and Haneta—*Japan 137,699*.
  - Ipposya K. K.—*Japan 130,091*.
  - Miss Jabonski—*Fr. 848,459*.
  - Jasco Inc.—*U. S. 2,227,659, 2,247,741*.
  - Johns-Manville Corp.—*U. S. 2,241,790*.
  - Kao Sekken K. K.—*Japan 130,123, 132,621, 133,770, 133,774-5*.
  - Mathieson Alkali Works—*Brit. 530,040*.
  - Monsanto Chemical Co.—*U. S. 2,232,117, 2,267,687*.
  - National Aniline & Chem. Co.—*U. S. 2,223,363, 2,249,757*.
  - National Oil Products Co.—*Brit. 526,699, 526,960*; *U. S. 2,241,421, 2,266,843*.
  - N. V. Chemische Fabriek Servo—*Dutch 49,219*; *Ger. 692,729 Cl. 12o*; *U. S. 2,224,360*.
  - Penn. Refining Co.—*U. S. 2,236,933*.
  - Petrolite Corp. Ltd. *U. S. 2,252,957*.
  - Procter & Gamble Co.—*U. S. 2,231,979*.
  - Reed—*U. S. 2,239,974*.
  - Sandoz—*Ger. 693,324 Cl. 8a*.
  - Sharples Solvents Corp.—*U. S. 2,210,962*.
  - Shell Development Co.—*U. S. 2,243,331-2*.
  - Standard Oil Development Co.—*Brit. 523,520*; *Fr. 845,847*; *U. S. 2,243,994*.
  - Soc. pour l'ind. chim. a Bale—*Ger. 699,655 Cl. 8k*.
  - Tokyo Senzai K. K.—*Japan 130,140-1*.
  - Watanabe and Kawamura—*Brit. 530,415*.
  - Windaus—*Can. 392,387*.
- Detergents were also prepared by sulfonation of nitrogen containing compounds such as ammonium salts, indoles, proteins, amines, imides, etc.
- Am. Cyanamid Co.—*U. S. 2,251,768, 2,252,401*.
  - Chemische Fabrik vorm. Sandoz—*Fr. 847,001*; *Ger. 692,925 Cl. 8o*.
  - E. I. du Pont de Nemours & Co.—*U. S. 2,212,171*.
  - Emulsol Corp.—*U. S. 2,236,515, 2,236,518, 2,236,528-30, 2,236,541, 2,238,902, 2,251,940*.
  - General Aniline & Film Corp.—*U. S. 2,225,960, 2,243,437, 2,255,082*.
  - Imp. Chem. Ind. Ltd.—*U. S. 2,259,602*.
  - I. G. Farbenind. A.-G.—*Brit. 512,022, 518,656*; *Ger. 701,642*; *U. S. 2,242,086, 2,247,921*.
  - Katz—*U. S. 2,216,617*.
  - Miyosi Kagaku Kogyo K. K.—*U. S. 2,251,536*.
  - Monsanto Chem. Co.—*U. S. 2,236,825*.
  - Procter & Gamble Co.—*U. S. 2,253,179, 2,265,838*.
  - Shell Development Co.—*Can. 399,050*.
  - "Unichem." Chemikalien Handels A.-G.—*U. S. 2,267,101*.
  - Waldmann and Chwala—*Ger. 700,371 Cl. 12p*.
- Among nitrogen containing compounds with detergent action were alkylolamides, amines, amides, quaternary ammonium derivatives, amidines, urethans, etc.:
- Alframine Corp.—*Brit. 515,882*.
  - Chemische Fabrik von Heyden A.-G.—*U. S. 2,242,211*.



Deutsche Hydrierwerke A.-G.—*Ger.* 692,927, *Cl.* 12p.

E. I. du Pont de Nemours & Co.—*U. S.* 2,268,395.

Emulsol Corp.—*U. S.* 2,238,901, 2,238,927-9, 2,239,706, 2,239,720, 2,239,997, 2,245,593, 2,248,089.

J. R. Geigy A.-G.—*Brit.* 513,663; *Fr.* 848,003; *Swiss* 206,594, 206,718, 207,299-303; *U. S.* 2,211,280, 2,214,971, 2,221,914, 2,229,803.

General Aniline & Film Corp.—*U. S.* 2,211,001, 2,218,939, 2,222,208, 2,230,591, 2,231,502, 2,267,725.

Imp. Chem. Ind. Ltd.—*U. S.* 2,237,296.

I. G. Farbenind. A.-G.—*Fr.* 847,599, 849,018-20; *Ger.* 697,170 *Cl.* 8k, 697,730 *Cl.* 12o; *U. S.* 2,210,442, 2,215,367, 2,251,892.

Katz—*U. S.* 2,216,618.

Neu—*Ger.* 688,083 *Cl.* 12p.

No. Am. Rayon Corp.—*U. S.* 2,242,223-4.

N. V. de Bataafsche Petroleum Maatschappij—*Fr.* 849,399.

O'Connor—*U. S.* 2,244,721.

Petrolite Corp. Ltd.—*U. S.* 2,228,985-9.

Pollak—*U. S.* 2,257,481.

Purdue Research Foundation—*U. S.* 2,247,106.

Resinous Products & Chem. Co.—*U. S.* 2,210,831, 2,260,967.

Reichold Chemicals Ind.—*U. S.* 2,215,038.

Röhm & Haas Co.—*U. S.* 2,229,024.

Searle & Co.—*U. S.* 2,252,863.

Shell Development Co.—*U. S.* 2,247,266.

Soc. pour l'ind. chim. a Bale—*Brit.* 527,008, 527,012; *Fr.* 849,147; *Swiss* 208,530 *Cl.* 12o, 208,534 *Cl.* 36p, 209,972 *Cl.* 36p; *U. S.* 2,226,057.

Squibb & Sons—*U. S.* 2,251,946.

A miscellaneous group of detergents included various organic esters and phosphated, borated and some halogenated compounds:

Chemische Fabrik Joh. A. Benckiser—*U. S.* 2,252,479.

Colgate-Palmolive-Peet Co.—*Brit.* 514,053.

Deutsche Hydrierwerke A.-G.—*Ger.* 694,944 *Cl.* 12o.

Doelling—*U. S.* 2,255,916.

E. I. du Pont de Nemours & Co.—*U. S.* 2,254,124.

Emulsol Corp.—*U. S.* 2,236,516.

J. R. Geigy A.-G.—*U. S.* 2,212,224.

General Aniline & Film Corp.—*U. S.* 2,217,846, 2,228,929.

I. G. Farbenind. A.-G.—*Ger.* 693,028 *Cl.* 8i, 696,317 *Cl.* 12o.

Röhm & Haas Co.—*U. S.* 2,249,111.

Soc. pour l'ind. chim. a Bale—*Swiss* 207,645.

## Glycerin Recovery — The Soap Kettle

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### Introduction

In these times it is of great importance that the greatest feasible amount of glycerin be recovered from the fats in the soap kettle.

According to the bulletin of the U. S. Department of Commerce "Animal and Vegetable Fats and Oils" for the years 1936-1940 inclusive, the amount of fats consumed in soap manufacture was, roughly, 5,745,000,000 pounds. The amount of 80 per cent crude produced for the same period of years was 865,000,000 pounds, which is equivalent to 692,000,000 pounds of 100 per cent glycerol. About 23 per cent of the fats consumed were in the coconut oil group which contains a greater proportion of glycerin than the usual animal and vegetable fats. On the assumption that the fats consumed in the soap kettle averaged 94 per cent glycerides, the theoretically available glycerol was about 864,000,000 pounds (as 100 per cent glycerol). The efficiency of recovery of the soap industry was 80 per cent of the theoretical. It is true that glycerin was completely lost in the so-called cold-made soaps and in soft and liquid soaps. This loss was probably more than offset by the high efficiency attained in the large-scale fat-splitting operations. Therefore, it is probably a fair assumption that the average countrywide recovery of glycerin, using the soap-boiling method of manufacture, is in

the order of 80 per cent or less. A rise from 80 to 85 per cent in recovery would be equivalent to a yearly increase of 9,000,000 pounds of C. P. and dynamite grade glycerin. This is a mark for the soap industry to shoot at. This paper will show that an increase to a 90 per cent recovery or better is entirely within the range of the individual soap factory with no more than the usual existing kettle facilities.

### Preliminary

It has been established that for practical purposes, glycerol is of equal concentration (1, 2) both in the lye and in the aqueous portion of the curd. To put it more simply, if the watery portion of the curd contains 5 per cent glycerol, it follows then that if the weight of the lye and the weight of the aqueous portion of the curd is known, it can be estimated what percentage of free glycerol has been removed from the kettle by the lye. Conversely, by regulating the amount of lye relative to the size of the kettle, a definite percentage of glycerol can be removed from the kettle. Extending the latter idea to its end, it is evident that a definite kettle recovery of glycerin can be obtained by being able to regulate the weight of the "washes" relative to the weight of the curds. (The curd under ordinary kettle operation will hold 35-38 per cent of its weight in "entangled lye.")