

REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1936

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(Section 2)

Deterioration of Fats and Oils

REVIEWS on the spoilage of fats and oils were contributed by K. Täufel (*Angew. chem.* 49, 48-53, and *Z. Untersuch. Lebensm.* 72, 287-99), Richard Neu (*Chem.-Ztg.* 60, 205-7), and I. H. Schmalfluss, H. Werner and A. Gehrke (*Fette u. Seifen* 43, 211-4, 243-7).

L. H. Lampitt and N. D. Sylvester (*Biochem. J.* 30, 2237-49) recorded analyses of oxidized fats and correlated their findings. These results included data on the Kreis test, Issoglio value and peroxide value. The technic for the determination of peroxides by Lea's method, and new and improved methods for the other tests, were described. During the course of the determination of the Issoglio value, the fats lost 16 per cent of their peroxide value, about 55 per cent in intensity of the Kreis test and 55 per cent of the aldehyde value. The figures were not dependent upon the degree of oxidation of the fats. The Issoglio value appeared to be proportional to the reduction in the aldehyde value and also to the aldehyde value of the original fat. The aldehyde value and peroxide value varied in approximately direct proportion.

E. Freyer (*OIL & SOAP* 13, 227-9) made observations on the color changes that occurred in cottonseed oil during the stability test, which led to the development of a simplified Wheeler-Swift procedure. Just before rancidity developed in the test the oils became darker, after which they began to bleach. During the latter change rancidity became organoleptically apparent. The darkening occurred just before a peroxide value of 125 was reached, which is the adopted minimum value at which cottonseed oil is considered to be non-rancid. This characteristic was used with the new apparatus, thus eliminating the necessity of judg-

ing the end point by determining the peroxide value. The principal feature of the new apparatus is a glass bath vessel, which permits examination of the tests without removal of the tubes.

Rape seed oil, wheat germ oil, cod liver oil and oleic acid were studied by J. M. Aas (*Fettchem. Umschau* 43, 52-5) with a special apparatus which allowed correlations to be made between oxygen uptake, gain in weight and loss in iodine value. Wheat germ oil and oleic acid took up 3 atoms of oxygen per double bond affected. Rape seed and cod liver oils took up 2-2.2 oxygen atoms per double bond. Only 0.64 per cent volatile product was given off in 124 days of oxidation. General information on oxidative deterioration and the mechanism of antioxidants in oils were presented by E. L. Lederer (*Öle, Fette, Wachse* 1935 [1] 2-5 and *Petroleum* 31, No. 40 and 44).

Studies of the factors which influence the stability of fats during storage were reported by G. R. Greenbank (*OIL & SOAP* 13, 140-1), M. R. Coe (*OIL & SOAP* 13, 197-9), F. R. Robertson and J. G. Campbell (*OIL & SOAP* 13, 172-3) and N. N. Godbole and Sadgopal (*Z. Untersuch. Lebensm.* 72, 35-45). The information by G. R. Greenbank was presented graphically. The accelerating action of light was most pronounced in the presence of air followed by moisture and heat, respectively. Removal of free fat acids from butter by steam distillation followed by storage for three years under vacuum and in diffused light resulted in a negative Kreis test. M. R. Coe recorded correlations on the induction period and rancidity development between oils protected from light by a green wrapper delimited by 4900 to 5800A and non-protected oils. The development of peroxides in the protected oils was no indication of the rate at which rancidity developed in un-

protected oils. Rancidity of an oil had no necessary correlation with the development of peroxides. There was a relationship between the numerical increase in the peroxide value of an oil, previously protected from the time it was exposed to light until it became rancid, and the peroxide value of a fresh sample of the same oil when it became rancid. Robertson and Campbell studied the possible effect of storing cottonseed oil in containers made of the following commercial alloys and metals: Hastelloy A, tinned Everdur A, Everdur A, deoxidized copper, nickel, Monel, Inconel, high-purity aluminum, commercial aluminum, Armco 18-8, Armco 17, Armco ingot iron, Allegheny metal, galvanized iron and glass (enameled black to exclude light). The peroxide values of oils stored in Everdur A and deoxidized copper containers were reduced in 2 weeks from 12.8 to 4.5 with improvement in flavor, but the sample in the copper container developed rancidity in 16 weeks. The oils held in Everdur and the copper became rancid at peroxide values of 49.0 and 84.0, respectively. All the other metals reacted nearly alike. N. N. Godbole and Sadgopal tabulated results of tests on the influence of light, air, moisture content, metals and rancid ghee on the stability of Indian buffalo butter fat (ghee).

H. Schmalfluss, H. Werner and A. Gehrke (*Margarin Ind.* 28, 43-4; 29, 4-8) studied the effect of heat on aldehyde formation in fats. They observed that lauric acid on heating became aldehydic easier than unsaturated oils; whereas, the reverse was expected. This prompted the authors to investigate whether or not some of the aldehydes formed were decomposed on heating. Tests were made by treating oils at 120, 150 and 180° and periodically determining the aldehydes by the von Fellenberg and Kreis tests which were modified to

give some quantitative aspects. Coco fat, palm kernel fat, glycerin, and paraffin oil gave good von Fellenberg tests which first increased and then decreased. Soy bean oil, peanut oil, lauric acid, methyl esters of lauric and caprylic acids acted similarly but in a lesser degree. The Kreis test was positive only in coco fat, palm kernel fat, soy bean oil and peanut oil. The intensity of the Kreis reaction rose to a maximum and then decreased. The decreases were about 100 times slower than the increases.

Several communications dealt with the action of micro-organisms on fats. J. R. Vickery (J. Council Sci. Ind. Research 9, 107-12, 196-8) tested the activity of several strains of *Achromobacter*, *Pseudomonas* and *Asporogenous* yeast on a synthetic medium containing 80 per cent beef fat in water-in-oil emulsion. All the strains of yeast and *Pseudomonas* tested were responsible for appreciable lipolysis, but only one strain of *Achromobacter* had this power to a slight degree. He therefore contended that the level of free acidity in beef fat does not apply generally as an index of spoilage occurring in beef fatty tissue. Where *Achromobacter* slim was present on stored fatty tissues, there was little lipolysis even where off-flavors and off-odors had developed. S. H. Jenkins (J. Soc. Chem. Ind. 55, 315-9T) described experiments which showed that decomposition and biological oxidation of stearic acid takes place in percolating sewage filters if available nitrogen, phosphorus and potassium are present. R. F. Boan (J. Proc. Sydney Tech. Coll. Chem. Soc. 6, 16-17) observed that considerable splitting occurred in linseed oil following storage in containers that previously contained honey. The splitting was attributed to ferments from the honey.

Keeping tests on fats stored for a year and a year and a half were reported by Louise Stanley (Report of chief of the Bureau of Home Economics 1935). After a year 3 kettle rendered lards, a prime steam lard, corn oil and a peanut oil showed some deterioration. At the end of a year and a half the fats were used as shortening in biscuits and judged for taste and odor. Two kettle-rendered lards made from fat of hogs fed, respectively, on a peanut and a corn ration were most frequently marked by judges as stale or rancid. Cottonseed oil also scored low

in flavor. The prime steam lard ranked among the best. The corn oil gave the most desirable flavor although the peroxide value of this was the highest of all the fats.

Biscuit and cracker manufacturers prefer using lard in their products from the standpoint of flavor and texture, but the poor stability of lard has limited its use in these products. R. M. Bohn (OIL & SOAP 13, 302-3) recommended mixing lard with more stable shortening for this purpose. In this manner the disadvantage to lard was partly obviated, while the preferable qualities were transmitted to the crackers or biscuits. Various mixtures of lard and shortening for this purpose were listed with data relative to their stability.

Investigations on antioxidants and autoxidation were reported in a series of papers by H. S. Olcott and H. A. Mattill (OIL & SOAP 13, 98-100; J. Am. Chem. Soc. 58, 1627-30, 2204-8) and L. A. Hamilton and H. S. Olcott (OIL & SOAP 13, 127-9). Antioxidants for lard, derived from the unsaponifiable lipid fraction of vegetables or vegetable oils, were named inhibitols. These inhibitols can be concentrated from wheat germ or cottonseed oils by processes used for preparing vitamin E concentrates followed by further fractionating the inhibitols from the concentrated mixture. These products were transparent oils. Their activity was destroyed by reagents which attacked the hydroxyl groups or saturated ethenoid linkages, but the inactive esters could be hydrolyzed to regenerate the activity and the chlorine and bromine addition products could be reactivated with zinc and hydrochloric acid. The concentrates had a strong absorption band at 2940A, which was roughly proportional to their activity. The inhibitols were more effective antioxidants in lard than in any other compound for which use of antioxidants had been suggested. The inhibitols protected purified fat acids and esters but did not protect the vegetable oils from which they were obtained. Commercial preparations of lecithin had a moderate antioxygenic action on cottonseed oil and lard and none on mixtures of lard and cod liver oil. The activity of the commercial lecithin was attributed to presence of cephalin because purified cephalin was active while purified lecithin was not. Other experiments included in this series dealt with the evaluation of several antioxidants

on methyl and ethyl esters of fat acids and a preliminary classification of inhibitors. The crude methyl and ethyl esters of vegetable oil fat acids were protected to a remarkable degree by several organic dibasic acids, phosphoric acid, sulfuric acid, cephalin and some phenolic inhibitors. Hydroquinone was slightly effective and inhibitols were inactive. When esters were partially purified by vacuum distillation, they were only slightly protected by acids and cephalin but were protected by hydroquinone and the inhibitols. They proposed a tentative classification of inhibitors into three groups: (1) acid type inhibitors; (2) inhibitols and hydroquinone; and (3) other phenolic inhibitors. Hamilton and Olcott postulated that phenolic inhibitors and inhibitols induce their effect by inhibiting formation of the initial active moloxide and that they are entirely destroyed before the start of rapid oxidation. Pro-oxidants were said to decrease the period before rapid oxidative deterioration by virtue of their destruction of natural inhibitors.

A comprehensive investigation on antioxidants and preservation of edible fats was made by C. H. Lea (J. Soc. Chem. Ind. 55, 293-302T; Dept. Sci. Ind. Res. Rept. Food Investigation Board for 1934, 38-43). The oxidation of the oils in contact with water was followed by determining the peroxide oxygen content, and the results were presented in charts. The oxidation of lard in glass vessels in contact with water was much more rapid at an alkaline than at an acid pH. It was suggested that this effect was due to dissolution of copper from the glass. At pH values below 5, nitrite was found to be a powerful pro-oxidant. Copper and iron in aqueous solution accelerated the oxidation of lard; the copper was 20 times as active as iron. Iron in alkaline solution, *i. e.*, colloidal ferric hydroxide was inactive. The various antioxidants tested were grouped according to their strength as follows: (1) Inactive—mannitol. (2) Weak—glycerol, glucose, sucrose, fructose. (3) Moderate—lactic, glycolic, and maleic acids or their sodium salts, ethanalamines and maleic acid. (4) Powerful—Polybasic hydroxy-acids and aliphatic amino-acids. The stability of oils containing the antioxidants was greatest in the presence of acids. The pro-oxidant effect of copper in concentration up to one part per million was completely inhibited by

several antioxidants. For some antioxidants increasing the amount of water beyond 0.01% produced an increased effect, for others it did not. In some cases, appreciable advantage was secured by using a mixture of two antioxidants. H. N. Holmes, R. E. Corbet and E. R. Hartzler (Ind. and Eng. Chem. **28**, 133-5) also recommended the use of more than one antioxidant. They reported that the combination of hydroquinone and lecithin afforded greater protection to vitamin A of cod liver oil than would be expected from the additive effects of both.

The effect of menthol, camphor, borneol, terpine, carvene and turpene on the oxidation of linseed oil was studied by A. Castiglioni (Ann. chim. applicata **26**, 249-51). The data which showed that menthol definitely catalyzed the oxidation of linseed oil seemed to be new among the observations.

The new antioxidants patented were as follows: A. E. Briod (U. S. 2,050,689), methoxyhydroquinone; I. Davidsohn and R. Strauss (Ger. 619,928 Cl. 23a 3), chlorinated or brominated paraffins; C. S. Marvel (U. S. 2,047,642), organic ester of tyrosine; H. E. Buc (U. S. 2,031,930), phenolic compounds containing a tertiary aliphatic hydrocarbon as a side chain; W. D. Richardson, D. P. Grettie and R. C. Newton (U. S. 2,031,069), condensation product of pyrogallol and acetone, stearylated pyrogallol, pyrogallol dimethyl ether and 1, 4- and 1,5-dihydroxy naphthalenes; R. M. Reed (U. S. 2,029,506), *p*-butyl (or amyl) phenol; C. E. Macke (U. S. 2,058,162), the aqueous extracts of sage or celery which have a solubility preference to oils and fats; R. C. Newton and D. P. Grettie (U. S. 2,060,587; Ger. 618,836 Cl. 53h; Can. 348,488), crude cottonseed oil; D. P. Grettie (U. S. 2,052,289) crude soya bean oil; Industrial Patents Corp. (Ger. 628,690 Cl. 53h), hydrogenated sesame seed oil; and D. P. Grettie (Brit. 446,792 a modification of Brit. 395,971), a heavier-than-water liquid distillate secured by the deodorization of hydrogenated sesame seed oil. Special treatments to improve stability of oils were patented by S. Musher (Fr. 785,927; Brit. 451,340; U. S. 2,049,017) and W. Ekhard (Fr. 797,099; Brit. 452,682). Musher treated the oils or fats with cereal material, such as oats, rye, barley, flour, sesame seeds or like material at about 60° for 15 minutes. The

vegetable material was removed after the treatment. Ekhard improved stability of oils by mixing them with a fermentable substratum which was brought into active fermentation by micro-organisms that produced both lactic acid and alcohol. The oils were separated after the fermentation ceased.

Some interest prevailed toward improving containers to yield maximum protection to stored fats or oils. L. A. Pelton (Food Industries **8**, 65-6) recommended use of glass lined steel tanks and drawing a vacuum in the head space of each tank after filling. W. L. Morgan (U. S. 2,043,860) developed transparent cellulose wrapping sheets for protection of fats, oils and waxes from rancidity. The sheets were made from transparent cellulose containing special dyes in a concentration sufficient to render it transparent to light having a wave length other than 2900 to 4700A. S. Musher (U. S. 2,038,752) coated flexible packaging material in sheet form with antioxidants selected from the group consisting of cereals and grains. Fat or oil products in contact with such a surface were protected against oxidation. A general discussion on protective coatings for fat or oil containers was presented by H. A. Levey (OIL & SOAP **13**, 199-201). The following topics were treated: properties required, method of application, formulas and their preparation, function of ingredients, methods of testing, and trend of development.

Correlations between the peroxide value of cod liver oil and vitamin A destruction were graphically recorded by Dorothy V. Whipple (OIL & SOAP **13**, 231-2). Vitamin A was destroyed at lower peroxide values when rancidity developed at room temperature than when it was accelerated by aeration at 100°C. It was suggested that not only vitamin A but other biological properties are not equally affected by rancidity produced in different ways and at different rates.

The development of the so-called tallowiness, fishiness or flavor reversion is a form of deterioration of fats and oils, the mechanism of which seems to have resisted all attempts toward a solution. Investigations on this problem were reported by W. L. Davies and E. Gill (J. Soc. Chem. Ind. **55**, 141-6T). It was shown that various oils, notably linseed oil, on long standing with casein, betaine, leci-

thin or other nitrogen sources or by heating with trimethylamine oxide at 105° for a short time, can react with the nitrogen compounds and develop a "fishy" odor. Glycerol, cholesterol, and unsaponifiable matter of vegetable and animal fats do not acquire a "fishy" odor or flavor under the same conditions. It was postulated that fishiness was associated with traces of peroxides, formaldehyde, and tertiary nitrogen either in the form of volatile bases, trimethylene, or its oxide.

Composition and Characteristics of Fats and Oils

Much work has been done to determine the composition of various natural fats. A review with general discussion of current methods for identifying and determining the various fat acids in food fats was presented by J. Grossfeld (Chem. Ztg. **60**, 913-7). T. P. Hilditch (Fette u. Seifen **43**, 97-100) described a scheme for determining per cent fat acids. The method was based on separation of liquid from solid acids by a modified Twitchell procedure, preparing methyl esters, fractionating and analyzing the fractions. S.-S. Ueno and coworkers (J. Soc. Chem. Ind., Japan **38**, 602-3, 691-2) determined the percentage of various fat acids in several completely hydrogenated oils by fractional distillation. This method yields an estimate of the fat acids of various carbon chain lengths in the oils. Data on several oils were reported. S. Lepkovsky, G. V. Feskov and H. M. Evans (J. Am. Chem. Soc. **58**, 978-81) improved a still that had been devised several years ago by H. M. Evans and applied it to the fractionation of fat acids of coconut oil and separation of erucic acid from rape oil. They claimed that complete separation of palmitic from C₁₈ acid was possible by distillation of the methyl esters.

The composition of jojoba, *Simmondsia californica*, seed oil appears to be one of the most unusual of any of the vegetable oils yet recorded. R. S. McKinney and G. S. Jamieson (OIL & SOAP **13**, 289-92) analysis of this oil was: saturated acids 1.64, palmitic acid 0.24, oleic acid 0.66, eicosenoic acid 30.30, dicosenoic acid 14.20, eicosenol 14.60 and dicosenol 33.70 per cent. These results indicate that the oil is not a glyceride fat but a liquid wax, composed almost entirely of esters of high molecular

weight monoethylenic acids and alcohols. Due to the unusual composition of this oil the means of arriving at the composition was complicated. Two saponifications were necessary to separate the acid constituents; the first saponification was carried out with sodium ethylate and the unsaponifiable matter remaining after this treatment was subjected to saponification for several hours with strong alcoholic potash. The acids were converted to the ethyl esters, fractionated, the fractions hydrogenated and further separation of the individual acids was carried out by fractional crystallization. The alcohols were converted to the acetate esters and separated by fractional distillation followed by fractional crystallization after hydrogenation. The individual acids and alcohols were identified by the physical and chemical characteristics.

T. P. Hilditch (Ann. Rev. Biochem. 5, 101-16) reviewed the recent literature on component fat acids and other substances present in natural fats and oils. This investigator with W. J. Stainsby (J. Soc. Chem. Ind. 55, 96-101T) and with T. P. Green (J. Soc. Chem. Ind. 55, 4-8T) also made additions to this type of information. The first mentioned paper pertained to the component glycerides of cacao butter. The composition of the butter in per cent by weight was: oleopalmitostearin 52, oleodistearin 19, stearodiolein 12, palmitodioleins 9, oleodipalmitins 6 and palmitostearin 2. Green and Hilditch recorded data on the amounts of polyethenoid C_{18} acids present in marine animal oils. The unsaturated C_{18} acids of whale oil consisted of about 90 per cent oleic and isomers of same, 3 per cent tetraethenoid and the remaining 7 per cent might have been octadecadienoic acids with but only small amounts of ordinary linoleic acid. Linolenic acid was absent. For cod liver oil the results were 70 per cent oleic and isomers of same, 10 per cent tetraethenoid stearidonic acid; the remaining 20 per cent probably were di- or triethenoid in character but linolenic was not found; and ordinary linoleic, if at all, was present in extremely small amounts. The unsaturated acids of grass-fed carp contained 11 and 6 per cent, respectively, of linolenic and linoleic acids. J. Pritzker and R. Jungkunz (Pharm. Acta Helv. 11, 177-83) produced evidence to confirm a statement of Bömer and Ebach that laurel oil contained 30

per cent trilaurin. They also proved the presence of 0.8 to 1.8 per cent caprylic acid in this oil. Using the methyl ester fractionation method of analysis, Y. Volmar and B. Hansen (Compt. rend. 201, 968-70), reported that there was from 0.19-0.23 per cent arachidic acid and about 1 per cent linoleic acid in various samples of olive oil.

Several analysts investigated butter fat and produced new additions to our knowledge of its composition. T. P. Hilditch and H. Paul (Biochem. J. 30, 1904-13) fractionally distilled butter fat acids. They found that there was no detectable amount of any unsaturated acid of lower molecular weight than decenoic acid, and the position of the double bond relative to the carboxyl group was the same in the C_{10} , C_{14} , C_{16} and C_{18} fat acids. They suggested that these observations indicated that the lower saturated glycerides of milk fats have been produced from preformed oleoglycerides, and that the lower unsaturated components may be degradation products of oleoglycerides which escaped complete saturation to lower saturated groups. Hexacosanoic (cerotic) acid and monohydroxypalmitic acid were isolated from butter fat by G. E. Holz and A. W. Bosworth (J. Biol. Chem. 112, 489-92; 116, 203-8). They also reported some of the characteristics of these acids. R. W. Riemenschneider and N. R. Ellis (J. Biol. Chem. 113, 219-33) analyzed goat milk fat for the fat acid present. The fat contained decenoic, tetradecenoic, palmitoleic, oleic, caproic, caprylic, capric, myristic, palmitic and stearic acids as indicated by a study of the distillation data. Subsequent examination of fractions established the presence of the above acids, also arachidonic acid and traces of an unknown acid which formed octabromides. A mixture of saturated acids with higher molecular weights than stearic acid was also isolated; this consisted principally of tetra-cosanoic acid along with traces of cerotic acid.

The variation in characteristics of several oils and fats was surveyed. R. T. M. Haines and J. C. Drummond (Analyst 61, 2-7) and N. Evers, A. G. Jones and W. Smith (Analyst 61, 7-11) tabulated the various characteristics of the halibut-liver oils of the 1935 season. The maximum, minimum, and average values of each of the characteristics were given. J. A. Lovren (Biochem. J. 30, 2023-6) analyzed

the fats from different parts of tunny fish. He showed that the content of stearic acid was inversely proportional to the degree of unsaturation of the remaining C_{18} acids. Western Canadian flaxseeds of the 1935 crop, according to W. F. Geddes (Can. Dept. Trade & Com., Dominion Grain Rev. Lab., 9th Ann. Rept. 1935, 77-80) had an oil content of from 38.3 to 45.2 per cent and averaged 42.1 per cent. Iodine value ranged from 172 to 201.7. His data indicated that the highest quality flaxseed was produced under environmental conditions which favor low protein content of wheat. J. F. O'Kelly and M. Gieger (Assoc. Southern Agr. Workers Proc. 34th, 35th and 36th Ann. Conventions 1933-35, 460) recorded the effect of variety, maturity and soundness on certain soybean seeds and oil characteristics. The beans of the Laredo variety contained less oil than other varieties, and this oil usually had a higher index of refraction and iodine value than did the others. Beans harvested before maturity contained more oil than did mature beans. The oil of immature beans had a higher index of refraction and lower iodine value than the oil of mature beans. Decomposition of beans was accompanied by a considerable increase in lipid content; the index of refraction of the oil increased slightly; the iodine value decreased considerably, but the saponification value showed no distinct trend. A difference in composition of kapok oil obtained from Java seeds and that from the Philippine seeds will be noted by comparing the data reported by G. S. Jamieson and R. S. McKinney (OIL & SOAP 13, 233-4), with that reported several years ago by A. O. Cruz and A. P. West. The proportions of stearic and palmitic acid differed in the samples, also myristic acid was reported in Philippine oil while Jamieson and McKinney did not detect this acid in the Java seed oil. Hans Mann (Fette u. Seifen 43, 153-6) made analyses on the body fats of bats at the beginning of hibernation and those of bats after 100 days of hibernation. The results from male and female bats were tabulated. The per cent of fat remaining in the females was greater. The melting point of the fat and unsaponifiable matter increased; the iodine value, saponification value and ester value decreased; and the acid value remained practically the same. All changes were greater in the male

animals. It was postulated that the same changes also occurred in other hibernating animals.

Technically important characteristics of Chinese and English cottonseed oils were studied, respectively, by P. E. Ronzone (OIL & SOAP 13, 165-7) and W. G. McLeod (OIL & SOAP 13, 67-8). The Chinese cottonseed oil was highly colored and gave high refining losses. Winterizing the oil was impossible unless it was mixed with 25 per cent of domestic oil. Data on some of the English crude cottonseed oil handled in this country suggested that it was obtained from poor quality seeds. A method for successfully refining the oil was presented.

L. J. Reizenstein (Am. Paint J. 20, June 22, 7-9, 46, 48, 50) reviewed the characteristics of a number of fish oils and discussed the general application of the oils together with possible future development. The Russian investigators, M. P. Belopols'kii, O. B. Maksimov and E. A. Lagovskaya (Bull. Far East Branch Acad. Sci. U. S. S. R., No. 16, 65B) contributed a study of the oils from fresh water fishes inhabiting the Amur River and Lake Khanka. The iodine values of whale oils were compared by J. Lund (OIL & SOAP 13, 148-50). The oils from the "right" whales had the highest iodine values; oils from humpback and sei whales had mean iodine values and the lowest were found in oils from blue and fin whales.

Interest in the identification of new component fat acids and work on the less widely distributed fat acids has continued. A survey on the methods of identification of minor component fat acids of natural fats was given by J. B. Brown (OIL & SOAP 13, 303-6). W. B. Brown and E. H. Farmer (J. Chem. Soc. 1935, 1630-2) reported that the α -licanic acid, oiticica fat and kernel oil of *Licania rigida* were converted by irradiation in the presence of iodine or sulphur to the iso- or β -acid. S.-S. Ueno *et al.* (J. Chem. Soc. Japan, 57, 180-2, 322-5, 462-8; Bull. Chem. Soc. Japan 11, 437-42) identified thynic acid ($C_{26}H_{40}O_2$) and shibic acid ($C_{28}H_{42}O_2$) in tunny oil and showed that hokke (*Pleurogrammus monoptygius*) oil contained 40 per cent of highly unsaturated acids with more than 20 carbon atoms per molecule. These latter acids were scolioic, thynic, shibic and C_{28} acids containing 4, 5, 6 or 7 double bonds. Y. Toyama and

coworkers (J. Soc. Chem. Ind. Japan 38, 680-4B; J. Chem. Soc. Japan 56, 1054-7, 1072-80, 1313-5 and Bull. Chem. Soc. Japan 10, 433-51) identified several unusual fat acids in fish and marine animal oils. The acids that were isolated and whose structures were established, were: tetradecenoic ($C_{14}H_{26}O_2$), decenoic ($C_{10}H_{18}O_2$), and dodecenoic ($C_{12}H_{22}O_2$) from sperm oil; and clupanodonic ($C_{22}H_{34}O_2$), docosahexenoic ($C_{22}H_{32}O_2$) and nisinic ($C_{24}H_{36}O_2$) from sardine oil. Evidence was presented to show that cetoleic ($C_{22}H_{42}O_2$), docosatetraenoic ($C_{22}H_{36}O_2$) and scolioic ($C_{24}H_{38}O_2$) acids may also be present in sardine oil. Y. Toyama with T. Tsuchiya (J. Soc. Chem. Ind. Japan 39, 220-1B) also isolated trichosanic acid from balsam pear seed oil.

Developments in the knowledge of cis-trans isomerism of monoethenoid fat acids, *i.e.*, conversion of oleic acid into elaidic acid and erucic acid to brassidic acid proved to be of both theoretical and technical importance. G. Rankov (Ber. 69B, 1231-8) studied various catalyzers for the conversion of oleic to elaidic acid. Heating oleic acid in a sealed tube to 200° with red phosphorus resulted in 60-70 per cent conversion while ordinary phosphorus was inactive. Olive oil, palm oil, beef tallow and beef bone fat, when heated 3 or 4 hours at 220° in the presence of 1 per cent sulphur or 3 per cent phosphorus and 50 per cent water in sealed containers, were almost completely decomposed into free acids and glycerol, and the fat acid mixture obtained had a considerably higher melting point than fat acid obtained by saponification. This indicated that elaidization had taken place. The process is of technical importance for the manufacture of soap. The use of selenium or tellurium for elaidization catalyst was patented by the N. V. Ned. Research Centrale (Fr. 794,529). S. H. Bertram (Chem. Weekblad 33, 3-5) prepared elaidic acid using selenium as a catalyst. Under all conditions, *i.e.*, using pure oleic or mixtures of oleic with stearic acid or paraffin, only 67 per cent conversion occurred, giving a 2:1 ratio for elaidic and oleic acid. This was explained by assuming that oleic acid was the trans form and elaidic acid the cis form, since the probability of cis formation is twice that of trans when starting with the activated intermediary

stage. Characteristics of several alcohol esters of elaidic acids were determined by A. K. Plisov and V. P. Galendeev (Rep. U. S. S. R. Fat and Margarine Inst. 1935, 3-11, 12-21). They found that the hydrogenation velocities of esters of oleic acid were slightly greater than those of elaidic, which led them to conclude that oleic acid has the cis configuration. This conclusion does not agree with that of Bertram. K. Hashi (J. Soc. Chem. Ind. Japan 39, 18B) prepared the chlorohydrins of both oleic and elaidic acid. The melting point of that from oleic acid was 38 to 38.3, while elaidic acid yielded chlorohydrins melting at 49.5 to 51 and 68 to 69.5. L. Keffer and A. M. Maiden (Bull. Soc. Chim. Belg. 44, 467-72) prepared brassidic acid by isomerizing erucic acid. This brassidic acid melted at 59.9.

H. A. Boekenoogen (Allgem. Oel-u. Fett-Ztg. 33, 461-8) contributed a brief summary of the information regarding phosphatides and non-glyceride constituents of fats giving their structural formulas and properties. New data on these constituents were also published. According to a communication by B. Rewald (J. Soc. Chem. Ind. 55, 1002-3) nearly 63 per cent of the phosphatides in wheat germ oil were bound to sugar, protein or other substances. The total amount of phosphatides was 0.611 per cent, 80 per cent being of the lecithin type and 20 per cent of the cephalin type. B. Sullivan and C. H. Bailey (J. Am. Chem. Soc. 58, 390-3) studied the unsaponifiable lipids of wheat germ. This fraction amounted to 4 per cent of the lipids. Approximately 70 per cent of the fraction consisted of sterols, about 56 per cent of which occurred in the free state. A few characteristics of the fractions were reported. H. Hotta and M. Kawaji (Nogoya J. Med. Sci. 9, 23-4) analyzed several liver oils for cholesterol; 3.4 to 5.4 milligrams per milliliter of oil were found. Alcohols were reported in oils by the following: Y. Toyama and coworkers (J. Chem. Soc. Japan 56, 1055-7, 1072-8, 1316-19) identified tetradecenol and hexadecenol in sperm whale oil; from the same oil, S.-S. Ueno (J. Soc. Chem. Ind. Japan 38, 608-11B) separated alcohols containing 8, 10, 12 and 14 carbon atoms; and S.-S. Ueno with R. Koyama (J. Chem. Soc. Japan 57, 1-9) repeated the separation of the above alcohols and proved that both the saturated and unsaturated

forms were present. J. Nakamiya (Sci. Papers Inst. Phys. Chem. Research, Tokyo, 28, 16-26) obtained gadusene (C₁₈H₃₂), an unsaturated hydrocarbon from fish-liver oils. H. Marcelet (Bull. Soc. chim. 3, 1156-60); Compt. rend. 202, 867-9, 1809-11) isolated hydrocarbons from the unsaponifiable portion of peanut and olive oils. Peanut oil contributed hypogeene (C₁₅H₃₀) and arachidene (C₁₉H₃₈). The chemical names of the hydrocarbons from olive oil were prefixed by "olea"; these hydrocarbons were: oleatridecadiene (C₁₃H₂₄), oleahexadecadiene (C₁₆H₃₀), oleanonadecadiene (C₁₉H₃₆), oleatricosatriene (C₂₃H₄₂), oleaoctacosatetrene (C₂₈H₅₀) and oleatetracosane (C₂₄H₅₀).

Observations on the gossypol contents of cottonseeds were recorded by W. D. Gallup (OIL AND SOAP 13, 191-4). Variations in single varieties appeared to be related to environmental factors of the regions in which the seeds were produced. High potash fertilization was beneficial to the development of gossypol. Factors which altered the gossypol content of seeds produced a corresponding, although less proportionate, change in the oil content. The oil-gossypol ratio was much wider in seeds of low oil content than in seeds of high oil content. The practical significance of this ratio pertained to the decreased re-

fining loss shown by certain grades of crude cottonseed oil with increasing gossypol content.

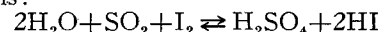
A preliminary survey of the oil yield and oil content of certain oleaginous materials was prepared by Anne Dewees and O. C. Stine (U. S. Dept. of Agr., Bureau of Agr. Economics, June, 1936). The data included the actual percent yield obtained by several processors over a year's period. Tables appended to this division of the review contain additional data on oil content of substances, characteristics of the oils and the component fat acids.

The analyses of several tung fruit, grown in the state of Mississippi, were recorded by R. S. McKinney and G. S. Jamieson (OIL AND SOAP 13, 71). The oil content of the fruit kernels of two cultivated trees was 64.7 and 70.1 per cent; whereas that from other samples ranged from 53.6 to 67.6. For comparison, tung fruit kernels grown in Florida gave 67 per cent oil. An extremely low moisture content of the high oil-bearing seeds accounted in part for their high oil content. The iodine values (Wijs) of the oils ranged between 163.1 and 165.5.

New methods for determining the oil content of seeds have aimed mainly at speeding up the determination. C. E. Weakly (Ind. Eng. Chem. Anal. Ed. 8, 388-9) designed a new 20 unit modified Soxhlet ap-

paratus. Other communications on fat and oil content analyses dealt with refractometric methods. J. P. Groenhof (Pharm. Weekblad 73, 1002-16), D. C. Ingraham and T. H. Simpson (OIL & SOAP 13, 222-4) and W. F. Geddes and F. H. Lehberg (Can. J. Res. 14, 48-61) described improved Coleman Fellows procedures, based on index of refraction using halowax as the solvent, for the analysis of various seeds. W. Leithe (Z. Untersuch. Lebensm. 71, 33-8) preferred bromonaphthalene to chloronaphthalene as a solvent in this procedure. The refractometer was also recommended by F. J. Squire (OIL AND SOAP 13, 2-5) for determining the rosin acids in fat acids, and by W. F. Geddes (Can. Dept. Trade & Com. Dominion Grain Research Lab. Ann. Rept. 1935, 76-7) for predicting the drying values of cold pressed linseed oil.

The new method for determining moisture in materials, including oils and fats, by K. Fischer (Angew. Chemie 48, 394-6) and Richter (Angew. Chemie 48, 776) can be completed in much shorter time than the old drying method. This new method depends on the amount of iodine absorbed by materials in sulfur dioxide-methyl alcohol solution. The reaction which takes place is:



CHARACTERISTICS REPORTED FOR VARIOUS OILS DURING 1936

Oil or Fat Source	% of oil or fat in source	Density	Refr. Index	Acid No.	Sapon. No.	Iodine No.	R.-M No.	Polenske No.	Acetyl No.	% Unsap.	Thioacyl anogen No.
<i>Asclepias cornuti</i> seed ¹	0.9286 ^{15.5}	10.2	188.9	122.9	1.6	28.17	75.62
Astrakhan Whitefish body ²	0.9232 ^{20/4}	1.4756 ^{20/D}	14.53	194.33	146.21	1.46	11.28	0.60	94.58
<i>Atropa belladonna</i> seeds ³	28.0	146.5	2.5
<i>Balanites aegyptiaca</i> fruit (of Africa) ⁴	Kernel 46.8	0.9220 ^{15/15}	1.4640 ⁴⁰	0.9	191.6	98.0	0.3
Balsam fir seeds ⁵
<i>Abies balsamea</i>	10.69	0.9279 ^{25/25}	1.4783 ²⁵	0.88	185.6	141.0	0.53	0.21	15.4	4.8
Balsam pear seed kernel ⁶
<i>Momordica charantia</i>	40.9	0.9153 ^{40/4}	1.5010 ^{40/D}	0.63	189.9	140.1	0.91
Beechnut kernel ⁷
<i>Fagus silvatica</i>	43	111.9	0.27	79.2
Black walnut (of America) ⁸
<i>Juglans nigra</i>	1.4730 ²⁵	7.8	193.5	135.1	0.42	86.0
Bushale seed ⁹
<i>Lebrunea bushale</i>	65.23	0.9156 ¹⁵	1.4708 ²⁰	7.41	182.82	83.39	4.3	0.8	31.48	0.53
<i>Celastrus paniculatus</i> seed ¹⁰	52.2	0.9586 ^{25/25}	1.4747 ³⁰	44.4	239.2	102.9	62.8	130.1	5.7
<i>Clerodendron cyrtophyllum</i> seed ¹¹	0.9110 ^{30/4}	1.4631 ^{30/D}	90.27	196.25	84.75	2.06
Chile seed ¹²
<i>Capsicum annuum</i>	26.1	0.9132 ^{4.5/25}	1.4738 ²⁵	2.18	192	133.5	7	1.7
Cocklebur ¹³	4.63-	0.8938-	1.4746-	44.6-
<i>Xanthium commune</i>	7.45	1.0088 ²⁵	1.499 ²⁵	103
Croton seed ¹⁴
<i>Croton tiglium</i>	0.9338 ¹⁵	1.4732 ^{21/D}	204.0	115.1	1.3
Cucurbitaceae seed kernels (various species) ¹⁵	39.7-49.2	0.9194-0.9248 ^{15/4}	1.4738-1.4789 ^{15/D}	1.0-5.56	189.7-191.8	102.9-145.2	0.77-0.95
Date stones ¹⁶
<i>Phoenix dactylifera</i>	6.8-8.5	0.9201 ^{15.5}	1.4580 ^{40/D}	212.6	54.5	1.1	3.0	1.98
<i>Datura stramonium</i> seeds ¹⁷	16.6	0.9184 ^{25/4}	1.4735 ^{25/D}	5.6	187.1	122.6	0.44	25.6	2.6
<i>Datura stramonium</i> seeds ⁸	6.7	115.8	1.9
<i>Duranta plumeri</i> seed ¹¹	0.9439 ^{30/4}	1.4736 ^{30/D}	58.62	210.91	101.30	0.40
Eel (during spring) ¹⁸	2.11	197.01	146.22
Eel (during summer) ¹⁸	6.30	193.09	158.89
Elderberry seed oil ¹⁹	28.1-	0.9320-	1.4781-	188.1-	1.5-	98.9-

(Table Continued on Following Page)

SUPPLEMENT TO CHART ON CHARACTERISTICS

Material	Hehner No.	Melting Point	Solidification Point	Titer	Ester. No.	Hexabromide No.
<i>Gallarynchus gallorynchus</i> and <i>antarticus</i>	-10
<i>Genypteris blacodes</i> and <i>chilensis</i>	-3
Grape seed (of Argentina) ²³
<i>Vitis vinifera</i>	-10.5
<i>Jatropha curcas</i> (of Belgian Congo) ²⁵	93.6-94.7
<i>Juglans manshurica</i> fruit kernel ²⁷	187.57
<i>Lagenaria vulgaris</i> ²⁹	93.2	-11
<i>Lophira alata</i> seed kernel (of Uganda) ⁴	24.5	43.8
Margosa seed ³¹
<i>Azadirachta indica</i>	39.6
Mink fat ³²	36.5
Nitonga nuts ³³
<i>Cryptocarya latifolia</i>	26.0	39.5	7.52
Olive (of Japan) ³⁵
<i>Olea europa</i>	-15°
<i>Palaquium formosanum</i> seeds ³⁷	57-60	27
<i>Peganum harmala</i> ³⁸	93.85	171.25	0
Poke root ³⁹	67.46
Po-Yok fruit (of Africa) ⁴
<i>Afrolicania elaeosperma</i>	30-50
<i>Psidium guajava pyrifera</i> seed (of India) ⁴⁰	17
Rice ⁴³
<i>Oryza sativa</i>	23.9
<i>Salvadora persica</i> fruit (of Sudan) ⁴¹	34.8	28.8
<i>Sapucahynda</i> seed ⁴⁴
<i>Carpotroche brasiliensis</i>	10-11
<i>Sapucahynda</i> seed ⁴⁵	22	13-15
Stickleback fish ⁴⁸
<i>Gasterosteus aculeatus</i>	91.0	180.15
Wheat germ ⁵¹
<i>Triticum vulgare</i>	89.0	2.28
<i>Xanthium strumarium</i> , L. seed ⁵³	92.52

COMPONENT FATTY ACID CONSTITUENTS OF THE OILS REPORTED 1936

Fat Source	Saturated Acids			Unsaturated Acids			Other Acids
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
<i>Asclepias cornuti</i> seed ¹	7-11	35	53.5
*Astrakhan whitefish body ²	22-13	43.8	3.91	12.45	Clupanodonic 6.71 Undetd. 3.0
**Black walnut (of America) ⁸
<i>Juglans nigra</i>	0.4	3.4	1.8	35.6	48.6	7.4	Lignoceric 0.04
<i>Atropa belladonna</i> seeds ³	5.9	1.8	25.5	66.8
<i>Datura stramonium</i> seeds ³	1.3	10.8	1.2	33.1	53.6
*Essang seed ²¹
<i>Escimodendron heudelotii</i>	9.7	16.0	11.0	10.0	Eleostearic 46.0
<i>Hyoecyanus niger</i> ³	6.5	0.4	11.1	82.0
<i>Juglans manshurica</i> fruit kernel ²⁷	2.9	0.6	18.69	76.27	2.24
**Kapok seed ²⁸
<i>Celba pentrandra</i>	10.2	8.4	45.2	32.9	Lignoceric 0.04
<i>Lagenaria vulgaris</i> ²⁹	17.62	28.25	15.26	30.74	Arachidic 0.68
*Linseed (of Egypt) ³⁰
<i>Linum usitatissimum</i>	6.34	7.57	38.44	42.33
Margosa seed ³¹
<i>Azadirachta indica</i>	13.6	19.1	49.1	15.8	Arachidic 2.4
**Oiticica nut ³⁴
<i>Licania rigida</i>	10.7	5.9	Licanic 78.2
<i>Psidium guajava pyrifera</i> seed (of India) ⁴⁰	16	55.8	27.8	0.4
Rape seed ⁴¹	3.5	14	24	2	Behenic 0.8 Erucic 55
Rice ⁴³	39.56	39.91
<i>Oryza sativa</i>	15.64
*Telfairia pedata seed kernel ⁵⁰	24.3	18.2	11.4	32.6	5.0	3.3 Volatile matter
Wheat germ ⁵¹
<i>Triticum vulgare</i>	16	28.14	52.31	3.55
*White Whale body ⁵²	50.95	0.08	Clupanodonic 1.22
*White Whale head ⁵²	0.70	C ₁₆ H ₃₀ O ₂ 30.25, clupanodonic 0.56 C ₁₈ H ₃₄ O ₂ 0.34
*White Whale jaw ⁵²	1.19	Clupanodonic 1.35
<i>Xanthium strumarium</i> , L. seeds	1.5-2.0	7.0-7.5	26.7	64.7

*Based on total oil. **As glycerides.

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E. Pyhälä (Öle, Fette, Wachse 1935, [1], 13-4) used the H. Cru-sell apparatus for determining the consistency of fats. The apparatus is similar to a viscosimeter. Results were reported in terms of the weight of fat that could be extruded during a standard time period under application of a constant fixed pressure and temperature. The data showed that there was no close relationship between the melting points and consistency of a fat. W. D. Gallup (Ind. and Eng. Chem., Anal. Ed. 8, 123-4) developed an apparatus for measuring the hardness of fats, principally of butter fat. With this device, hardness was expressed in grams of mercury required to force a plunger 5 mm. in diameter and weighing 50 grams through a disk of fat 6 mm. in thickness. The hardness figures on butters revealed marked differences in them which were less apparent when judged by iodine value or melting point.

A. Koss (Przemysl. Chem. 19, 139-47) studied the relationship between melting point and composition of various animal fats in an attempt to apply the information for identifying fats. The melting point data on fats, fat acids and mixtures of fats showed no regular relationship that could be used in identifying a mixture of two animal fats. Cooling curves for 16 hardened and 13 natural oils, fats and waxes were plotted by S.-S. Ueno and S.-S. Nakaguchi (J. Soc. Chem. Ind. 39, 79-82). Remarkable temperature elevation was observed after superfusion for each hardened oil and fat. The solid waxes and paraffin did not show a temperature rise. N. Spasskii (Seifensieder-Ztg. 63, 3) recommended seeding with solid material during the titer test on tallow to reduce the unfavorable influence of undercooling. Heats of crystallization of methyl and ethyl esters of several monobasic fat acids were determined by M. A. King and W. E. Gardner (J. Chem. Soc. 1936, 1372-6). Heats of crystallization of C_{14} to C_{22} acids ranged from 10.63 to 19.68 kilogram calories per gram mol; the specific heats of these acids varied between 0.51 and 0.54 for the liquid form and were slightly lower for the tilted form.

H. N. Brocklesby (Can. J. Research 14B, 222-36) revealed by the ebullioscopic method that saturated fat acids in benzene solution show a decreasing degree of association with increasing carbon content up to lauric acid, after which association re-

mains almost constant. The association constant for linseed oil indicated the normal molecular weight when determined either cryoscopically or ebullioscopically in a number of various solvents. Polymerized oils, by these methods, also showed identical molecular weights in different solvents. These data indicated that polymerized esters of unsaturated fat acids cannot be assumed to be associated.

During the past few years several writers have suggested including viscosity among the characteristics normally reported for an oil. A. R. Rescorla and F. L. Carnahan (Ind. Eng. Chem. 28, 1212-3), G. B. Ravick (Kolloid-Z. 76, 341-5), and G. N. Bhattacharyya (Indian J. Physics 10, 209-25) responded to this encouragement by supplying viscosity data for several oils at various temperatures, with other characteristics of the oils tested. The possible effect of impurities such as mucilaginous substances or oxidation products in viscosity measurements were discussed by W. Normann (Fettchem. Umschau 43, 9-10).

Theoretical bases for color measurements by various instruments in current use on fats and oils were discussed by L. Ivanovszky (Öle, Fette, Wachse, 1936 [4], 1-8). A modified Bailey instrument for this purpose was devised by H. B. Stevenson (OIL AND SOAP 13, [1], 18-20). The improvements pertain to mechanical detail in which color glasses are attached to disks and are manipulated by hand wheels. The use of the instrument obviates the danger of breaking standard glasses. Conditions which may affect the Lovibond readings on cottonseed oil, according to P. M. Shuey (OIL AND SOAP 13, 174-5), are: (1) Variations in color of the light source, (2) nonsymmetry in the instrument which may contain reflecting surfaces, owing to dirt or yellowing of transmitting surface, (3) temperature of the sample, (4) nonsymmetry of the eye, (5) unsymmetrical reflection, and (6) brightness differences in the field.

The Mackey test for spontaneous combustibility of oils was studied by W. Garner *et al.* (Analyst 61, 337-8, 519-28) and Kehren (Z. ges. Textil-ind. 39, 256-7). Garner suggested precautions that are necessary in the technic and also recommended the use of the apparatus for testing the sensitivity of oils to metallic oxidizing agents. Kehren pointed out several flaws in the apparatus built under German speci-

fications. His results indicated that English apparatus was much superior.

Two methods for determining acidity of oils were described. R. N. Evans and J. E. Davenport (Ind. and Eng. Chem., Anal. Ed. 8, 287-91) outlined a potentiometric method for the titration of the acids in insulating oils in which the glass electrode and *n*-butanol solvent were used. Fedchenko and Kashin (Masloboino Zhirovoe Delo 11, 498) added the sample of oil to 15-20 cc. of 10 per cent salt solution and titrated with 0.1 *N* potassium hydroxide in presence of phenolphthalein. This method was recommended for very dark oils. A method for determining the neutral equivalent of a fat acid of high molecular weight described by R. B. Sandin, M. Kulka and D. W. Wooley (Ind. and Eng. Chem., Anal. Ed. 8, 355-6) involved titrating the acid in absolute alcohol solution with sodium ethylate as the base and using thymolphthalein as the indicator.

The American standard method for determining sediment and material causing turbidity in vegetable oils was modified by E. Mirer (Anal. Methods in Oil and Fat Ind., U. S. S. R., 1936, 62-86, and Z. Untersuch. Lebensm. 71, 345-57). An improved sample container was devised by which, after centrifuging the sample, the sediment volume may be read in a graduated portion of the container. Sediment obtained by this method from linseed oil was analyzed by V. I. Shafraonovskaya (Anal. Methods in Oil and Fat Ind., U.S.S.R., 1936, 89-98). It contained 20 per cent phosphatides, 16 per cent albumins, 7.5 per cent carbohydrates, and 12.9 per cent mineral substances.

H. P. Kaufmann (Fette u. Seifen 43, 218-22) reported the unified work on the unsaponifiable material, which was carried out under the German fat organization, "D. G. F. I." The petroleum ether, Centralburo and English methods were compared in several laboratories. The conclusions were that the petroleum ether method is quick; it yields good results for fats with low unsaponifiable percentage; however, it is not generally applicable to fats of high unsaponifiable percentage. The use of ether as a solvent is more generally applicable but is tedious. Retaining the petroleum ether method for fats with low unsaponifiable percentage was recommended. Further work will be done toward selection of a method

best suited for difficultly saponifiable fats.

Data from tests comparing various iodine value determination methods were tabulated by N. N. Godbole (*Fette u. Seifen* 43, 155). The Hubl method required too much time. In the Wijs method the halogens were found too active and substitution occurred. The method of Hanus and Kaufmann gave results which agree with each other and were not appreciably affected by substitution when a longer time was allowed for the halogens to react. The Kaufmann method was most favored by the investigator. New modifications and improvements for the bromine vapor method for iodine value determination were proposed by H. Thoms (*Analyst* 61, 177-8), H. N. Brocklesby and K. F. Harding (*Can. J. Research* 14B, 237-42) and H. Wollschitt (*Arch. exptl. path. Pharmokol.* 179, 260-5). A potentiometric determination method for iodine value was devised by K. Drewski (*Przemysl Chem.* 19, 63-75). The main feature of the method was the use of an apparatus which was similar in shape to a Weston normal cell, for determining the potential differences in the reactive materials contained in it. L. Zeleny and D. A. Coleman (*OIL AND SOAP* 13, 253-6) revealed that the correlation between iodine value and refractive index of fresh linseed oil was sufficient to warrant the use of the refractometer for determining the iodine value. Equations and graphs were presented for this purpose. Test shows that standard errors amount to ± 0.82 iodine number.

Difficulty is usually encountered in obtaining consistent iodine values by various methods or under various conditions of the same method on some oils. The iodine values of tung oil obtained under various conditions can be corrected to standard conditions with the use of a nomograph which was prepared by C. S. Wan and K. Ho (*Ind. and Eng. Chem., Anal. Ed.* 8, 282-3). R. Klatt and G. Margosches (*Fettchem. Umschau* 42, 183-90) reviewed the literature pertaining to the abnormal behavior of castor oil toward iodine value determination. They concluded that with certain methods the abnormalities are due to an effect exerted on the double bond of ricinoleate radical by its hydroxyl group. R. S. McKinney and G. S. Jamieson (*OIL AND SOAP* 13, 10-11) reported interesting observations from their investigations of the characteristics and composi-

tion of oiticica oil. The iodine value by the Hanus method was considerably influenced by the weight of the oil taken, the quantity of Hanus reagent used, and the time allowed for the reaction. Since no evidence of the presence of any unsaturated constituents other than oleic and licanic acids was obtained, the investigators determined the true iodine value from the quantity of oleic acid and thiocyanogen value. The amount of oleic acid was determined by a modified Lapworth and Mottram procedure. The quantity of licanic acid as the glyceride in the oil was calculated using the equation

$$86.8x + 86.04y = 100 \times \text{SCN value}$$

in which x equals per cent licanic acid and y that of oleic acid glyceride. The analysis of the oil is presented in the chart appended to this part of the review.

Most recent methods for determination of unsaturation are based on amount of hydrogen absorbed by the oils by catalytical hydrogenation. Apparatus and procedures for these were described by A. S. Ginsberg (*J. Gen. Chem. U. S. S. R.* 5, 1169-90, 1252-4) and T. Maruyama (*J. Agr. Chem. Soc., Japan*, 12, 395-400).

E. Rossman (*Fette u. Seifen* 43, 224-8) slightly modified the Eibner-Muggenthaler method for hexabromide value of fats or oils. Various other methods in current use were discussed from the standpoint of their limitations, time required, etc.

Contributions to the technic for determining thiocyanogen value of oils and data on some oils, with favorable criticism of this method for determining fat acid composition were presented in communications by S. L. Ivanov *et al.* (*Schriften zentral Forschunginst. Lebensmittelchem., U. S. S. R.* 4, 185-91), P. O. Burlachenko (*ibid.* 4, 192-5), F. Charnley (*J. Biol. Board Can.* 2, 285-97), S. K. Sharma (*J. Indian Chem. Soc.* 13, 1514) and N. N. Godbole and Amarenda (*Allgem. Oel- u. Fett-Ztg.* 33, 7-10). The last two contributions contain methods of calculating the fat acid composition of the oils which included corrections for glycerin and unsaponifiable.

Two new characteristics which depend on certain types of unsaturation have apparently found a place among procedures for fat and oil analyses. The "diene value," originated by H. P. Kaufmann and J. Balthes (*Fette u. Seifen* 43, 93-7) shows the greater promise for improving the characterization of oils. The diene value was described as

the amount of maleic acid anhydride that reacts with 100 parts of oil calculated in equivalent amounts of iodine; it yields a measure of the conjugated double bonds and hence aids in identification of the structure of some of the fat acids. Detailed methods for analysis and data on several oils were presented. A newer procedure for this method was described by B. A. Ellis and R. A. Jones (*Analyst* 61, 812-6). These investigators prefer calling this characteristic the "maleic acid value" (M. A. V.) because it makes no assumption as to the mechanism of the reaction. The other characteristic, bromine-binding value, originated by K. Meimel (*Naturwiss.* 23, 721; *Fette u. Seifen* 43, 250-2) measures changes in the amount of conjugated double bonds. It was described as the ratio of the amount of bromine that adds to an oil to the amount that is converted to hydrobromic acid when an excess of oil is treated with a solution of bromine in methyl alcohol. Data on several oils and on oils in the course of heat treatment were presented.

A collaborative study of the Andre-Cook, the Roberts-Schuetz and West-Hoagland-Curtis methods for determining acetyl value of fats and oils was reported by W. L. Roberts (*J. Assocn. Official Agr. Chem.* 19, 420-7). The Andre-Cook method shows poor agreement with normal samples and was inaccurate on samples containing volatile fat acids. The Roberts-Schuetz method was the simplest of the three tested; collaborators obtained suitable individual checks with each other. Using the West-Hoagland-Curtis methods, individuals were able to obtain duplicate checks, but the same individuals did not check each other. P. G. Hafner, R. H. Swinney and E. S. West (*J. Biol. Chem.* 116, 691-7) made slight improvements on the West-Hoagland-Curtis technic for acetyl value of fats, which were claimed to improve the accuracy. They revealed for the first time that a number of common fats and oils contained small amounts of hydroxylated acids. Some acetyl values determined are: butter 2.7, castor oil 125.6, coconut 1.3, corn 3.6, cottonseed 4.4, lard 1.5, linseed (raw) 5.3, linseed (boiled) 7.9, neat's-foot 9.0, olive 3.1, peanut 2.6 and salmon 3.7. A simplified method was described by K. Hinsberg (*Biochem. Z.* 285, 185-9). The determination was carried out in an apparatus consisting of two small vessels connected with

an L-shaped tube. Acetylation with acetic anhydride was carried out in one vessel, after which the liberated acetic acid was distilled into the other, which contained a known amount of standard potassium hydroxide solution. Distillation was carried out by immersing the vessel containing the reacted mixture in a bath at 100°, while the other vessel was maintained at 15°.

In regard to most of the characteristics of oils, A. Eisenstein (*Ole, Fette, Wachse, Seife, Kosmetik* 1936 [7], 1-4) called attention to variations due to the presence of free fat acids. For example, a palm oil, 58 per cent free fat acid, gave a saponification number of 203.7; since 1000 mg. of this oil corresponds to 1027.2 mg. of neutral oil, the saponification value calculated to the neutral oil basis is 198.3. Mathematical formulas for converting characteristics of acid oils to the neutral oil basis were presented. Characteristics of various palm oils showed lesser variations if reported on the neutral oil basis.

Unified methods for fat analysis were reported as follows: V. Vesely (15me Congr. chim. ind. Bruxelles 1936, 1139-41), S. Fachini (14me Congr. intern. quim. pura applicada, Madrid, 6, 339-51), and F. Sporer (*Ole, Fette, Wachse, Seife, Kosmetik* 1936 [10], 4-7; [12], 8-11) reported methods approved by the International Commission for the Unification of Methods for the Analysis of Fats and Allied Products. W. H. Irwin and committee members on the analysis of commercial fats and oils, American Chemical Society (*Ind. and Eng. Chem., Anal. Ed.* 8, 233-7), reported their studies and made recommendations for adoption of several methods.

The outstanding achievements in testing for adulteration of oils were the methods originated to identify the presence of tea seed oil in olive oil. These methods have been responsible for the removal of large amounts of adulterated olive oils from our market. J. Fitelson's method (*J. Assocn. Off. Agr. Chemists* 19, 493-7; *Food Indus.* 8, 359) depends on a color change of tea seed oil from brown to an intense green in the presence of acetic anhydride, carbon tetrachloride, concentrated sulfuric acid and anhydrous ether. The method described by W. Siebenberg and W. S. Hubbard (*OIL & SOAP* 13, 194-7) was almost identical to Fitelson's. B. Berisso (*Rev. col. farm. nac. Rosario*, 2, 59; *Anales farm. bioquim.*, 6, 89-90B) re-

vealed that adulteration of olive oil with as low as 3 per cent peanut, cottonseed, rape or sunflower seed oil can be detected by examination of the fluorescence produced by irradiation with light 365 wave length. Other tests on olive oil dealt with distinguishing different types of oil. W. Ciusa (*Chimica e industria* 18, 13-4) suggested measurements of the optical activity and unsaponifiable substances for distinguishing pure and expressed oils. H. Kringstad (*Angew. Chem.* 49, 423-5) studied the ultraviolet absorption capacity of refined and pressed virgin oils, as well as oils obtained by solvent extraction. The extinction curves for the unsaponifiable matter and the fat acids of these oils were presented. The data can be used to characterize olive oils as virgin, extracted or pressed, raw or refined, pure or adulterated and fresh or rancid. J. F. Reith and C. P. van Dijk (*Chem. Weekblad* 33, 501-2) described a method for differentiating refined and unrefined fats, which depends on their electrical conductance. D. Mangrane (*Anales soc. espan. fis. quim.* 33, 707-9) compared the various types of olive oil and some of their characteristics. B. B. Cunningham and L. G. Saywell (*Food Research* 1, 457-64) maintained that to date no infallible test for virgin olive oil has been reported. They also reported that it does not appear likely that a substance such as virgin olive oil, defined upon a basis of its manner of preparation rather than its physical or chemical properties, can be uniquely and quantitatively estimated by any physical or chemical test.

J. Grossfeld (*Fette u. Seifen* 43, 100-3) reviewed the analytical tests used on margarine and butter and discussed their significance for identifying constituents of margarine and adulterants of butter. A method for determining butter fat in food fats in general, as described by T. von Fellenberg (*Mitt-Lebensmittel. Unters. Hyg.* 27, 133-57) depends on the difference in the amount of alkali necessary to titrate the free fat acids distilled from the hydrolyzed fats under definite conditions.

Fats extracted from foods during the fat determination usually do not yield accurate Reichert-Meissl values; hence, the use of this value for estimating the amount of butter in food products was not reliable. F. Hillig (*J. Assocn. Official Agr. Chemists* 18, 454-9) pro-

posed a fat determination procedure which obviates the difficulty. The principal steps were: (1) addition of paraffin to collect fats liquid at room temperature, (2) acid hydrolysis of material, (3) incorporating fat and hydrolyzed material in filter, and (4) extraction of fat and paraffin with petroleum ether. The material extracted is corrected for the amount of paraffin added.

Recent literature for the determination of the A and B values of butter does not consistently describe the procedure. Since no adequate reasons have been given for the changes, N. N. Godbole and Sadgopal (*Z. Untersuch. Lebensm.* 71, 252-3), suggested that the original procedure of Holde should be most acceptable. These determinations are used to detect adulteration of butter. A new index for butter, which was proposed to replace the Reichert-Meissl test, was originated by R. Lucentini and E. Drago (*Ann. chim. applicata* 25, 388-9). This index is a measure of the acids soluble in a saturated solution of potassium sulfate and is in terms of cubic centimeters of 0.1 N sodium hydroxide. Genuine butters gave values of 18 or over while common adulterants had values of 3.5 to 4. Adulteration of butter could be masked against this new index and several other methods which depend on short carbon chain acid by adding acetic esters to the adulterated mixtures. A method for identifying presence of this constituent was described by S. Bezzi and S. Sacconi (*Annali Chim. Appl.* 25, 407-17). This procedure was based on the different volatilities in steam of acetic acid and volatile acids normally present in butter.

Methods for detection of hydrogenated fats in other fats have been improved. P. J. Vanderkelen (15me Congr. Chim. ind. 1936, 597-9) suggested that the Bömer method be used in conjunction with determination of iso-oleic acid. Procedures for identifying hydrogenated fats by detection of nickel were described by M. Struszynski (*Przemysl Chem.* 19, 48-9) and J. Ranedo (*Anales soc. espan. fis. quim.* 33, 813-4). Prevention of the interference of ferrous salts on color produced by nickel salts with dimethylglyoxime and ammonium hydroxide was the object of the improved procedure.

Detection of adulteration of rape or mustard oils or adulteration of other oils with these oils usually depends on the behavior

of the erucic acid present. According to S. Neogi (Analyst 61, 597-601) the insoluble lead salts of the fat acids of these oils have an iodine value of 42.8 to 49.7, but very low values (0.2-2.4) are obtained with the usual adulterants. Technic for the estimation of erucic acid which was described by J. Grossfeld (Phar. Ztg. 81, 397-9) pertained to detection of adulteration of oils with rape oil.

V. C. Mehlenbacher (OIL & SOAP 13, 277-82) has revealed that fat and oil microscopy may lead to a simpler means of identifying fats and oils and detecting adulteration. Before the microscope can take a prominent place in laboratory routine, the methods should be made more comprehensive; and the data on crystal habits, forms and physical properties of those fats that may be encountered in industry should be recorded as completely as possible so that the records can be used as a basis for comparison. Mehlenbacher was highly successful in obtaining good microscopic photographs of crystals of several fats and their acids. The crystal structure of the various fats differed sufficiently to allow microscopic examination to serve as a method of identification.

In addition to the tests already reported for identification of oils, several color tests have been developed which can be applied in analytical schemes on fats and oils. H. Jesser and E. Thomae (Angew. Chem. 49, 846-7) recorded the color reactions of 23 oils obtained by 3 procedures: (1) 1 cc. of oil in benzol was treated with 1.5 cc. of arsenious chloride and (3) 0.1 cc. of oil was treated with 2 cc. of a mixture of acetic anhydride and chloroform and 0.05 cc. of concentrated sulfuric acid. Several of the color reactions could be applied toward detection of oils or adulteration. According to V. C. Mehlenbacher (OIL & SOAP 13, 136-8) kapok oil may be differentiated from cottonseed oil by treating the sample dissolved in chloroform with a solution of silver nitrate in absolute alcohol. In presence of kapok oil a brownish-black color develops on standing. A qualitative test for linoleic acid was described by G. J. Martin (J. Am. Chem. Soc. 58, 364-5). The reagent used was arsenophosphotungstic acid as prepared for the determination of uric acid according to Benedict's method. When 1 cc. of oil was layered over 5 cc. of reagent and heated in a boiling water bath for one hour, a

deep blue color developed in the reagent layer in the presence of linoleic acid. This test may serve as an indication of adulteration with certain oils or for detection of rancidity in some oils.

Soaps and Detergents

Recent physicochemical investigations on the behavior of soaps in solution have resulted in information which is of both technical and theoretical importance. N. N. Godbole and Sadgopal (Kolloid-Z. 75, 193-201) reported that an increase in the number of the carbon atoms of the saturated fat acid soaps up to myristic acid was accompanied by increase of foam value, and decrease of surface tension and gold number; and that beyond myristic acid, the trend was reversed. These results agree with the detergent properties of the soaps. P. A. Rebinder (Vsesoyuznuii Nauch.-Issledovatel Inst. Zhirovoe Unters. Physikochemie der Washwirkung 1935, 5-34), E. K. Vestrem and A. B. Taubman (*ibid.* 35-48), N. N. Petrova *et al* (*ibid.* 49-66, 93-115, 126-37), N. N. Serb-Serbina and G. V. Zakharova (*ibid.* 67-92) and N. M. Smirnov (*ibid.* 116-25) published a series of papers on physicochemical investigations of the washing action of soaps. It was said that the surface activity of aqueous solutions of sodium oleate, palmitate and stearate increased with temperature, since the degree of dispersity rose. At 40° the surface tension decreased in the order oleate, palmitate, and stearate; at 60° this order was reversed. Solutions of soaps, like tallow soap, which contained large amounts of saturated fat acids had greater surface activity at 60° than at 20°; this was due to variations in solubility. Soaps containing mostly unsaturated acids did not show the temperature effect so strongly. In very little dilute soap solutions the surface activity was increased by addition of sodium carbonate, but in more concentrated solutions, addition of sodium carbonate decreased the degree of foaming and increased the surface tension. This effect was more noticeable with soaps of saturated fat acids than with those of unsaturated acids. In weak solution castor oil soap lowered the surface tension more than palm kernel or coconut oil soap. In foaming power, palm kernel oil soap led, followed by coconut oil and then castor oil soaps. Emulsifying capacities of soaps toward the system water-in-benzene in decreasing order were:

castor oil soap, sodium oleate, coconut oil soap. For foam formation, this series was exactly reversed. In a reversed phase, *i.e.* benzene-in-water, the hydrophilic order of the soaps was the same as the order for the emulsifying power.

Several investigators reported the influence of alkalinity on the surface tension of soap solutions. J. Powney (Trans. Faraday Soc. 31, 1510-21) plotted the surface tensions of sodium and potassium salts of oleic, lauric, and myristic acids. The measurements were made at 20°. Small changes in alkalinity produced very large changes in surface tension, especially in the case of laurates. The discrepancies that may occur in this type of measurement were listed by N. K. Adam (Trans. Faraday Soc. 32, 653-6). It was pointed out that addition of alkali raised the surface tension as the result of suppression of hydrolysis, and excess alkali diminished surface tension in consequence of salting out of soap. Strict control of pH was recommended for suppressing hydrolysis. H. L. Cupples (Ind. Eng. Chem. 28, 60-2; 27, 1219) compared the surface tension, interfacial tension and spreading coefficients of sodium carbonate-oleic acid mixtures with sodium hydroxide-oleic acid mixtures on refined paraffin oil. The sodium hydroxide-oleic acid mixtures were much more sensitive to variations in ratios than the carbonate-oleic acid mixtures.

The decomposition of soap in contact with textiles had been explained as due to the action of atmospheric carbon dioxide. G. Baroni and C. Cola (Bol. Staz. sper. seta 6, 4-7) showed that this decomposition does not occur with glass wool and hence should be attributed to the surface effect of porous fibers. In commercial laundries, this effect along with other influences such as differences between loads of soiled clothes, the hardness of the water used and other factors create difficulties in buffering the washing medium to the desired pH. C. E. Lennox and J. S. Sandtner (OIL & SOAP 13, 257-61) have investigated this problem by commercial scale tests. A number of alkalis which are being used commercially for this purpose were compared from the standpoint of their buffering capacity and the pH which they maintain in washing media. The information was presented graphically. These graphs gave the limitations of some of the products and also indicated the amounts required for certain effects.

A review on soap which treats the colloid aspects from a theoretical viewpoint was contributed by P. A. Thiessen (*Fette u. Seifen* 43, 149-52). A review comparing the colloid and washing properties of aluminum hydroxide, starch, casein, and tragacanth with soap was presented by K. Lindner (*Fette u. Seifen* 43, 214-8). W. M. Urbain and L. B. Jensen (*J. Phys. Chem.* 40, 831-2) have shown that suspended inert particles and oil droplets in soap solution carry a high electric charge, as measured by the zeta potential. They postulated that a relationship exists between this effect and the dispersing action of soaps, thus furnishing a measure of detergent action.

W. Seck (*Angew. Chem.* 49, 203-6) recorded data on the structure of soaps of various fat acids. The material presented by him was severely criticized by P. A. Thiessen *et al* (*Angew. Chem.* 49, 640-2) and by R. Brill (*Angew. Chem.* 49, 643-5). A check of the work indicated several experimental errors in Seck's work.

B. Tjutjunnikow and N. Kasjanowa (*Allgem. Oel- u. Fett-Ztg.* 33, 204-16, 323-9) contributed a large number of photomicrographs of various soaps and a study of the effect of mechanical processes on soap structure. All soaps displayed a crystalline structure. Milling and plodding of soap tended to orient the fiber-like crystals in parallel positions. The greater plasticity of milled soap was attributed to its oriented structure.

The germicidal properties of soaps were investigated by M. Bayliss (*J. Bact.* 31, 489-504; *J. Infectious Diseases* 59, 131-6). The effectiveness of various fat acid soaps and sulfate esters against several organisms were recorded.

Several papers on soap technology treated the choice of stock and possibilities of some interchanges. Y. Kawakami (*J. Electrochem. Assoc. Japan* 3, 389-94) recommended hardened soybean and rice oils having iodine values of about 70 as substitutes for tallow in soap manufacture. Means for making hardened fish oils suitable for soap-making were described by Kawakami and by Grann (*Seifensieder-Ztg.* 62, 486). N. Kumagai (*Japan* 111,341-2) patented methods of making fish oils suitable for soap manufacture. The fat acids of the oils are converted to butyl, amyl or like esters and hydrogenated to iodine values between 40 and 100. Alternatively, the oil may be hydrogenated first and then heated

with an alcohol to cause interesterification. This material was subsequently saponified. According to a patent issued to Y. Tanaka (*Japan* 111,200) hydrogenated fish oil was suitable for soap making after it had been chlorinated. L. A. Rouget and J. D. Rouget (*Fr.* 795,220-1) claimed that soaps made from fats of *Litsea sebifera* or plants of the same family were especially adaptable for use with sea water. He also claimed special qualities for this product when chlorine was added. Methods for making suitable soaps from soybean oil are described by A. A. Horvath (*J. Soc. Chem. Ind.* 55, 691-3). R. L. Datta and R. S. Das Gupta (*Soap Perf. Cosmetics Trade Rev.* 8,[4] 34-6) revealed that soap made from a properly mixed stock had a greater detergent power than that of any single fat acid soap or greater than that calculated as the additive effect of the individual components.

During each year, many communications appear on detergents, which it seems advisable to mention only by title. These articles are reviews, descriptions of well-known processes, collections of formulas and other material of general nature. Those that appeared recently, listed according to their subject, are as follows:

Triethanolamines and other alkylolamines: E. J. Flischer (*Allgem. Oel- u. Fett-Ztg.* 32, 489-95).

Washing of Textiles: R. S. Shane (*J. Chem. Ed.* 13, 563).

Soap in tanning: P. I. Smith (*Soap* 12 [7], 23-5, 33).

Soap manufacture: R. Sansone (*Nuova Rev. Olii vegetali Saponi* 36, 91-4).

Cold made soap: E. G. Thomssen (*Soap* 12 [9], 23-7, 35).

Manufacture of soap from fat acids: E. P. Zwicker (*15me Congr. Chim. Ind. Brussels* 1936, 151-4) and C. H. Keutgen (*Seifensieder-Ztg.* 63, 155-6, 187-8, 208-9).

History of soap making: H. P. Kaufmann (*Fette u. Seifen* 43, 178-83).

Theories of soap: I. Davidsohn and A. Davidsohn (*Ole, Fette, Wachse, Seife, Kosmetik* 1936 [12], 1-7).

Saponification with sodium carbonate: R. L. Datta and A. Das. (*Soap Perfumery, Cosmetics* 1936, 451-3).

Catalysis in soap manufacture: H. Silman (*Soap* 12 [3], 63-5, 93).

Mechanical technology of soap: K. Rossner (*Fette u. Seifen* 43, 160-3, 194-6, 228-31, and *Seifensieder-Ztg.* 63, 293-4); C. R. Kemp and E. G. Thomssen (*Soap* 12 [6], 27-31, 37, 73) and G. Knigge (*Seifensieder-Ztg.* 63, 475-6, 498-9).

Continuous soap manufacturing processes: A. Ranuiseho (*Masiobolna Zhirovoe Delo* 12, 298-9) and J. M. Vallance (*Soap* 12 [2], 65-6, 75).

Medicinal soaps: E. G. Thomssen (*Soap* 12 [10], 29-32) and G. Gatti and R. Cajola (*Nuova Rev. Olii vegetali Saponi* 36, 95-7).

Dry cleaning soaps: C. A. Tyler (*Soap* 12 [5], 31-33, 61) and S. W. Putnam (*Soap* 12 [1], 25-8, 63).

Oils, fats and fatty acid in cosmetics: R. H. Auch. (*Oil & Soap* 13, 58-9).

Soap fillers: A. Lottermoser (*Angew. Chemie* 49, 104-6); F. Ohl. (*Gelatine, Leim, Klebstoffe* 3, 168-71); H. Zilske (*Seifensieder-Ztg.* 63, 186-9); K. L. Weber (*Seifensieder-Ztg.* 63, 189-90, 209-10, 230-1, 252-3); E. Walter (*ibid.* 56-7); W. Kroner and G. Steinhoff (*ibid.* 272-5); P. Brettschneider (*ibid.* 311-2); W. Schvieta. (*ibid.* 391-2); K. Kiefer (*ibid.* 413-4), and J. G. Vail (*Ind. Eng. Chem.* 28, 294-9).

Perfume for soap: A. Wagner (*Seifensieder-Ztg.* 63, 422-3); F. Schulz (*ibid.* 63,

143-5); R. Farnet (*ibid.* 63, 644-6); and J. Herold (*Fette u. Seifen* 43, 156-9).

Glycerin recovery: O. H. Wurster (*Oil & Soap* 13, 246-53, 283-6); J. Altenburg (*Chem.-Ztg.* 60, 113, 136-7); P. Andronov (*Masiobolna Zhirovoe Delo.* 11, 353-5); and Z. Askinazi and E. Tobler (*Masiobolna Zhirovoe Delo* 12, 301-3).

Metallic soaps: H. Silman (*Soap* 12 [11], 36-7, 77; [12], 31-3, 39); H. C. Bryson (*Chem. & Ind.* 55, 781-4); H. S. Land (*Chem. Industries* 39, 538-5); and I. H. W. Chatfield (*Paint Manuf.* 6, 70-2).

Sulfonate or sulfate detergents: A. Bresser (*Z. ges. Textil-Ind.* 38, 508-9); J. Davidsohn (*Ole, Fette, Wachse* 1936 [5], 1-8); M. J. Hausman (*Soap* 12 [5], 23-7, 61); J. Pinte (*Chimie & Industrie* 35, 1166); and Weiwart (*Seifensieder-Ztg.* 62, 841-2, 882).

Soap stock may be improved as described in a patent issued to Metallgesellschaft A.-G. (Ger. 625,606 Cl. 23a 3) by washing with aqueous solutions of alcohol and salt to remove the last traces of impurities. S. H. Bertram and E. C. S. Kipperman (*Chem. Weekblad* 32, 624-7; *Ole, Fette, Wachse* 1936 [6], 1-4) contributed evidence to show that the soaps of elaidinized fat acids have in many respects a better cleansing action than soaps of non-elaidinized acids, and they recommended elaidinization of soap stock. Data on the surface tension, suds formation, wetting power, and emulsifying power of several fat acids and oils and their elaidinized isomers were tabulated.

Several suggestions were made toward selection of materials or addition of substances to soap stock to obtain special qualities in the finished products. H. Nitschke (*Seifensieder-Ztg.* 63, 497-8, 517-8, 536-7) recommended stocks containing 25-30% palm or coconut oil and 10% rosin for manufacture of soap for hot climates. He also suggested adding sodium sulfate when water glass was used as a filler. F. B. Downing and R. G. Clarkson (*U. S.* 2,033,125 and 2,033,819) patented the use of soaps of fatty acids containing 5 to 12 carbon atoms, in mercerizing baths for textiles; the use of sodium laurate was especially recommended. Soaps made from fats of molecular weights less than 210 were recommended by L. A. Rouget and J. D. Rouget (*Fr.* 795,220) for use with sea (salt) water. An addition to this patent (*Fr.* 795,221) pertains to the addition of sodium hypochlorite to the soap. S. Gelert-Nielsen (*Norw.* 56,620) prepared shaving soap by saponifying stearic acid with an excess of ammonium hydroxide, added glycerol and buttermilk and cooled the mixture immediately to avoid loss of ammonia. R. H. Fash (*Brit.* 450,221) added chromate salts to shaving soaps or creams to render the steel of razor blades passive, hence preventing them from rusting. R. H. Fergu-

son (Can. 356,799) patented a process for making soap cream from hydrogenated oils. Disinfecting soaps prepared by W. Schulenburg (Ger. 632,825 Cl. 23e) contained silver compounds or silver powder.

A few innovations in the saponification procedures were reported. Time of saponification was reduced, as cited in patent of Soc. Mury (Fr. 795,163) by adding just sufficient water for saponification, heating the fats to little above the melting point and adding hydrogen peroxide before adding the alkalis. According to a patent of Inzersdorfer Chemische Industrie G. m. b. H. (Brit. 448,930) soaps may be prepared by mixing the fats or oils with caustic alkali and passing the mixture through an emulsifier or homogenizer. Wax soaps were prepared by L. A. Barthelemy (Fr. 795,765) by saponifying the melted waxes with a strong caustic. W. Schrauth (U. S. 2,027,936) saponified sperm oil at 200-280° with the use of about 2% excess alkali; during this process the alcohols formed are oxidized. As an economical measure, C. Leyst-Küchenmeister (Brit. 442,046) used waste sulfite-cellulose lyes for saponifying fats. The sulfite-lye was first freed from sulfur dioxide by heat and agitation and from calcium by sodium carbonate. A. S. Kluchevich and L. T. Averko-Antonovich (Ind. Eng. Chem. 28, 949-52) reported the characteristics of lumps formed during industrial boiling of 40% soap. The data show causes of frequent differences between the analyses of samples and the real content of the kettles. Means of remedying some faults occurring in soap making are suggested. Continuous processes for soap manufacture were patented by B. Clayton (U. S. 2,037,006) and R. E. Burns (U. S. 2,037,004).

Additions of glycerol and water soluble phosphates stabilized soap against deterioration as cited in patents of H. Krause (Austrian 143,654). For the same purpose E. Crocker and L. F. Henderson (U. S. 2,040,430) added zinc sulfide. J. P. Kane (U. S. 2,042,104) protected soap cakes against deterioration by coating them with rubber. J. Leben (U. S. 2,055,581) added 5-20% alkylolamine salts of salicylic acid to soap to reduce hydrolysis. Alkyl esters of glycolic acid or lactic acid were cited as superfatting agents in a patent issued to Henkel & Cie (Ger. 633,871 Cl. 23e). C. Cronquist (Swedish 80,963) prepared a mixture of wool

fat, spermaceti and whale oil for superfatting.

W. Kling (U. S. 2,057,959) patented a process for removing the carbolic or iodoform odor of bleached soaps, which pertains to heating the soap to 120-160° under 2-16 atmospheres pressure in the presence of sodium sulfite.

Several patents dealt with new mechanical features of equipment or new apparatus for use in the soap industry. A. Welter (Ger. 620,391 Cl. 23e) patented a means of heating with super-heated steam. Details of an apparatus for making liquid soap from concentrated material were described in a patent of A. L. Bobrick (U. S. 2,032,524). F. Fetterer and K. Wiemer (Ger. 618,003 Cl. 23f) invented a combined extrusion through sieve, and milling apparatus. M. Igarashi and H. Hatto (U. S. 2,043,378) described a simple apparatus for preparing fibrous soap. W. A. Hutton (U. S. 2,057,192) devised means for connecting, mixing, cooling, extruding and printing processes so that the manufacture of bar soap was continuous. C. T. Walter (Brit. 436,828; 448,123; 449,683 and U. S. 2,043,681) patented an apparatus for making tubular soap. These patents claimed invention of a new form of soap, novel features for extrusion apparatus and method of drying. A patent issued to A. Imhausen and W. Prosch (Ger. 635,091 Cl. 23e) dealt with means of removing carbon dioxide, hydrogen sulfide and other injurious gases from the atmosphere in soap driers. A soap dispenser which grates ordinary bars was invented by C. Iaggi (U. S. 2,037,329).

Some soap and detergent inventions pertained to mixtures of substances. A shaving soap formula of Etablissements Pilex (Fr. 800,548) was a mixture of soap, magnesium carbonate, sodium bisulfite, gelatine, citric acid, aluminum acetate and water. This formula was similar to that of G. Sarbach (Fr. 794,380) except that starch was used in place of gelatine. For the same purpose V. Scheffer (Hungarian pat. 114,137) prepared a mixture of ammonium and alkali metal soaps. C. Ellis (U. S. 2,058,781) plasticized soap by incorporating into it a petroleum distillate of a boiling range between 300 and 400° F. Soap prepared by W. Bleck (U. S. 2,056,916) for removing paint, lacquers or varnish was a mixture of cellulose lacquer solvent, soap, glycerine, abradant and water. Soap was coated with alkaline salts

by the Electric Smelting & Aluminum Company (Brit. 440,952) so that during a washing operation, on addition of this soap the materials got a prealkaline treatment. V. Boulez (Brit. 444,165) added glue, pectin, gelatine or like agents to soap. A soap containing products formed by the decomposition of silk by alkali was the subject of P. Küller's (U. S. 2,048,797) patent. A. L. Sodergreen (U. S. 2,049,476) patented the addition of hydrolyzed cereals to soaps. A mixture prepared by G. Roux and A. Delemer (Fr. 790,722) containing sodium and potassium carbonates, soap, glucose, glycerin and saponin was said to be noninjurious to linen when used as soap. Borax, soap and other materials were used in detergents prepared by A. A. Fowler & R. M. Otis (U. S. 2,059,449) and A. Parodi (Italian patent 318,624). For the same purpose C. R. Garnsey and W. R. Manning (Austrian 24,156) patented a special mixture of carbonate salts, soap and pumice. The inventions, with patentee or assignee's name, dealing with special mixtures of soaps containing alkali silicates or phosphates or in some cases both and other material for wetting, emulsifying or detergent uses are as follows:

- Henkel & Cie G. m. b. H.: Brit. 435,317; 435,465; 436,213; 437,128; 439,493.
- Chemische Fabrik Joh. A. Benckiser G. m. b. H.: Fr. 786,332; Brit. 448,608.
- P. R. Johnson: U. S. 2,044,246.
- C. Ellis: U. S. 2,046,449.
- R. Weissbach: Brit. 451,559; Fr. 798,437.
- R. S. Sutton: U. S. 2,034,361.
- T. K. Cleveland: U. S. 2,044,467.
- J. P. Hansel: Brit. 436,332.

Those patents which pertain to addition of alkali phosphates or silicates or both to sulfated or sulphonated wetting agents, are as follows:

- Henkel & Cie G. m. b. H.: Brit. 443,486; 443,487; 447,072.
- Deutsche Hydrierwerke A. G.: Ger. 629,644 Cl. 12s; 629,403 Cl. 12s.
- I. G. Farbenindustrie A. G.: Brit. 444,071.
- O. Drapal: U. S. 2,030,859.

K. Winokuchi and M. Toriyama (J. Soc. Chem. Ind. Japan 39, 94B, 94-6B) contributed some studies on sulfonating oils. They found that sulfonation of unsaturated oils was somewhat selective in nature. The selectivity increased with lowering of the temperature and reducing the amount of sulfuric acid used. Considerable amounts of the sulfuric esters were decomposed during the course of the sulfonation. K. Nishizawa (J. Soc. Chem. Ind. Japan 39, 234-5B) prepared pure 10-hydroxystearic acid, sulfonated the compound and reported some of its characteristics. This product resembles the sulfonates derived from oils containing high percentages of oleic acid. R. M. Reed and H. V.

Tartar (J. Am. Chem. Soc. 58, 322-32) recorded considerable data on alkyl sulfonic acids. The calcium and magnesium salts were much less soluble in water than had been claimed previously. The interfacial tensions between benzene and solutions of sodium alkyl sulfonates showed changes with time. The conductivities of sodium alkyl sulfonates were analogous to those of the potassium soaps. According to a patent issued to Böhme Fettchemie-G. m. b. H. (Ger. 619,386 Cl. 8i) precipitation of calcium soaps of sulfonated oils was prevented by adding alkali salts of citric acid.

Surface tension data on solutions of various sulfated fat acids were recorded by S. Ueno *et al.* (J. Soc. chem. Ind. Japan 38, 603-8B) and Weltzier and H. Ottensmeyer (Fette u. Seifen 43, 91-3). Weltzien and Ottensmeyer reported that the lowering of the surface tension by commercial products was perceptibly greater than by pure products when compared in like concentration.

Methods for analysis and grading of sulfonated or sulfated oils were reported by R. Hart *et al.* (OIL & SOAP 13, 13-18; Am. Dyestuff Repr. 25, 122-5, 696-707). E. L. Lederer (Öle, Fette, Wachse, Seife, Kosmetik 1936 [10], 1-3) reviewed methods for measuring the calcium dispersing capacity of these and other materials. A simple method for determining oil in sulfonated oils was contributed by D. Burton and C. F. Robertshaw (Fette u. Seifen 43, 152-5). The sulfonated oil sample was treated with hydrochloric acid, extracted with carbon tetrachloride, and after evaporating the solvent, the amount of oil was weighed. Amount of rosin in sulfonated oils may be determined according to W. Riess (Collegium 1936, 348-9) by treating the sample dissolved in methyl alcohol with sulfuric acid, adding acetone, washing with saturated salt solution until neutral to litmus, adding ethyl alcohol and finally titrating with standard sodium hydroxide solution.

Among the analytical methods for soap, the determination of free alkali seems to be the most troublesome. R. M. Lingle (J. Am. Pharm. Assoc. 25, 286-8) found objections to all current methods. He concluded that the United States Pharmacopoeia method was most convenient and gave results sufficiently accurate for medicinal soft soaps. E. R. Luckow (OIL & SOAP 13, 287-9) devised apparatus for excluding atmospheric influences

on the solutions during analyses of soaps for free alkali. It was reported that exclusion of carbon dioxide increases the accuracy of the determination. H. H. Uhlrig and F. C. Duemmling (OIL & SOAP 13, 307-14) reported a very comprehensive study on free alkali determination. Current methods were compared. The most accurate results were obtained by using a solvent comprising 100 volumes of benzene, 75 alcohol and $2\frac{1}{2}$ water, and titrating with 0.1 *N* acid.

Gravimetric, volumetric, and refractometric methods for determining fat acids in soap were respectively described by A. Korenova (Masloboino Zhirovoe Delo 12, 253-4), A. Rosam (Öle, Fette, Wachse 1935, [2], 10-12) and W. Leithe and H. J. Heinz (Angew. Chem. 40 412-14). A refractometric method for the determination of rosin in fat acids, for soap manufacturing control, was described by F. J. Squire (OIL & SOAP 13, 2-5). A review of methods for the fat acid content of soap was contributed by L. Hartman (Seifenseider-Ztg. 63, 95-97).

An apparatus for the determination of volatile hydrocarbons in soap was developed in the laboratories of Procter & Gamble Company (OIL & SOAP 13, 9-10). A simple method of determining clay in soap, with the use of centrifuge, was described by M. T. Bolshakova (Vsesoyuz. Nauch. Issledovatel Inst. Zhirovoe. Analyse-methoden in der Oel- u. Fett. Ind. 1936, 108). An extraction method for the determination of free iodine in medicinal soaps was contributed by J. Glenn, Jr. (Soap, Perfumery, Cosmetics 1936, 531).

Methods for evaluating the detergent capacity of soap were reviewed by J. Hetzer (Fettchem. Umschau. 43, 4-8) and T. Ruemele (Allgem. Oel- u. Fett-Ztg. 33, 17-18). Hetzer also proposed a method by which the wetting power may be evaluated. He defined the wetting number as the concentration of wetting agent in a definite liquid that will allow a standard piece of textile material, at a designated temperature, to sink in two seconds. An apparatus for producing foam for the analysis of soaps was devised by E. L. Lederer (Seifenseider-Ztg. 63, 331-2). The apparatus yielded a measure of the foaming capacity and allowed measurement of the rate of foam decomposition.

Throughout the year various committees of the American Oil Chemist Society reported their studies of

analytical methods and recommended unified methods in their official journal (OIL & SOAP).

There appeared a vast number of new patents entitled wetting, emulsifying, textile, etc., agents which have not yet been reported in the present survey. A few of these may become of commercial importance. The majority of these in their present form or because of economic or other factors are quite impractical; however, since these reflect a high degree of interest, ingenuity, and imagination, and since they may present some new information that may lead to later fruitful inventions, they are being recorded. An effort was made toward classifying these so that the list may be more useful for reference work.

The patents on derivatives of sulfuric acid, fat acid, or fat alcohol were as follows:

H. Bertsch: U. S. 2,026,816; 2,046,242.
A. Beyer: Brit. 448,804; Fr. 782,621.
H. Th. Böhme A.-G.: U. S. 2,032,313; 2,061,468.
Böhme Fettchemie G. m. b. H.: Ger. 628,064 Cl. 12o; Ger. 633,082 Cl. 12o.
Chemische Fabrik vorm. Sandoz: Swiss. 177,938 Cl. 36o.
Deutsche Hydrierwerke A.-G.: U. S. 2,056,272; Brit. 450,515.
E. I. du Pont: U. S. 2,049,975.
C. E. Every-Clayton: Brit. 449,132.
E. Franz: Brit. 445,350.
I. G. Farbenindustrie A.-G.: U. S. 2,037,974; 2,043,476; Ger. 626,491 Cl. 23e; 629,996 Cl. 28a; Brit. 443,559; 443,631-32.
Fettsäure & Glycerin-Fabrik G. m. b. H.: Ger. 632,481 Cl. 23c.
M. de Groot & Bernhard Keiser: U. S. 2,020,998-99.
B. R. Harris: U. S. 2,023,387; 2,029,168.
Imperial Chemical Industries: Brit. 436,209; U. S. 2,053,424.
H. Jahn: Ger. 622,728 Cl. 12o.
D. Lacy-Hulbert: Brit. 436,866.
E. A. Mauersberger: U. S. 2,041,560; 2,042,952; Brit. 443,668; Fr. 757,679.
Oranienburger Chem. Fab. A.-G.: Ger. 622,268 Cl. 12o; 623,948 Cl. 12o; 625,637-8 Cl. 12o.
Procter and Gamble Company: U. S. 2,049,670.

Patents dealing with the sulfonation process:

H. Th. Böhme A.-G.: U. S. 2,032,313-4.
Chem. Fabrik Stockhausen & Cie: Ger. 631,910 Cl. 12o.
Chemical Works of Basel: U. S. 2,044,400; Brit. 450,368.
Chem. Fabrik vorm. Sandoz: Brit. 450,368; U. S. 2,044,399.
Deutsche Hydrierwerke A.-G.: Brit. 441,601.
I. G. Farbenindustrie A.-G.: Ger. 626,521 Cl. 12o; 629,182 Cl. 12o.
Fettsäure-Glycerin-Fabrik G. m. b. H.: Ger. 623,632 Cl. 12o.
H. Grabbe: Fr. 796,463.
A. Gressner: U. S. 2,039,989.
R. Huttenlocher & R. Hess: U. S. 2,029,073.
P. Kaplan: U. S. 2,052,570.
Unichem. Chemikalien Handel A.-G.: U. S. 2,044,919.
O. K. Seikaku K. K.: Japan 113,952.
Zschimmer & Schwarz Chem. Fabrik Dölu: Ger. 634,951 Cl. 12o.

Patents on sulfuric acid derivatives of by-products from the coal, or the mineral oil industries, intended for detergent uses:

A. Beyer: Fr. 799,344.
E. I. du Pont: U. S. 2,061,617-20.
I. G. Farbenindustrie A.-G.: U. S. 2,042,747; 2,045,015; Ger. 630,679 Cl. 12o; Brit. 435,385; 441,878; 450,467; Fr. 798,106; 789,993.
L. H. Flett: Brit. 447,898.
B. R. Harris: 2,052,027.

Henkel & Cie G. m. b. H.: Fr. 794,422.
K. Keller & E. Gofferjé: Ger. 622,296 Cl. 12o.
J. O. Peirce: U. S. 2,042,410.
Rutzgerswerke A.-G.: Fr. 787,546.
E. Segessmann: U. S. 2,054,140.
Standard Oil Development Co.: U. S. 2,-049,055; 2,059,838; Brit. 449,169; 446,314.

Patents on sulfuric acid derivatives of compounds containing nitrogen, *e.g.*, amines, imides, amides, etc., intended for detergent use:

W. E. Billingham: Brit. 443,719.
Böhme Fettchemie G. m. b. H.: Ger. 622,640 Cl. 12s; 627,055 Cl. 12s; 628,828 12p.
I. G. Farbenindustrie A.-G.: Ger. 623,-296 Cl. 8o; Fr. 789,522; Ger. 635,241 Cl. 8o; Brit. 446,269; Fr. 787,819.
B. R. Harris: U. S. 2,052,027.
Henkel et Cie G. m. b. H.: Brit. 436,-862; 442,135; 443,486; Fr. 789,578.
Imperial Chemical Industries, Ltd.: Brit. 435,039; 443,902; Fr. 794,578; 797,-631; 786,625.
F. Pospiech: U. S. 2,055,588.
Soc. pour l'ind Chem. à Bâle: Brit. 449,-043; Fr. 785,475; 799,220.
E. Waldmann & A. Chwala: Brit. 434,-358.
J. Worslup: Brit. 450,672.

Patents on phosphoric acid deriv-

atives of organic compounds intended for detergent use:

Böhme Fettchemie G. m. b. H.: Ger. 619,019 Cl. 12o.
B. R. Harris: U. S. 2,052,029; 2,026,785.
H. Bertsch & G. Rauchalles: U. S. 2,-049,758.

Patents on nitrogen containing detergent; differing from those reported above under sulfuric acid derivatives of the compounds in that sulfonation was not claimed:

Deutsche Hydrierwerke A.-G.: Brit. 435,290; 443,265.
I. G. Farbenindustrie A.-G.: Brit. 438,-793; 443,632; 446,416; 446,912; 449,081; Fr. 789,004; 795,662; 799,093.
Gesellschaft für Chemische Industrie; Brit. 449,209.
B. R. Harris: U. S. 2,023,075.
Henkel & Cie G. m. b. H.: Brit. 446,737.
H. Hunsdiecker & E. Vogt: U. S. 2,-051,947.
F. W. Johnson: U. S. 2,040,997.
F. Munz and O. Bayer: U. S. 2,043,329.
Röhm & Haas Co.: U. S. 2,036,916; 2,-045,517.
Soc. pour l'ind Chim. à Bâle: U. S. 2,-043,164; Brit. 449,209; 449,661; Fr. 786,911; 796,192.

Patents on detergents from coal and mineral oil products differing

from those previously reported in that none of the sulfuric acid derivatives are listed here:

A. Th. Böhme Chemische Fabrik: Ger. 628,062 Cl. 8k.
H. A. Bruson: U. S. 2,036,916.
I. G. Farbenindustrie A.-G.: Ger. 627,-808 Cl. 23e; Brit. 449,865; Fr. 798,728; 798,-941; U. S. 2,020,453; 2,054,979; 2,055,095; Brit. 433,305; 433,780; Fr. 798,970.
H. T. Ferrell et al.: U. S. 2,056,913.
H. Franzen: Ger. 627,808 Cl. 23e.
R. Heuter: U. S. 2,050,969.
J. Robinson: U. S. 2,040,673.
W. Schrauth: U. S. 2,036,438.

Miscellaneous detergent patents:

Deutsche Hydrierwerke A.-G.: Ger. 626,-904.
I. G. Farbenindustrie A.-G.: Fr. 800,079; 787,785; Ger. 623,404 Cl. 12s.
B. R. Harris: U. S. 2,025,984.
Henkel & Cie G. m. b. H.: Brit. 446,498.
Imperial Chemical Industries, Ltd.: Fr. 785,800.

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CHANGES IN THE PHOSPHATIDE CONTENT OF CRUDE SOYBEAN OIL DURING STORAGE*

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A PAPER PRESENTED AT THE FALL MEETING OF THE AMERICAN OIL CHEMISTS' SOCIETY, AT CHICAGO, OCTOBER 8-9, 1936

WHEN domestic crude soybean oil began to appear on the market in this country much of it was cloudy and inferior to the crude soybean oil imported from the Orient^{2, 6}. Three explanations have been offered to account for this difference between the Oriental and the domestic product. Junker⁵ stated that modern methods of oil extraction removed a large amount of other materials along with the fat while the crude Manchurian press method removed only the oil. Pickard⁶ and Eastman² attributed the poor quality of the domestic oil to failure of the producers to master the art of filtering the oil. Gardner³ compared several domestic and imported oils and reported that some samples of domestic oil showed a considerable amount of flocs, indicating that the oil had not been allowed to settle long enough.

Smith and Kraybill⁷ showed that the material responsible for the "break" in soybean oil consists of crude phosphatides. They removed these materials by two different methods and obtained "non-break"

soybean oil. When the product removed was added to this "non-break" soybean oil the soybean oil was again converted into "break" oil. Jamieson and McKinney⁴ found that the precipitate that separated from expressed crude soybean oils on standing consisted chiefly of crude phosphatides.

An opportunity to study the changes in the phosphatide content of crude soybean oil during storage was presented in Lafayette, Indiana, on January 28, 1933. At that time fifteen carloads of soybean oil which had been produced at a local mill within a period of four months were held on track in the railroad yards. This mill was crushing principally Manchu and Dunfield soybeans. The oil was obtained by the use of Anderson expellers, filtered immediately through a filter-press, stored for not more than three days in the mill, and then loaded into tank cars. Some of the cars had been steamed out just before being loaded and probably contained more moisture than the others, but these cars could not be identified from the data available. Movement due to switching provided a small amount of agitation of the oil during the storage period.

Sampling. The tank cars of soybean oil were sampled through the

trapdoor in the turret. The sampler used had a diameter of four inches and was fitted with a sleeve valve. In sampling the oil the valve was closed and the sampler placed in the car to the desired depth, the valve was opened and quickly closed again, and the sampler withdrawn. The oil in the sampler was mixed well and a two-ounce bottle filled from the mixed sample.

Three samples were taken from each car as follows: (1) the surface oil, (2) the middle layer of oil, and (3) the material on the bottom of the car. In some cases the material on the bottom was so thick that it would not run into the sampler and in these cases the sample was taken as deep in the car as the sampler would operate.

A description of these samples was obtained immediately and is included in Table 1. The samples were then carefully mixed and worked to a uniform consistency with a spatula. The total phosphorus contained in each sample was then determined in duplicate.

Determination of Total Phosphorus. Approximately five grams of the sample was placed in a weighed ten centimeter porcelain evaporating dish and the exact weight of the oil determined, ten

*These data are from a thesis submitted by G. E. Halliday to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, August, 1934.