

REVIEW OF SCIENTIFIC LITERATURE ON FATS AND OILS FOR 1935

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SECTION 2

Composition and Characteristics of Fats and Oils

Among the contributions to our recent knowledge of fats and oils, the work of T. P. Hilditch and associates is outstanding. Reviews presented by this investigator in a few lectures (J. Soc. Chem. Ind. **54**, 139-45, 163-7, 184-9 and Fettchem. Umsch. **42**, 105-17) give evidence which seeks to substantiate the claim that the composition of natural fats is available in many cases in fuller detail than other natural groups such as carbohydrates or proteins. The illustrations to show this are drawn from recent contributions to such topics as component acids and glycerides of fats, the manner in which their chemical constitution determines the properties and uses to which they may be put, their transformation when subjected to hydrogenation under different conditions and the evolution of a new group of strongly detergent compounds from fatty derivatives. Data in tabular form on the principal component acids and the manner in which these are assembled into triglycerides show that "even distribution" is in most cases the dominating principle in natural fats and oils. Additions were made to these data in his most recent communications on palm oils (J. Soc. Chem. Ind. **54**, 77-82 T), piqui-a fat (J. Soc. Chem. Ind. **54**, 109-11 T) and rape oil (J. Soc. Chem. Ind. **54**, 331-6 T).

A contribution toward application of absorption spectra in fatty oil research is presented by L. J. N. van der Hulst (Rec. trav. Chim. **54**, 639-50). Absorption curves are presented for several fat acids, and some of their ethyl and methyl esters. The differences between the curves of the impure and the purified materials indicated that the absorption spectrum might be used for detection of impurities. The author proposed equations for approxi-

mately estimating the amounts of strongly absorbing compounds present in a mixture. Investigations of this type will probably meet complications when applied to oils that either polymerize or form cyclic compounds during the splitting of the acids from glycerine by saponification at high temperatures. Evidence on this point was submitted by J. R. Edisbury, R. A. Morton, and J. A. Lovern (Biochem. J. **29**, 899-908) who indicated that the change from a diastinic in a natural glyceride to a highly selective absorption of the acids prepared by saponification of fish oils is due to the cyclisation resulting from the heating during saponification.

C. Lutenberg and T. Dudkina (Fettchem. Umsch. **42**, 91-5) compared the Twitchell, Grossfeld, and Cocks, Christian and Harding methods for determination of solid unsaturated fat acids in the presence of saturated acids. It was concluded that none could succeed or be made successful for quantitative separation of solid acids.

The methods for determining saturated acids in fats and oils are evaluated by D. Nikitin (Trudui VNIIZh **1934**, No. 2, 35-59). The Kaufmann method is best in absence of linolenic acid or the Bertram method in absence of the unsaturated acids of high molecular weight, cyclic acids, and isomers of oleic acid or its homologs. The Twitchell method gives lower results than either, and the Holde-Selim-Bleyberg is still less accurate. The Grossfeld method is not recommended, but it finds use for separating binary mixtures. A. Lutenberg and T. Dudkina (Trudui VNIIZh **1934**, No. 2, 60-2) modified the Bertram procedure so that the iodine numbers of the precipitates obtained are approximately zero. This is brought about by carrying out the oxidation at a temperature lower than is usually recommended and omitting the extrac-

tion of the aqueous layer with petroleum ether.

T. G. Green and T. P. Hilditch (Biochem. J. **29**, 1552-63) studied the various methods proposed for characterizing linoleic and linolenic acids. The results are summarized by the statement that no better method was found than the original process of oxidation with alkaline permanganate as proposed by Hazura; and this procedure, at best, leads to the isolation of crystalline tetra- or hexahydroxystearic acids in yields which respectively correspond to only about 40% and 15-18% of the theory for linoleic and linolenic acids. The investigation was for the purpose of forming a preliminary to the further investigation of butter fat (Biochem. J. **29**, 1564-75). The results of the latter investigation indicated that the C₁₈ acid with two double bonds of peanut oil and cow butter fat are structurally similar, and that the latter is a different geometrical isomeride (or mixture of isomerides) of the linoleic acid of seed fats.

The evaluation of the amount of fat acids less saturated than oleic by means of the difference between the iodine and thiocyanogen value is recommended by O. J. Hill and L. S. Palmer (J. Dairy Sci. **18**, 455) as a technic for studying the effect of oil seed cake feeds on the composition of butter fat produced. Usual values for butter fat are 2.49-4.16; much higher values are obtained when cattle rations are supplemented by seed cake feeds containing highly unsaturated acid glycerides.

The first naturally-occurring ketonic unsaturated fat acid was identified by W. B. Brown and E. H. Farmer (Biochem. J. **29**, 631-9). The acid and an isomer were discovered in oiticica oil and were found to be identical with an acid obtained from *Licania rigida* kernel oil. This suggested *Licania rigida* as the source of oiticica

oil and hence the name licanic acid was applied to the acid. The structural formula of the acid was shown to be $\text{CH}_3-(\text{CH}_2)_3-(\text{CH}:\text{CH})_3-(\text{CH}_2)_4-\text{CO}-(\text{CH}_2)_2-\text{CO}_2\text{H}$. This acid is probably the same material as the "couepic acid" of van Loon and Steger, who ascribed to it the formula $\text{CH}_3-(\text{CH}_2)_3-(\text{CH}:\text{CH})_3-(\text{CH}_2)_7-\text{CO}_2\text{H}$. Additional evidence supporting the ketonic structure of the acid is presented by C. P. A. Kappelmeier (Fettchem. Umsch. 42, 145-52).

Our knowledge of the composition of marine oils was supplemented during the period under survey by the separation and identification of several new acids from sardine oil by Y. Toyama and T. Tsuchiya (Bull. Chem. Soc. Japan 10, 192-9, 232-41, 241-8, 296-300, 301-4). The marine animal oils were reviewed by W. Kumura (Proc. 5th Pacific Sci. Cong. 5, 3663-71) from the standpoint of the highly unsaturated acids present; and by T. P. Hilditch (ibid. 647-61) who discussed some characteristic features of the glycerides present.

In addition to those already mentioned, several other reports have appeared in regard to fat acids other than those normally reported. E. E. U. Abraham and T. P. Hilditch (J. Soc. Chem. Ind. 54, 398-404 T) stated that acids of the normal series, i.e., myristic, palmitic, stearic, etc., are not present in wool grease. It is suggested that the acids of sterol waxes secreted by sebaceous and other glands are derived from an isoprene or a terpene foundation. Several series of acids are reported, some of which give evidence of lactone or internal anhydride formation when boiled with dilute mineral acids. E. H. Farmer and E. Sunderland (J. Chem. Soc. 1935, 759-63) obtained an acid with formula $\text{CH}_3-\text{CH}_2-(\text{CH}:\text{CH})_4(\text{CH}_2)_7-\text{CO}_2\text{H}$ from oil of the *Parinarium laurinum* kernel, and also identified alpha-eleostearic acid in *Parinarium macrophyllum*. F. J. E. Collins (J. Soc. Chem. Ind. 54, 33-5 T) compared the acids distilled from Chinese wax with those of esparto grass. The acids of the latter averaged a larger carbon content. Since erucic acid is rarely found in nature outside of the cruciferous family plants, K. Taufel and H. Thaler (Fettchem. Umsch. 41, 196-8) questioned its reported occurrence in grape seed. This

doubt was confirmed by a series of chemical experiments, none of which yielded positive evidence.

A survey of the phosphatides content in American soy beans and oils by G. S. Jamieson and R. S. McKinney (OIL AND SOAP 12, 70-2) discloses that, with but few exceptions, the beans grown in the East contained less phosphatides than those from the West. A high concentration of the lipides is found in the precipitate separating from clarified expressed crude oil. Regardless of whether or not a separation took place, all the crude soy bean oils contained notable quantities of phosphatides. The marine oils are reviewed from the standpoint of the lipides by E. Andre and A. Block (Bull. soc. chim. 2, [5] 785-802).

L. Schmid and S. Margulies (Monatsh. 65, 391-8) determined the decomposition point of gossypol and some of its derivatives. A sample extracted from cottonseeds decomposed at 184°. M. Podol'shaya (Masloboino Zhirovoe Delo. 11, 128-31 and Fettchem. Umsch. 42, 96-100) reports the influence of gossypol on the color of cottonseed oil. When oil solutions of gossypol are heated, the color intensity rises to a maximum at about 90° and then falls to a minimum between 120° to 150°, after which it rises to a higher maximum. The amount of analytically determinable gossypol and the color intensity of the recooled oil are lowered by increasing the temperature or duration of heating and there is a further decrease during storage.

A. E. Gillam and I. M. Heilbron (Biochem. J. 29, 834-6) examined the unsaponifiable matter of several butters by combined chromatographic and spectrographic methods in order to ascertain the relative ratio of the amounts of alpha- and beta-carotene present. The ratio varied considerably in samples from different cows. There was a similarity between the lipoid pigments of the blood serum of cows and those of the butter produced; consequently, it is argued that the carotenoids in milk fat must come from the food ingested by the cow via the blood. F. Richter's (Milchwirtschaft. Forsch. 17, 72-86) photometric measurements on several butter colors show a marked similarity between the color curves of butter fat and carotene, while those of all other

colors were decidedly different. He also reports that the stability of carotene in oil solution is better than that of other vegetable colors. Because of these results, he proposes a fixed carotene content of butter as a standard of color. Methods for differentiating carotene from vitamin A by chemical reagents are reviewed and discussed by V. E. Levine and G. E. Bien (Proc. Soc. Expt. Biol. & Med. 32, 873-6).

Sei-ichi Ueno and associates (J. Soc. Chem. Ind. Japan 38, 113-6B, 189-90B, 345-52B and 352-6B) and M. Tsuyimoto and H. Koyanogi (J. Soc. Chem. Ind. Japan 38, 118-20B, and 271-2B) report work on identifying the unsaponifiable constituents of several marine animal, fish and vegetable oils. The per cent of cholesterol in the samples varied; several alcohols were identified and some hydrocarbons were separated. Gresvald (J. Am. Pharm. Assoc. 24, 214,290) separated a sterol of 130-1° melting point from the leaves of wild bergamot and sitosterol from *Pinus sabiniana* seeds.

T. Thorbjarnarson, A. S. Ruiz and J. C. Drummond (Analyst 60, 382-8) recommend aluminum oxide for the selective adsorption of pigments from the unsaponifiable matter of fish oils. After acidifying, the pigments may be eluted from the adsorbent with chloroform. This work is published to aid the workers who are attempting to identify unsaponifiable constituents of oils.

Several hydrocarbons were identified in natural oils. Y. Toyama and T. Tsuchiya (J. Soc. Chem. Ind. Japan 38, 254-8) separated pristane (octadecane) from sardine, herring, and sperm oils; heptadecane was also obtained from sardine oil. T. Thorbjarnarson and J. C. Drummond (Analyst 60, 23-9) report hydrocarbons of formula $\text{C}_{20}\text{H}_{40}$, $\text{C}_{31}\text{H}_{62}$ and $\text{C}_{30}\text{H}_{50}$ present in the unsaponifiable matter of olive oil.

Analytical fat extraction methods are investigated from the standpoint of speeding up the determination and devising methods for special needs. P. M. Ivanov (J. Applied Chem. U. S. S. R. 7, 1523-6) finds the Ban method requires 6-7 hours in comparison to 15 hours for the Soxhlet extraction. The results by the former are 0.5 to 0.9% less than those of the latter method. V. Puzanov (Masloboino Zhirovoe

Delo. 11, 169-70) devised an apparatus by which it is claimed the extraction is complete in 30 minutes. The application of the refractometer for per cent oil analysis in industry and food control is discussed by W. Leithe (Chem. Ztg. 59, 325-7) with special reference to the materials to which it may be applied. V. V. Illarionov and P. Demkovskii (Masloboino Zhirovoe Delo 11, 171-3) recommend chlorobenzene as a solvent for the refractometric per cent oil method when applied to oil seeds. According to A. Ermakov (Masloboino Zhirovoe Delo 11, 282-4) good results are obtained with use of alpha-bromo-naphthalene in the same procedure. A description of the acid method for determining fat in pastry is presented by T. von Fellenberg (Mitt. Lebensm. Hyg. 25, 316-8). He recommended boiling ten grams of sample with 100 c.c. of hydrochloric acid for five minutes, grinding the dry, filtered residue with sand and dry sodium sulfate and extracting with acetone. A. Baader (Allgem. Oel-u. Fett-Ztg. 32, 381-4) finds the usual method of determining fat in mixed mineral oil-fat lubricants unsuitable, because the concentration of caustic ordinarily used is too low for complete saponification in presence of the hydrocarbons. Best results are reported with half normal sodium hydroxide in 2:1 benzene: alcohol solution.

A colorimetric method using copper sulfate as a reagent for determination of moisture in oil is described by I. Sonkhotzkii (Masloboino Zhirovoe Delo 11, 48-9). A control method for moisture in lard is proposed by F. Graf (Scientia Pharm. 6, 42). According to the description, one gram of sample dissolved in 5 c.c. of benzene at 20° results in a turbid solution if the water content is greater than 0.5%.

The free fat acid determination received consideration in two contributions. I. Petrjajew (Masloboino Zhirovoe Delo 11, 137) recommends a mixture of alcohol and benzene (1:2) as solvent for the oil. A potentiometric method is described by O. Tomicek and J. Feldman (Collection Czechoslov. Chem. Communications 6, 408-22).

The various iodine value procedures are compared by S. Yushkevich, (Trudui VNIIZh 1934, No. 2, 9-34), Y. Yoyama and T. Tsuchiya (J. Soc. Chem. Ind.

Japan 38, 32-5), T. Fink and T. Hadacek (Casopis Ceskoslov. Lekarstva 15, 103-12) and N. Evers and W. Smith (Pharm. J. 134, 417). The prevailing decision is that the Rosenmund-Kuhn-benn method is most suitable and that the Wijs gives values higher than other standard methods. The first named writer recommends the Stiepel method for routine work where rapid determinations are required. K. Ho, C. S. Wan and S. H. Wen (Ind. and Eng. Chem Anal. Ed. 7, 96-101) found it impossible to check iodine values on tung oil by the Wijs method according to the procedure specifications of the different authorities, so they made investigations on the relation of the various factors; i.e., time of contact, temperature, etc., with iodine value obtained. As a result of the data accumulated they propose equations for converting the value obtained under laboratory conditions to the standards of the various specifications. The rapidity of the Hübl method is increased, according to Klyuchevich and A. Vishnevskaya (Masloboino Zhirovoe Delo 10, No. 11, 50-2) by holding the sample in contact with the reagent for only 20 minutes at 60°; this temperature is higher than that usually specified. K. Drewski (Przemysl Chem. 19, 63-75) describes a potentiometric method for iodine value. E. Rossman (Angew. Chem. 48, 223-6) and J. Boeseken and R. Pols (Rec. trav. chim. 54, 162-6) propose methods by which the value is obtained by means of determining the bromine vapor uptake; the latter method is a micro-method. A modification of the Margosches, Hinner and Friedmann method is described by W. Ruziczka (Mikrochemie 17, 215-21).

In the determination of iodine value of oils containing free hydroxyl groups the formation of hydrogen iodide may occur to give erroneous results. R. Klatt and K. G. Margosches (Fettchem. Umsch. 42, 183-90) suggest that such errors are prevented when the determination is made on the acetylated fat.

L. Margaillan and M. Carriere (14me Congr. Chim. ind. Paris Oct. 1934) called attention to the fact that higher hexabromide values of fats are obtained when precipitation is carried out in the absence of acetic acid. They explain this by assuming that in presence of acetic acid the beta-

isomers of linolenic acids do not precipitate. M. C. Tuyn (Verf. kroniek 7, 233-7) finds best results are obtained when the hexabromide determinations are made on the isolated fat acids.

H. Taufel, M. de Mingo and H. Thaler (Fettchem. Umsch. 42, 141-4) give evidence showing that the "Wizoff" or Verley-Bolsing acetylation methods give less accurate acetyl values than the Franchimont procedure for di-, tetra- and hexa-hydrostearic acids and for neutral castor oil. The Franchimont method is also less affected than the others by presence of free fat acids. A report of the Association of Official Agricultural Chemists' committee on acetyl value of fats and oils (J. Assoc. Official Agr. Chemists 18, 434-9) gives a comparison between the Andre-Cook, Roberts-Schuetz and West-Hoagland-Curtis acetylation methods. The West-Hoagland-Curtis gave the lowest results; the other methods agreed more closely although the Roberts-Schuetz acetylation values were higher than the Andre-Cook. E. S. West, C. L. Hoagland and G. H. Curtis (J. Biol. Chem. 104, 627-34) modified the Verley-Bolsing method so as to lessen the difficulty in determining the acetyl value of lipids due to presence of free fat acids.

Tables appended to this division of the review give the data on per cent oil or fat from various sources with the characteristics and fat acid composition as were presented during the year.

A new colorimeter constructed by E. R. Bolton and K. A. Williams (Analyst 60, 447-54) evaluates the color of oils by passing a light from which the infra-red rays are eliminated, through the oil; and by means of accurate instruments the light transmitted is measured. The figures are reported in the per cent of light extinguished. G. E. Halliday and H. R. Kraybill (OIL AND SOAP 12, 22-4) consider it most convenient to express the color of soybean oil in milligrams of free iodine per 100 cc. dissolved in a 2 per cent potassium iodide solution of which a five centimeter column just matches a like column of oil. The contribution of J. M. McNichols (OIL AND SOAP 12, 167-77) on the spectrophotometric analysis of 125 vegetable oils is presented as an aid in developing better color grading methods. McNichols considers the Lovi-

bond the best instrument.

The Finkener method is judged by A. Koss (*Przemysl Chem.* **19**, 75-85) as the most accurate for determining the temperature of solidification of fat acids. He cautions that measurements should be made immediately after saponification.

The methods for determining viscosity of oils are summarized by H. A. Boekenoggen (*Fettchem. Umsch.* **42**, 177-80) and a comparison of data on several oils is presented. It is suggested that since viscosity measurements are relatively easy to carry out they should become important as characteristics of oils and fats.

New methods of characterizing fats are proposed by R. Lucentini and E. Drago (*Annali chim, appl.* **25**, 388-91), P. Rehbinder and L. Solowjewa (*Masloboino Zhirovoe Delo* **11**, 60 and *Allgem. Oel- u. Fett-Ztg.* **32**, 277-82) and R. Stronbecker (*Z. Untersuch. Lebensm.* **69**, 521-43). The first named method pertains to determining the number of cubic centimeters of tenth normal sodium hydroxide required to neutralize the fat acids (mainly PrCO_2H) obtained by hydrolyzing five grams of fat in 100 cc. of saturated potassium sulfate solution. This varies from 18.7 to 20.85 for butter and is 3, 5.3, 4.15 and 3, respectively, for tallow, cacao butter, hydrogenated cacao butter and hydrogenated whale oil. Rehbinder and L. Solowjewa characterize the polarity of fats by an indirect measurement of the interfacial tension between a solution of fat in a nonpolar solvent and a series of weak alkali solutions. The value is reported in concentration of sodium hydroxide necessary to form a single phase and gives an indication of the ease of saponifiability or emulsifiability of the fats and oils. The criterion of Stronbecker pertains to evaluating the kinetic saponification velocity by use of conductivity decrease curves. This is recommended as a practical method for detecting adulteration.

With but few exceptions, determinations on the solubility of gases in oils and fats have been neglected until the work of F. C. Vibrans (*OIL AND SOAP* **12**, 14-5). The solubilities of the various gases in corn, linseed and cottonseed oils and lard did not vary appreciably; the values in cc. per 100 cc. of oil or lard are:

air 7.1-7.3, oxygen 10.8-11.2, nitrogen 6.1-6.7, hydrogen 4.1-4.3 and carbon dioxide 102-134.

Three criteria are described by A. Castiglioni (*Ann. fals.* **28**, 24-7) for differentiating cacao butter extracted by solvents and that by means of pressure. The solvent extracted gives a yellow green fluorescence when dissolved in acetic acid; it gives a pink color when dissolved in alcohol and treated with hydrochloric acid and antipyrine; and it also gives a characteristic violet coloration in the Marawskii sulfuric acid-acetone test.

Two methods have been proposed for distinguishing refined from crude oils. S. H. Bertram (*Chem. Weekblad* **32**, 296-7) finds that refined oils have a much higher electrical resistance than the unrefined and suggests this as a means of identification. J. Guillot (*Ann. fals.* **28**, 69-75) suggested a refractophotometric method for distinguishing virgin from refined olive oils or other crude oils from the refined product. The absorption coefficients of crude oils are less than for the refined or heated oils.

The detection of adulteration of olive oil still seems to be a problem. G. Tommosi (*Ann. staz. chem. agrar sper. Roma No.* **305**) finds the refractive index, iodine value and maumene value the most useful. Negative color reactions were considered no proof of absence of adulterant. R. Macille (14me congr. chim. ind. Paris 1934) recommends a technic for carrying out Bellier test with special reference for its use in detecting peanut oil in olive oil. G. Leoncini (*Boll. ist super agrar Pisa* **10**, 405-17) reports that Tuscany olives attacked by some micro-organisms gave the reaction of Marowski-Fachini, but not the Bellier reaction.

Rape oil can be detected in linseed oil by determining the iodine value of the insoluble lead salts of the fat acids; i. e., erucic acid. According to Grossfield (*Chem. Ztg.* **59**, 935-6) the value for rape oil is sixteen times that of linseed oil; this variation is greater when the lead salts are absorbed in lead palmitate during the separation. As little as two per cent rape oil may be detected in linseed oil on this basis.

The adulteration of lard with vegetable seed oil is detectable according to L. Kofler and E.

Schaper (*Fettchem. Umsch.* **42**, 21-6) by determining the melting point of the acetylated sterols from the sample in question. They present curves and charts of the variations caused by additions of vegetable oils to lard. Two per cent peanut oil could be readily detected. Difficulty is experienced in detecting coconut oil in lard owing to the low sterol content of the former. A. C. Bose (*Analyst* **60**, 160-3) recommends the development of the sterol iodine value of Bolton and Williams for classifying animal and vegetable oils. This method is also not applicable to determining presence of coconut oil in animal fats.

The Tortelli and Jaffe's test for identifying hydrogenated fish and marine animal oils was modified by M. N. Ghose and H. K. Pal (*Analyst* **60**, 240-1), so that the transient rose color obtained becomes a persistent pink. This was accomplished by reducing the amount of test sample and adding a ten per cent solution of bromine in chloroform instead of the pure liquid bromine as in the usual method.

An improvement in the detection of nickel in fat is given by M. Struszynski (*Przemysl Chem.* **19**, 48-9). The advantage is obtained by extracting the metal with use of dilute solutions of hydrochloric acid containing a small amount of nitric acid or potassium chlorate.

Investigations on the effect of baking ingredients and process on butter fat are submitted by G. Prange (*Z. Unters. Lebensm.* **69**, 548-55). The effect of wheat flour fat, egg oil, and baking are not so great that one may confuse the butter with a foreign fat.

Wood oil or tung oil may be characterized according to Fa-Wu Cheng (*Trans. Sci. Soc. China* **8**, 97-101 and 758-63) by the difference between the index of refraction of the original oil and the polymerizable fraction multiplied by 10^4 . These figures are comparatively low for the oils; and adulteration with as low as three per cent of rape oil, poppy oil, tallow or rosin increases the figure enough to detect additions of the foreign fatty materials. A simple test by Z. Leppert and Z. Majewska (*Przemysl Chem.* **18**, 471-3) pertains to detection of wood oil in other oils. A drop of ninety per cent sulfuric acid is placed on a drop of oil; when this contains

CHARACTERISTICS REPORTED FOR VARIOUS OILS DURING 1935

Oil or Fat Source	% of oil or fat in source	Density	Refr. Index	Acid No.	Sapon. No.	Iodine No.	R-M No.	Acetyl No.	% Unsap.	Hegner No.	Thiocy- anogen No.
Acorns (of India) ¹											
<i>Quercus incana</i> Roxb.		0.9081d ²⁵	1.4576 ³⁰	13.0	192.2	81.5	14.8	0.8	96.1
<i>Quercus dilatata</i> Lindl.		0.9034d ²⁵	1.4588 ³⁰	22.2	188.4	90.3	21.1	2.3	88.2
<i>Quercus ilex</i> Linn.		0.9079d ²⁵	1.4576 ³⁰	8.5	189.9	83.0	17.4	0.9	94.9
<i>Aleurites moluccana</i> nuts ²		0.9246 ²⁰075	196	154
Apple seed ⁴	18.0	B. Ref. 62.9 ⁴⁰	2.3	187.7	122.4	.22	1.10
<i>Austranella congolensis</i> De Wild. ⁵ seed (of Belgian Congo)		.9104 ³³	1.4662 ²⁴	1.94	190.4	74.27	14.46	0.85	94.1
Bael or Beli fruit seed (of India) ⁶ <i>Aegle Marmelos</i> Corr.	34.4	0.918 ^{80/4}	1.4647 ^{40/D}	0.42	193.6	108	1.58	93.7	70.4
<i>Blighia laurentii</i> Wild. seed ⁷ (of Lower Congo)		0.904d ^{15/15}	1.4620 ^{33.5}	35.5	181.7	73.47	1.6	95.29
Caper spurge seed kernel (of Ukraine) <i>Euphorbia lathyris</i> L. 58.3-63		0.920 ²⁰	1.4698 ^{20/D}	9.9	82.0	2.5	5.4	1.2	80
<i>Cassia absus</i> Linn. seeds ⁹		0.9276 ²⁵	1.4840 ²⁰	2.5	190.4	130.5	12.0	8.4
<i>Cortinellus shiitake</i> P. Henn. seed ¹⁰		0.9231	1.4918	74.44	176.38	133.59	8.5	30.	93.25
<i>Coula edulis</i> Baillon, nuts ¹¹	29.6 (kernel) 7.2 (nuts)	0.9879 ⁷⁸	1.4683 ²⁰	20.3	189.5	86	0.4	11	0.8	82.6
Digger pine seed ¹²		0.9177 ¹⁸	1.4713 ^{24/D}	189.8	120	4.95	83.0
Fig (Caprifed) seed ¹³		1.4775 ²⁵	0.87	190.1	169.4	6.1	1.07	108.4
Grape seed (of California) ¹⁴		1.4740 ²⁵	.03	192.1	129.1	18.8	0.53	80.03
Gray cress seed ¹⁵		1.4750	3.22	181.2	181.0	1.56	109.4
Green moog seed ¹⁶		171.2	111.9	12.3
Haddock liver ¹⁷ <i>Sebastes marinus</i>	4.	0.9233 ¹⁸	1.4820 ^{18/D}	180	170	3.95
Hipberry seed ¹⁸		0.9270 ¹⁵	4.1	187.5	155.2	0.3	1.04
Hyocyanus niger seed ¹⁹	28.9	1.4693 ^{40/D}	11.95	186.7	142.9	1.99	81.1
Itoyo fish ²⁰ <i>Gasterostens aculeatus</i> Lim.		0.9232 ^{20/4}	1.4789 ^{20/D}	.75	186.9	165.0	1.01
Jaboty beans ²¹	50 (kernel)										
<i>Erisma uncinatum</i> Warm.	23 (fruit)	0.8760 ^{78/4}	1.4360 ⁷⁷	20.0	233.0	5.4	0.93	10	.7
<i>Kabuli Chhola</i> seed ¹⁶		185.3	72.44	3.4
Kalumpang seeds ²² <i>Sterculia Foetida</i> Linn.		0.9231d ²⁰	1.4671 ²⁹	9.24	215	77.13	1.86	109	0.48
Kapok seed (of Sicily) ²³	12.20	0.918d ¹⁵	13.6	183.8	10647	92.5
Kapok seed (of It. Somaliland) ²³	17.36	0.9209d ¹⁵	7.4	183.8	9555	93.5
Millepedes ²⁴ <i>Strongylosoma tambanum</i>		1.6285 ^{15/D}	69.7
Oats ²⁵		0.916 ¹⁵	44.58-	193.4-	115.77-	6.82-	1.74-	91.5-
Bagilumbang nut oils ¹⁶		40.15	198.8	113.65	12.98	1.73	92.25
<i>Aleurites trisperma</i>	59.9 (kernel)	1.4971 ²³	.87	196	18750	69.9
<i>Omphalocarpum boyankombo</i> De Wild ⁶	48.8	.9128 ¹⁵	1.4672 ^{22.5}	1.21	206.06	81.70	15.46	1.17	93.0
Palm (of Sumatra) ²⁶		0.8703 ^{80/4}	1.4484 ^{70/D}	13.0	197.7	54.6-	0.40	11.7	45.3
Pear seed ⁴	19.4	B. Refr. 62.0 ⁴⁰	5.4	189.5	124.1	0.33	1.03
Peanut (of China) ²⁵	42.1-43.6	0.914-	1.4710 ^{20/D}	0.5-	194.5-	97-
<i>Pentadesma butyracea</i> Sabine ⁵		.9146d ²⁰	1.5	196.5	98.5
(of Tshuapa, Congo)	42.8	.9145 ¹⁵	1.4532	4.04	192.75	35.60	0.65	11.78	94.0
<i>Pentadesma butyracea</i> Sabine ⁵	
(of Kisantu, Congo)	36.9	.9137 ¹⁵	1.4517	9.85	190.0	36.77	0.82	24.85	93.4
<i>Pentadesma Lebrunii</i> St. ⁵	
(of Congo)	20.3	.9155 ¹⁵	5.85	218.8297
<i>Pinus pumila</i> Regel ²⁸	23.77	0.9276d ¹⁵	2.34	191.3	161.1	91.0
Piqui—a seed coat ²⁹	70	10.6	281.6	47.8	0.8
Piqui—a seed kernel ²⁹	
<i>Caryocar villosum</i>	59	0.9	284.0	48.6	1.7
<i>Plantago ovata</i> Forsk. seed ³⁰	1.75	.9212 ²²	1.4737 ^{28/D}	5.16	181.8	116.0	37.7	1.8-2.0	91.8
<i>Pongamia pinnata</i> Merr. ³¹	16.63	0.931	1.472	22.35	180	91-96	2.6
Ring snake ³² <i>Natrix natrix</i>		1.4630 ^{40/D}	198.5	87.98	2.2
Rose Mallow seed ³³ <i>Hibiscus Moscheutos</i> X. H.	
<i>Cocchineus</i>		0.9262d ²⁰	1.4760 ²⁰	24.13	186.55	107.8	1.8	22.92	1.34	63.29
Sandalwood seed ³⁴ <i>Santalum album</i>	13.9-49	0.928-	1.4760-	11-	185-	138-	20.4-	16.8-
		.945 ²⁵	1.4780 ^{20/D}	14.5	197	153	24.3	18.8
<i>Sarcostigma kleinii</i> seed ³⁵		0.9274 ^{29.5/4}	1.4650 ^{40/D}	11.89	196.6	71.82	0.55	0	94.2	49.48
Shark liver ³⁶ <i>Squalus sucklii</i> Girard	55.5-75.3	0.9149-	1.4739-	0.86-	161.2-	122.0-	9.80-
		0.9164 ^{15/4}	1.4760 ^{20/D}	1.77	168.9	137.9	16.23
Shark flesh ³⁶ <i>Squalus sucklii</i> Girard	2.16-3.29	0.9249-	1.4800-	3.16-	178.1-	173.7-	4.87-
		0.9168 ^{15/4}	1.4760 ^{20/D}	0.84	167.3	167.8	8.20
Sumac seed (of Sicily) ³⁷		0.9128 ²⁰	1.4772 ²⁰	191.9	97.5	1.63
Sunflower seeds (of Cyprus) ³⁸	24.2	0.9216d ^{15/15}	1.4655 ⁴⁰	2.8	192.2	115.8	1.0
Tea seed (of Ceylon) ³⁹		0.914 ³⁰	1.4674 ^{30/D}	0.83	196.0	88.7	76.3
Thorn apple seeds, unripe ⁴⁰	10.3	1.4675 ^{40/D}	20.42	227.6	131.1	78.6
Thorn apple seeds, half ripe ⁴⁰	38.7	1.4675 ^{40/D}	3.43	189.3	127.7	79.6
Thorn apple seeds, ripe ⁴⁰	2.4	1.4672 ^{40/D}	1.50	183.7	126.3	76.5
Tobacco seed ⁴¹	11.33	0.9302d ¹³	B. Refr. 66.39 ⁴⁰	190.49	139.74
Tung oil (American) ⁴²		1.5165 ²⁵	193.6	246.947	82.75
Whale shark liver ⁴³ <i>Rhinodon typicus</i> Smith		0.8977 ^{50/4}	25	182.5	108.6	.11	5.04
Ucuhuba seed ⁴⁴ <i>Viola surinamensis</i> Warb.	65.1	1.4446 ^{70/D}	8.4	223.9	10.9	1.6	2.2

SUPPLEMENT TO CHART ON CHARACTERISTICS

Material	Polenske value	Hexabromide No.	Titer	Melting Point	Viscosity
Apple seed ⁴	0.4
Bagilumbang nut oil ¹⁶
<i>Aleurites trisperma</i>	0
Grape seed (of California) ¹⁴	0.3	.29
Hipberry seed ¹⁸
Jaboty beans ²¹
<i>Erisma uncinatum</i> Warm.	3.1	41.5
Oats ²⁵	5.24-12.4
Palm (of Sumatra) ²⁶	.67	28°-33°
Pear seed ⁴	.3
<i>Pentadesma butyracea</i> Sabine ⁵	28-31.5
(of Tshuapa, Congo)
<i>Pentadesma butyracea</i> Sabine ⁵	28-32
(of Kisantu, Congo)

Ring snake ³²									
<i>Natrix natrix</i>86							25.5°
Sandalwood seed ³⁴									
<i>Santalum album</i>								35° C.
<i>Sarcostigma kleimii</i> seed ³⁶	0.19		0					solid at 20°	Engler 7.4 ³⁰
Ucuhuba seed ⁴⁴									
<i>Virola surinamensis</i> Warb.	4.0							51

COMPONENT FATTY ACID CONSTITUENTS OF THE OILS REPORTED 1935

Fat Source	Saturated acids			Unsaturated acids			Other acids reported
	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
<i>Amoora rohituka</i> seed ³	0.7	7.8	15.1	11.2	65.3	
*Bael or Beli fruit seed (of India) ⁸	..	15.6	8.3	28.7	33.8	7.6	
<i>Aegle Marmelos</i> Corr.	17.3	12.9	Elaeostearic 67.1
**Bangilumbang nut oil ⁴⁸	
<i>Aleurites Trisperma</i>	
Caper spurge seed (of Uralia) ³⁷	5.73	90.6	2.3	
<i>Euphorbia lathyris</i> L.	6.28	8.10	16.32	47.32	0.41	Oxyacids 0.75, Lignoceric 0.82
* <i>Cassia absus</i> Linn ⁹	1.6	87.1	2.7	
<i>Coula edulis</i> Baillon, nuts ¹¹	5.5	51.0	43.5	
Digger pine seed ¹²	5.23	2.18	18.99	33.72	32.95	Arachidic 1.05
*Fig (Caprifig) seed ¹³	5.98	2.67	52.1	51.9	2.3	Arachidic 0.07
*Grape seed (of California) ¹⁴	6.3-8.7	65.7-71.3	
<i>Hycosyamus niger</i> seed ¹⁹	
Jaboty bean fat ²³	52.8	18.9	2.8	Lauric 23.9
<i>Erisma uncinatum</i> Warm.	
Millepedes ²⁴	7	40	Propionic 28
<i>Strongylosoma tambanum</i>	9.5-10	49-55.7	15.1-19.7	Volatile acids 3-6
Oat ²⁵	42.9	4.7	39.8	11.3	Lower fat acids 1.5
Palm oil (of Sumatra) ²⁶	1.3	41.4	4.7	42.9	9.7	
Palm oil (Belgian Congo) ⁴⁶	1.6	32.3	5.5	52.4	8.2	
Palm oil (Cape Palmas) ⁴⁶	0.7	14.0	18.8	28.0	5.0	0	Arachidic 1.7, Palmitoleic 1.5, C ₂₀ -20, C ₂₂ -7.5
Pig liver ²⁷	
<i>Pinus pumila</i> Regel seeds ²⁸	5.09	17.52	71.84	5.55	
Piqui—a seed kernel ²⁹	1.4	48.4	0.9	46.0	3.3	
Piqui—a seed dried fruit coat ²⁹	1.5	45.1	1.8	49.6	2.0	
<i>Plantago ovata</i> Forsk. ³⁰	12.5	36.75	47.95	0.244	
* <i>Pongamia pinnata</i> Merr. ³¹	23.01	11.30	65.65	
**Rose Mallow seed ³³	15.60	33.12	45.53	
<i>Hibiscus Moscheutos</i> X. <i>H. Coccineus</i>	34	55.18	10.82	
<i>Sarcostigma kleimii</i> ³⁵	14.60	2.60	55.75	23.5	
**Sumac seed (of Sicilia) ³⁷	11.45	74.25	14.3	
Tea seed oil ³⁹	(including unsapon.)	
Thorn Apple seed, unripe ⁴⁰	9.1	30.3	60.6	
Thorn Apple seed, half ripe ⁴⁰	7.9	36.6	55.5	
Thorn Apple seed, ripe ⁴⁰	11.5	31.0	57.5	
**Tung oil (American) ⁴²	4.6	0.8	Elaeostearic 94.10
Ucuhuba seed ⁴⁴	63.2	8.4	1.5	6.3	2.8	Lauric 12.6, Resinous matter 5.2
<i>Virola surinamensis</i> Warb.	
*Based on total oil.							
**As glyceride.							

OIL OR FAT CONTENT IN VARIOUS MATERIALS REPORTED DURING 1935

Material	Oil or Fat Content
Sind (India) Oil Seeds ⁴⁸	
Soy Beans	
Pusa Yellow	16.8
Punjab	17.32
Pusa Chocolate	19.17
Lorido	17.36
Safflower	30.53
Linseed	37.15
Castor	47.04
Sunflower	29.18
Mustard	30.53
Rapeseed	39.20
Manchurian Oil Seeds ⁴⁹	
Perilla	
White seed	48.37
Black seed	45.75
Flax	31.92
Hemp	30.18
Sunflower	
Husk	1.42
Kernel	58.15
Soy Beans	
Green	16.70
Black	18.27
Red	18.58
Yellow	19.79
Sesame	
White	54.98
Black	44.71
Peanut	
Large	44.99
Small	46.56
Castor Bean	51.91
China Jute Seed	18.30
Olives of Cyrenaica ⁵⁰	16.54

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not less than ten per cent wood oil, the drop of acid does not spread but rapidly darkens and assumes a polygonal contour. The

reaction serves for mixtures with raw, boiled, or aerated linseed oils.

The movement for adoption of

standard methods is fostered by publications of several commissions. Reports of the analytical committees of the "American

Oil Chemist Society" appeared throughout the year in several issues of their official journal (OIL AND SOAP). Notes on the analytical methods used by the American paint industry are presented by J. R. Stewart (Nat. Paint, Varnish & Lacquer Assoc. Inc. Circ. 474, 378-410). The French text of the unified methods compiled by "International Commission for the Study of Fatty Substances" is reproduced into German by G. L. Voerman (Chem. Weekblad 32, 414-9) and reviewed in English by H. M. Langton (Food 4, 279-80).

Physiological Studies with Oils and Fats

Facts and theories regarding the liver in relation to fat metabolism are reviewed by H. H. Williams and W. E. Anderson (OIL AND SOAP 12, 42-4). These have been supplemented during the year by several writers. M. Jowett and J. H. Quastel (Biochem. J. 29, 2143-91) studied fat metabolism using the method of determining oxidation to acetoacetic acid by means of liver slices *in vitro*. The optimum pH for the oxidation of most of the acids is close to the physiological value. Acetoacetic acid is probably the only beta-keto-acid produced in significant quantities. Acids of even number carbon atoms produce acetoacetic acid more rapidly than those of odd number, and there is some evidence which suggests that the latter are completely burned to carbon dioxide and water. Benzoates, cinnamates and phenylpropionates strongly inhibit the oxidation of acids to acetoacetic acid. Kidney, spleen and testes produce acetoacetic acid in small quantities, but brain gives no measurable production. All the organs investigated destroy acetoacetic acid in the presence of oxygen, the testes and liver being the least active. The attempts of F. P. Mazza (Boll. soc. ital. biol. sper. 9, 667-9) to oxidize fatty acids with liver extracts were unsuccessful in the case of formic, acetic, butyric and caproic acids and only a slight oxidation occurred with palmitic, stearic and lauric while living liver sections oxidized all but formic acid.

R. O. Jones and I. Smedley-MacLean (Biochem. J. 29, 1690-1701 and 1877-80) studied the oxidation of phenyl derivatives of fat acids by means of hydrogen per-

oxide in the presence of copper catalyst in an attempt to deduce some knowledge of the manner in which fats are oxidized in the body and the nature of the intermediate stages of their oxidation. In the absence of the catalyst, with increasing length of the side chain more of the acid was oxidized; with catalyst phenylacetic acid was most readily attacked. The addition of glucose did not promote the decomposition of fat acids, and coupling with glycine renders them less susceptible to oxidation. It is suggested that the main path of the oxidation does not pass through the keto-acid as a preliminary stage, since beta-hydroxybutyric acid was much more readily oxidized than acetoacetic acid. Additional information is supplied by H. J. Deuel, Jr., J. S. Butts, and L. Hallman (Proc. Soc. Exp. Biol. & Med. 32, 1351-2) who are unable to form appreciable amounts of glycogen in the liver from even-carbon fatty acids. Beta-oxidation is fairly quantitative with odd-carbon acids. On the other hand, S. Skraup and S. Strieck's (Verh. Ges. Verdauungs- u. Stoffweckelkrankh. 1934, 132-6) experiments on dogs indicate that odd-carbon fatty acids are not oxidized in the body.

In recent years a majority of the attempts to test whether or not fat can be transformed into carbohydrate in the animal body have been in favor of the negative. Positive results are produced by C. L. Gemmill and E. G. Holmes (Biochem. J. 29, 338-49). The glycogen content of the livers of rats fed butter falls practically to zero on the first day of the diet; but this gradually rises, reaching a level of almost 1%, which is above normal, on the fourth or fifth day of butter feeding. This and in addition the lowering of the respiratory quotient are indications that conversion of fat to carbohydrate takes place in the liver of a rat fed on butter alone; and it is argued that such is also the case in normal liver. D. J. Levine (Z. Vitaminforsch 4, 92-105) fed young rats fat-free milk and noted that the formation of glycogen is markedly decreased. H. J. Deuel, Jr., J. S. Butts, L. F. Hallman, and C. H. Cutler (J. Biol. Chem. 112, 15-23) report that no significant glycogen deposition occurred in the livers of fasting rats following the administration of sodium

salts of acetoacetic, butyric, caproic, or oleic acids; but a deposition of glycogen followed administration of propionic, valeric, heptonic, and nonylic acids as the sodium salts. It was also here concluded that beta-oxidation proceeds in a relatively quantitative manner with odd-carbon fatty acids.

Reviews relative to this portion of the survey were presented by W. E. Anderson and H. H. Williams (OIL AND SOAP 12, 65-68 and 282-4) and R. E. Howe (OIL AND SOAP 12, 4-6). The first deals with the biochemical aspects and the latter treats the dietary value of fats.

The reports on the substitution of fat acids for the glycerides in the diet are conflicting. R. Lecoq. (Compt. rend. 200, 1979-80) finds that the fat acids with or without addition of glycerol could not be substituted for the glycerides in diet of pigeons, even when the vitamin content of the ration is increased. On the other hand, S. Lepkovsky, R. A. Ouer, and H. M. Evans (J. Biol. Chem. 108, 431-4) report that the free fat acids obtained from lard, their reesterified glycerol, methyl or ethyl esters produced good growth when substituted for the natural glyceride in rations fed to rats. The synthetic esters, with exception of the glyceride, were somewhat inferior to the untreated lard.

The experiments of Z. Maczarski and J. Bormann (Polish Agr. Forestal Ann. 33, 201-8, in English 208) show that the rape oil of rape cake cattle feeds reduces the amount of fat in the milk produced. This is also true in the case of cod-liver oil feeding of cattle as demonstrated by C. M. McCoy and L. A. Maynard. (J. Biol. Chem. 109, 29-37). Since this lowering is much less with shark-liver oil or salmon oil, the authors investigated cod-liver oil to determine whether the factor causing the effect was in the unsaponifiable or the triglyceride portion; the latter produced the effect.

The undesirable effects of highly unsaturated fat feeding to farm animals have been previously noted. Similar effects are produced in poultry according to E. M. Cruickshank (Agr. Progress 11, 147-8). Feeding hemp seed or linseed to poultry resulted in production of oily egg yolks, poor quality carcasses, and oily body fat. The effect of various cereal

diets on the composition of the body fat of rats was investigated by H. S. Olcott, W. E. Anderson and L. B. Mendel (J. Nutr. 10, 517-23). The iodine value of body fats produced by corn, oats, wheat and barley rations are 83, 79, 70 and 71 respectively.

Previously, H. M. Evans and S. Lepkovsky demonstrated a sparing action of fat on vitamin B, with young growing rats, by showing that vitamin B disappeared from tissues more slowly on high fat diet than on low fat diet. A recent publication by the same authors (J. Biol. Chem. 108, 439-55) ascribes the conflicting results obtained by Kemmer and Steenbock (J. Biol. Chem. 103, 353-62) to the use of adult rats, whose vitamin requirements are so high as to mask the sparing action of fat. Evans and Lepkovsky base their contention on the argument that when rats are reared without vitamin B, the muscles of those on low fat diet suffer a loss of vitamin B, both in absolute amount and in concentration per unit weight; but on the high fat diet, though the concentration per unit weight is reduced by about one-half, there is little loss in the absolute amount of this vitamin since the muscles weigh approximately twice as much.

A normal number of communications on comparison of the nutritive value of fats appeared. K. Pickat (Problems of Nutrition U.S.S.R. 3, No. 1, 107) reports that the nutritive value of sunflower oil is higher than either butter or suet when fed to young rats as 30% of the calorie intake, and attributes this to its content of unsaturated fat acids. B. B. Brahmachari (Indian Med. Gaz. 69, 327-9) claims that mustard oil is equal to other fats if supplemented by sufficient vitamin A; this statement is also made by H. K. Lassen (Acta Path. Microbiol. Scand. 11, 183-96) for peanut oil and W. Tange (J. Agr. Chem. Soc. Japan 11, 524-32) finds margarine equal to butter when fortified with the vitamin. Tange also reports that hydrogenated vegetable oils are superior to hydrogenated fish oils.

A. D. Holmes and coworkers (OIL AND SOAP 12, 86-8) promote the feeding of cod-liver oil to industrial workers to reduce the time lost due to colds and similar troubles. Another publication (J. of Dis. of Children 49, 94-100)

presents data showing that 10 c.c. of American cod-liver oil, if completely assimilated would supply the daily iodine requirements of an average human adult.

E. Agduhr (Upsala Lakareforem Forh. 39, 307-94) supplements his earlier reports on the toxicity of cod-liver oil, with evidence indicating that the toxicity is not associated with the vitamin content. Higher molecular alcohols and organic iodine compounds produce lesions corresponding to those developed in the adrenals, kidneys, liver and heart following consumption of 5 c.c. of cod-liver oil per kilo body weight per day. Contrary to some of these results, W. M. Cox and A. J. Roos (Bull. Johns-Hopkins Hosp. 54, 430-9) reported that no histological evidence of lesions is produced in the hearts of rats fed an adequate diet containing 75% of the calorie intake as cod-liver oil, which amount is sixty times that fed by Agduhr. Growth of rats was subnormal. Supplementing a rat diet with one per cent cod-liver oil according to C. B. Freudenberger and F. W. Clausen (J. Nutr. 10, 549-55) produces no difference in growth, body weight, tail length, incidence of infections or weights of the various glands, except the thyroid gland which was found significantly smaller in those rats that received the cod-liver oil.

A few reports consider the vitamin content of fats. J. H. Hilton, S. M. Hauge, and J. W. Wilbur (J. Dairy Sci. 18, 795-9) find butter produced from the milk of cows fed soy bean hay made from plants after the beans were well formed, is low in vitamin A content. Artificially dried alfalfa hay feeding yielded butter of exceptionally high vitamin A content. H. Topelmann and W. Schuhknecht's (Z. Vitaminforsch 4, 111-20) spectroscopic examinations did not reveal the presence of vitamin D in lanolin and other wool-fat preparations either before or after irradiation. R. S. Morgan and H. Pritchard (Analyst 60, 355-68) found that the average potency per gram of the medicinal cod-liver oils retailed in the various parts of the British Isles is 670 and 81 international units of A and D respectively. According to W. C. Russel, M. M. Taylor and D. E. Wilcox (J. Nutr. 9, 569-73) the response of the white rat to antirachitically equivalent amounts of cod-liver

oil and irradiated ergosterol determined curatively is the same when the sources of the factor are fed on a preventive basis. This result differs from that obtained with chickens, in which species the irradiated form of the factor is much less effective than the cod-liver oil when compared on a preventive basis.

The necessity of using biological methods of assay for determination of physiologically active gossypol in certain products prompted W. D. Gallup and Miss R. Reder (J. Agr. Res. 51, 259-65) to make a study of the dietary factors which influence the test in order to devise a more sensitive diet for toxicity evaluation. Alkaline diets high in calcium proved superior to any in allowing the rats fed gossypol to approximate a normal growth rate. The recommendation is therefore made that in biological assay, a basal diet be employed which is potentially slightly acid and contains only the amount of calcium and protein which is compatible with maintenance and moderate growth.

Detergents

Communications dealing with chemical and physical phenomena involved in the action of soaps are much fewer than those on the technical phase of the subject. H. A. Neville and M. Harris (Bur. of Standards J. of Res. 14, 765-70 and Proc. Am. Assoc. Textile Chem. Colorists 1935 200-2) report investigations on the selective adsorption of soaps from aqueous solutions. If the foam is continuously removed from an aqueous solution, the remaining liquid becomes more alkaline. When carbon black, paraffin oil and crude olive oil are brought in contact with soap solutions, acid material is adsorbed at the interfaces; and the aqueous medium becomes more alkaline. The results of these experiments are consistent with the theory of the existence of an acid soap, resulting from the hydrolysis of soap in dilute solutions. B. Tyutyunnikov and N. Kas'yanova (Allgem. Oel-u. Fett-Ztg. 31, 276-9) find that a determination of hydroxyl ion concentration is not a true measure of the amount of soap hydrolyzed in dilute solutions. This amount is always more than can be calculated from the pH, because of the adsorption of hydroxyl groups by certain constituents of the soap solution. This

adsorption of hydroxyl groups at a given soap concentration increases with the amount of alkali until a certain pH is attained, after which it suddenly falls. The critical pH and the amount of alkali needed to produce it depend on the nature of the soap.

The colloidal viewpoint of soap is reviewed by W. Prosch (*Kolloid-Z.* 70, 106-8). It is stated that soap properties begin with eight carbon-chain fat acids; consequently, it is suggested that soap can be classified according to the molecular weight of the acids. M. P. Volarovich (*Kolloid-Z.* 71, 22-8) suggests some relations on the colloidal properties of rosin soaps are obtainable from the flow velocities (viscosities) of the soap solutions. According to E. Angelescu (*IX Congr. intern. quim. pura aplicada* 2, 506-17) the viscosity of 0.2N sodium stearate in mixtures of cresol and water shows a maximum viscosity at a cresol concentration of 1.3% attributed to colloidal dispersion with maximum solvation. With higher cresol content up to 10 per cent the curve approaches a straight line at low viscosity, attributed to molecular dispersion. Sodium palmitate alone does not show the maximum and tends to eliminate the maximum of viscosity when added to the stearate. Stearic acid added to sodium stearate-cresol mixture increases the maximum.

The influence of various electrolytes on the properties of sodium oleate solutions was investigated by N. Petrova (*Masloboino Zhirovoe Delo* 1935, 142-8). The lathering power and surface tension were decreased by 2 per cent salt or sodium carbonate on basis of soap, while acids affected this unfavorably. Emulsifying power is increased by either 2 per cent salt or small amounts of hydrochloric acid. Sodium silicate or trisodium phosphate have little influence at low concentrations. The hardness of the soap itself according to J. L. Bowden and R. Thomas (*Trans. Faraday Soc.* 31, 164-82) falls to minimum and thereafter increases with increasing concentrations of salt, sodium carbonate or sodium sulfate.

General discussions, historical treatments, recommendations promoting raw materials and new detergents excessively dominate the publications relating to soaps and detergents. Historical surveys

are submitted by M. H. Ittner (*Ind. & Eng. Chem.* 27, 756-8) and Miss A. Tiffany (*Amer. Druggist Jan.* 1935, 52-3, 112). Patents on soap articles are extensively reviewed by J. Rossman (*Soap* 10 [12] 25-7, 52; *ibid.* 11 [1] 25-7, 65; [2], 25-7, 53; [3], 27-9, 57). Other articles of general nature are noted in the various paragraphs which follow.

Continuous saponification methods are receiving much consideration. G. Bogdanov and E. Elisafova (*Masloboino Zhirovoe Delo* 10 [9 & 10], 3-6) obtained best results by simultaneous use of powdered sodium carbonate and a 40-45° Be. caustic liquor, the proportions of which are such that the excess alkali in the soap produced by the Bogdanov continuous method, consist of sodium carbonate alone. The soap produced is claimed to be soft and homogeneous. C. M. Adcock (*The Industrial Chemist* 11, 181-2, 190; *Brit.* 367, 513) saponifies in a continuous process at temperature of about 300° and at 800 to 1500 pounds pressure per square inch. The patent issued to Garbinton Ltd. and Johnson (*Brit.* 423,188) deals with a method of heating by electricity in the above type process. Proportioning devices for mixing the material in a continuous saponification process were invented by R. J. Short (*U. S.* 2,024,478; 2,024,479; and 2,024,480).

A great trend toward use of alkylolamines in the soap industry is displayed in the patent literature. E. I. du Pont de Nemours (*U. S.* 1,994,467 and *Brit.* 428,142) are assignees of patents which deal with preparing soaps by saponification of fat acids with an alkylglucamine such as methyl hydroxyethylglucamine, arabamine, mannamine, galactamine, etc. I. G. Farbenindustrie patents (*Brit.* 419,588; 420,883; 420,884; 420,903; and *Ger.* 612,686) claim preparation of wetting and emulsifying agents by reactions of glycidol with a primary or secondary amine containing at least one hydrocarbon of more than eight carbon atoms, or glycidol with carboxylic acid amide and/or sulfonic acid amide or glycidol with fat acid amine. The use of triethanolamine or its derivatives as an admixture to usual soaps is claimed with slight variations by R. Bushley (*Brit.* 424,977), J. Leben (*Brit.* 414,077), and L. Szigethy (*Hung.* 111,897).

Other detergents containing nitrogen were invented by H. Hunsdiecker and E. Voght (*Brit.* 426,508) who propose *o*-alkyl and *o*-aryl derivatives of isourea or its salts. A later invention by the same authors (*Brit.* 428,091) pertains to preparation of monoacyl derivatives of cyanamide for use as wetting agents. Imperial Chemical Industry Ltd. (*Brit.* 420,066; 420,137 and 420,518) obtained a series of patents on products formed by reacting special types of amines, dimethylolurea and fat acids or amino alcohols and acid amides with ethylene oxide.

I. Davidsohn (*Seifensieder Ztg.* 61, 325-8, 939-41, 961-2 and *The manufacturing chemist* 6, 228-31) discusses exhaustively the manufacture of cold process soaps and submits several formulas. Various tests indicated that the unsaponified fat, present in the soaps made by using less than the theoretical amount of caustic is probably not unchanged triglyceride but rather mono- and diglyceride; such soap can be worked up advantageously into good toilet soaps. The technic of using tallow in the cold soap process is described. Practical suggestions of coloring cold process coconut-oil soaps are given by Oculus (*Seifensieder Ztg.* 62 649-50). To makes such soaps buoyant F. W. Blumenthal (*Soap* 11 [7] 59-60) recommends and describes a technic using powdered metals which with alkali produce hydrogen.

A series of papers describing the various technics used in the manufacture of fine milled soap containing large amounts of hardened fat appeared in the German literature (Akter, *Seifensieder Ztg.* 62, 201; A. Beyrick, *ibid.* 241-2; O. E. Steuer, *ibid.* 263-4; E. Seibt, *ibid.* 284; K. *ibid.* 297-8 and J. Schall, *ibid.* 387-8). It appears that large proportions, up to 85% of hardened fats of low titer can be successfully used for making soap. The communications of H. Silman (*Soap* 11, [6] 59-61) and H. Kranich (*Soap* 11 [7] 21-23, 49) discuss the manufacture of powdered soap and that of C. A. Tyler (*Soap* 11, [10] 31-33) discusses floor scrub soaps from the standpoint of adopting a soap to meet the type of floor and the floor conditions. Shaving soap also received attention in the way of suggestions, formulas, etc., by R. H. Auch (*Soap* 11, [3] 23-5, 67) and Maso-

in (Seifen-Oel-u. Fett-ind. 21, 191); the latter author presents formulas for liquid soaps.

Several improving agents have been patented. K. Stickdorn (Ger. 613,224) claims that liquid soaps containing 45 per cent fat acids are obtainable if the product is made so that it contains about 15 per cent mono- or polyhydric alcohol and some potassium or ammonium salts of carboxylic acids such as oxalic, adipic, succinic, or tartaric. M. H. Jolivet (Fr. 778,000) adds benzoic acid to the soap to neutralize the free alkali liberated during washing. Soap is stabilized by Leben and Ormul Products Co. (Brit. 414,077) by additions of alkylamines, salts of benzoic, salicylic and like acids; and per Dabsch and Franche (Fr. 781,641) by adding glycerine or other water soluble alcohol and trisodium phosphate.

New superfatting materials are patented by S. Stiepel (Ger. 609,634), Henkel & Cie (Fr. 773,246) and E. I. du Pont de Nemour & Co. (Brit. 424,283 and U. S. 2,004,874). Use of ethyl and methyl esters of fat acids is claimed by Stiepel; the others use high molecular weight compounds having free hydroxyl groups. Tallow or coconut oil are considered unfavorable superfatting agents by J. Augustin (Mfg. Chem. 6, 77-8) because these on rancidification become irritating. Vaseline, beeswax, and lanoline are listed among the suitable agents.

Soaps soluble in hydrocarbons which assist in dry cleaning and help reduce formation of explosive vapors are known commercially as benzine or marseilles soaps. J. Grosser (Ceskoslovensky mydlar a vonavkar 11, 21, 35-6) obtains enhanced results by adding chlorinated hydrocarbons to the soaps during preparation. H. E. Wassel (Can. 345,664) prepares such soaps by joint saponification with hydroxyalkylamine and inorganic alkali. The resulting soap is dissolved in a substantially anhydrous solvent.

Considerable attention is devoted by A. R. Cade (Soap 11, [9] 27-30, 115) to the synergistic action of soap on the germicidal efficiency of phenols. The germicidal action of phenols increases with decreased pH. At pH of ten or in high concentration of soap the germicidal effect of phenols is nil. This information is substantiated by S. L. Malowan (Seifensieder-

Ztg. 62, 567-8) who in addition, states that no great increase in disinfecting power can be expected by use of soap containing phenols. H. O. Halvorson *et al.* (Soap 11 [5], 25-8, 109, 111, 113) investigated several disinfectants in order to discover a suitable one for use with detergents at pH of 9.0. Best results were obtained with a detergent made of a mixture of 1% sodium chlororthophenyl phenolate, 3% fused sodium silicate, 15% dry sodium resinate, 13% sodium hexametaphosphate, 10.5% sodium carbonate and 57.5% sodium bicarbonate. Miss M. J. Hausman (Soap 11 [9], 23-6, 59) recommends a pure coconut oil soap as an antiseptic because it combines good germicidal activity with detergent properties. Methods of preparing germicidal soaps containing finely divided silver are patented by L. Latzin (Ger. 609, 336) and W. Schulenburg (U. S. 1,993,686). A review on the disinfectant and medicinal soaps is presented by P. Martell (Allgem. Oel- u. Fett-Ztg. 32, 366-8).

The tendency of some soaps to irritate the skin is attributed by Welwart (Seifensieder-Ztg. 62, 667-9) to removal of naturally occurring fats and oils. Means of obviating such deleterious effects is the addition of lecithin according to K. Braum (Dtsch. Parfum-Ztg. 21, 238 and Fettchem. Umsch. 42, 193) or by addition of glycerol or lanolin as per T. Ruemele (Allgem-Oel-u. Fett-Ztg. 32, 101-3). Special soaps for the care of the face are discussed with recommendations by J. Augustine (Parfumerie moderne 29, 105-13). D. H. Bothrill (U. S. 2,007,107) combines a soap with a massage article by unbedding a rubber facial massage device in a bar of soap.

Processes following the saponification are continually being improved. Methods of drying soap by spraying in a drying atmosphere are described by D. N. Snurnov, *et al.* (Lesokhimitskaya Prom. 3 [1-2] 24-6), F. E. Hall (U. S. 1,985,987) and E. F. van Suchtelen (Brit. 417,449). A. Welter (Ger. 606,366 Cl. 23a) mixes the liquefied soap with one or more salts and the mixture is extruded through nozzles to form filaments of less than 1.5 mm. in diameter. The filaments become brittle when cooled and dried and can be broken up into small rods. To obtain transparent soap containing a high per cent of fat

acids W. Pape (U. S. 2,005,160) makes use of special cooling process by which the soap is quickly cooled to prevent crystallization. J. W. Bodman (U. S. 2,005,333) invented a soap finishing apparatus by use of which a more homogeneous soap mass is obtained. Equipment for cooling soap is patented by A. O. Hurxthal (U. S. 1,994,360) and R. R. Bottoms and W. R. Wood (U. S. 2,013,025). Methods for increasing the buoyancy of soap have been proposed by J. S. Stone (U. S. 1,997,474) Mousson & Co. (Ger. 611,045) and L. F. Wilcox (Australia 14,431; 14,432 and 14,433). The method of Stone pertains to mechanical means, while the latter two are of chemical nature, *i.e.* respectively, use of powdered silicon to produce hydrogen gas, and use of hydrogen peroxide which liberates oxygen gas.

Since the soap-makers were forced to find cheaper raw materials an increasing amount of literature on soap constituents has appeared. C. Stiepel (Seifensieder-Ztg. 62, 138) suggested that technical stearic acid can be substituted for tallow in the manufacture of high grade soft soaps. The difficulties encountered on attempting to prepare soap from some technical soy bean oil fat acids are discussed by Welwart (Seifensieder-Ztg. 62, 504-5). "Tall oil," a by-product resin oil of the paper industry, when made into soap is claimed by A. Lamanovich and N. Tretyakova (Masloboino Zhirovoe Delo. 11, [12], 39-41) to have good foaming and emulsifying power. It is suggested that up to 25% of this product can be incorporated in household soaps. M. Petrov (Maslobinon Zhirovoe Delo. 11, 150) tabulated analysis of several pine gums, the intention being to promote their use in soap making. G. H. Hogg (OIL AND SOAP 12, 44-7) argued that wood rosin produces better soap than gum rosin from the standpoint of appearance and stability of the finished product. Soap containing up to 80% pine oil is prepared by J. Mehme (Ger. 616,029 Cl. 23e) by saponifying with excess solid alkali and finally neutralizing the excess with fat acids. A novel source of raw material is the benzene extract of air dried peat described by Roginskarja (Russ. 34, 675).

Important advances were made in utilizing petroleum products.

C. Ellis (U. S. 1,999,184) obtains advantages in saponification of oxidation products of hydrocarbons by using limited amounts of water. The Colgate-Palmolive-Peet Co. (Brit. 423,279) saponify without adding water. Heating and stirring are accomplished by high pressure steam, which also serves to remove the unsaponifiable. On the other hand I. G. Farbenind. A.-G. (Fr. 779,843) use a caustic solution to saponify paraffin oxidation products dissolved in water—immiscible solvents; advantages are claimed because the water layer takes up the soap, while the unsaponifiable and impurities remain in the water-immiscible layer. A. Deumshitz (Masloboino-Zhirovoe Delo. 11, 260-1) offers suggestion for removing resinous and asphaltic impurities from the naphthenic acid used in soap making. Distillation, evaporation and salting out processes are described. The common mineral-oil soaps are listed under their trade names with brief descriptions and definitions by T. Ruemele (Allgem. Oel-u. Fett.-Ztg. 32, 87-9).

Among the non-soap adjuncts the sodium silicates received most attention. A. Foulon (Allgem. Oel-u. Fett.-Ztg. 31, 483-5 and Seifensieder-Ztg. 62, 298-9, 321-2), I. Davidsohn (Seifensieder-Ztg. 62, 63-9), W. Prosch (Seifensieder-Ztg. 61, 938-9), C. Bergell (Seifensieder-Ztg. 62, 13-15) and V. Savvina (Masloboino Zhirovoe Delo. 11, 258-60) all emphasize the advantage of using water glass in soaps. Of the carbohydrates, K. Braun. (Seifensieder-Ztg. 62, 586-7) recommends starch; Khorassany (Austrian 138,923) uses agar, tragacanth and other gums; alkali salts obtained with oxidized starch, dextrin, hydrocellulose and the like have detergent properties according to the patent issued to Janser (Austrian 140,042); sulfited celluloses are added to the soap prepared by Zartler (Hung. 112,640) and in like manner van der Werth (Ger. 594,499) adds wood pulp to the raw materials for saponification. L. Ivanovo (Masloboino Zhirovoe Delo. 10 [9-10], 15-7) discloses that since bile and pancreatic enzymes exert a powerful hydrolytic action toward starch, they may find applications in the preparation of detergents or emulsifiers. Gelatine, albumin degradation products or synthetic polypeptides are con-

densed with cetyl chlorocarbonate or fat acid chlorides to form wetting agents according to the respective patents of I. G. Farbenind. A.-G. (Brit. 425,370) and F. Sommer (U. S. 2,015,912). Bonzli (Swiss 171,729) finds it economical to add fine saw dust or ground marble to soap. Technic for manufacture of powdered soap containing sodium silicate is described in patents issued to Swann Research, Inc. (U. S. 1,989,759 and 1,989,765). Caustic soda and sodium silicate are kneaded to a plastic mass, cooled to a solid product, disintegrated and covered with fat acids by spraying. The variation in the patents deals with addition of tri-sodium phosphate and treatment with chlorine gas before coating with fat acids. A detergent formula patented by Henkel and Cie (Brit. 428,961) contains a combination of alkalimetaphosphates, soap, modified soda and peroxide compounds. R. R. Fabregas and J. M. Ostheim (Swiss 172,342) find additions of sodium acid sulfate and sodium carbonate to soap will increase the foaming properties by releasing gas when in contact with water.

The characteristics of sodium hexametaphosphate and sodium sesquisilicate in regard to their detergent action and preparations are treated in the respective communications of B. H. Gilmore (OIL AND SOAP 12, 29-32) and C. H. Jeglum (Soap 11 [2], 31, 63-5). R. Hart (Am. Silk Rayon J. 54, [3], 40-2, 59, 60-1) finds pyrophosphates act similarly to metaphosphate but in a different degree. The former is less effective in dispersing lime soap but superior for magnesium soap. The effect of the alkaline detergents, *i.e.* carbonates, phosphates and silicates, on metals was studied by C. L. Baker (Ind. & Eng. Chem. 27, 1358-64). A considerable amount of data on several metals is presented. The silicates of soda impaired the surface of metals less than the other alkalis considered with exception of sodium carbonate solutions toward zinc. Among the sodium silicates themselves, an increasing ratio of silica to sodium oxide seems to give greater protection.

Technic for recovering glycerol in soap making is submitted by L. Klepikov and M. Irodov (Masloboino Zhirovoe Delo. 11, 262-3). In concentrating glycerol solutions M. Zaliopo (Masloboino

Zhirovoe Delo. 11, 260-1) eliminates scale formation by adding .005 per cent graphite to the charge.

Analysts have been active toward improving methods for analysis of soap and soap materials. A simple test for the probability of a fat to produce green soap is devised by C. P. Long and H. P. Stevenson (OIL AND SOAP 12, 7-8) who heat a sample of the fat containing a copper sheet at 110-5° for one hour; the color of the chilled sample indicates the color of the soap that may be derived from the original sample. On the other hand, J. A. Skogstrom (Can. Chem. & Met. 18, 274-5) maintains that the surest way is to make a small test sample of soap and note the color. Miss M. J. Hausman (Soap 11, [4], 21-4, 67, 69) recommends testing for oxidized acids and cold petroleum ether insolubles as the surest means of disclosing the soap making quality of olive oil foots; the latter test is claimed to be the most important. The same tests are proposed by C. Stiepel (Seifensieder-Ztg. 62, 161-3) for evaluation of the still residues from fat acid distillation processes.

The wetting and spreading properties of aqueous soap solutions can be evaluated by the visual test of H. L. Cupples (Ind. & Eng. Chem. 27, 1219-22). A drop or two of mineral oil is placed on a level sheet of celluloid and spread to a thin film; a drop of the aqueous soap solution placed on this will spread only if the spreading coefficient is positive with reference to the oil.

The rate of dissolution of soap may be characterized by two new methods. E. Sauer and W. Burch (Angew. Chem. 48, 171-4) pass a stream of water at fixed temperature and velocity over a standard portion of the soap surface and titrate a definite amount of the water solution to determine the amount of soap dissolved. The method of C. Stiepel (Allgem. Oel-u. Fett.-Ztg. 32, 63-5) accomplishes the same aim by hanging a linen bag containing a standard cake of soap in a small churn; churning under set standards of time, temperature, speed and amount of water. The soap dissolved is measured by acidifying the solution and measuring the volume of fat acids. A measure of the foaming power of the soap is also obtainable by noting the

amount of foam after the stirring is complete.

Several disputes have arisen in regard to the determination of free alkali in soap and soap solutions. This is because of various factors which seem to complicate the analytical methods making usual direct titrations or pH determinations inconclusive. Vizern and Guillot (14 me. Congr. Chim. ind. Paris Oct. 1934 and Ann. chim. analyt. 16, 446-9) investigated the pH and alkali relation in soap solutions and proposed procedures for determining free alkali. At equal concentrations the pH increases with the molecular weight, and with equal molecular weight the pH increases with the melting point of the fat acids. The pH can remain constant or vary but slightly for appreciable variations of free alkali; it therefore follows that the effects produced by soap solutions on the skin or on fabrics are not dependent on the pH. The method of analysis described is carried out by decomposing the soap with excess sulfuric acid, measuring the excess sulfuric acid and separately titrating the fat acids; the difference equals free alkali; or alternatively one may dissolve the soap in ethyl alcohol containing a quantity of fat acids; after saponifying the free alkali, the remaining free acids are titrated and the amount of free alkali calculated from results. B. Tyutyunikov and N. Kas'yanova (Masloboino Zhirovoe Delo. 11, 312-6 and Allgem. Oel- u. Fett.-Ztg. 31, 276-9) postulated that certain component parts of dilute soap solutions adsorb various substances including OH-ions and fat acids and convert them into different types of compounds. Hence hydrolysis of neutral soap and the resultant quantity of free alkali in dilute solutions are greater than can be calculated. W. Poethke (Fettchem. Umsch. 42, 180-90, 197-201) and I. Davidsohn (Rayon and Melliand Textile Monthly 16, 23-4, 83-4) review the existing analytical procedures for determining free alkali in soap and report their own investigations. When using propyl alcohol as a solvent Poethke finds the amount of hydrochloric acid necessary for titrating the free alkali is less than when ethyl alcohol containing sodium sulfate is used as the solvent; the titration is still smaller if sodium sulfate is added to the propyl alcohol.

Hence it is argued that the carbonates are less soluble in propyl alcohol and that in the determination of free alkali according to Davidsohn some carbonates are titrated. It is suggested that propyl alcohol is the most suitable solvent for exact determinations. J. Hetzer (Fettchem. Umsch. 42, 87-8) states that analysis for free alkali as control in soap making can be obviated if technicians would recognize the fact that excess alkali can be prevented with accurate control of reacting ingredients and the time of complete reaction reduced by referring to saponification velocity charts to ascertain complete reaction rather than making tests for such. A method for determining speed of saponification is presented, with data obtained on several oils.

J. R. N. van Kregten (Chem. Weekblad 32 81-3) reports a method for analysis of perborates in soap. Since the perboric acid is stable in acid solution, he recommended hydrolyzing the soap with sulfuric acid, removing fat acids by extraction with chloroform and titrating the aqueous layer with standard potassium permanganate solution. The iodometric methods are less suitable.

Soapless detergents obtained by the action of sulfuric acid on various fatty materials, have increased in production and diversifiability of use. Formerly they were only important to the textile industry; although this is the largest outlet for these products, they are by no means limited to use in that industry, for increased interest, improvements, and promotion have extended the applications. The properties of the products are recently discussed in lectures by R. J. Hannay (J. Soc. Dyers Colourists 50, 273-82), A. H. Grimshaw (OIL AND SOAP 12, 8-10) and R. A. Pingree (OIL AND SOAP 12, 182-6). These lectures deal principally with the textile uses. Current technic with review of patents on preparing these compounds from various raw materials are well reviewed with extensive descriptions by A. E. Sunderland (Soap 11, [10], 67-4); [11] 61-4, 71 and [12] 67-9) and briefly reviewed by E. H. Kadmer (Seifensieder-Ztg. 62, 180-3, 207-9).

The differences in the sulfur-containing detergents are sufficient to merit several comparative investigations. L. Szegoe (Giorn.

chim. ind. Applicata 16, 533-7 and Rev. gen. mat. color 39, 350-6) contends detergent power of sulfonated products is maximum at sixteen carbon atoms. Below and above this figure the effectiveness decreases. E. Franz's (Melliand Textilber 16, 277-82) investigations demonstrated no difference in efficiency of several commercial samples in solutions of various pH. Exception to this work was made by K. Lindner (Melliand Textilber 16, 436-7) who contends that the most recently developed sodium sulfated cetyl alcohol is not decomposed by boiling in dilute acids as is the sodium sulfated cetyl alcohol and hence is more efficient. The efficacy of the various products differs in dispersing action on insoluble soaps as is demonstrated by K. Lorenz (Monatschr. Textil-Ind. 49, 208) and I. K. Lindner (Monatschr. Textil-Ind. 50, 65-6, 94-5). Some are more efficient in regard to calcium soaps, while others are most effective with magnesium soaps. The relative value of sodium hexametaphosphate and "Igepon T" for dissolving calcium soaps is compared by G. Schwen and H. Kuckerty (Dyer 74, 117-8). The sulfonated product is better because of its superiority to the other when used in small amounts. Substitution of the new washing agents in regular household wash is regarded unthinkable by F. Ohl (Allgem. Oel-u. Fett.-Ztg. 32, 14-7) because they do not surpass soap for cleaning heavy soiled material; the advantages for special use is admitted principally, the washing and cleaning of finer textiles such as are quickly washed in the household and which have not been heavily soiled. Welwart (Seifensieder-Ztg. 61, 639-41) finds that the use of alcohol sulfonates in shampoos is attended with serious difficulties. Suggestions are made as possible means for making the customary soap shampoos suitable for use in hard water. Improvements in detergent action of the sulfated alcohols with addition of phosphate salts is claimed by W. J. Tennant (Brit. 431,682).

The action of several sulfonated agents on castor oil at various temperatures was investigated by K. Winokuti and associates (J. Soc. Chem. Ind. Japan 38, 25-7B, 27-30B, 31-32B). In most cases, except with concentrated sulfuric acid alone, when the castor oil is

treated with fuming sulfuric or other strong sulfonating reagents without dehydrating catalyst, a certain amount of acid product can be separated which is insoluble in acetone and not decomposable by boiling with hydrochloric acid. When low temperatures are employed, sulfonation occurs with less hydrolysis of glycerides. Data indicating most favorable conditions for maximum combination with sulfuric acid are graphically presented. Like data for sunflower seed oil are submitted by C. Otin and M. Dina (J. Intern. Soc. Leather Trades Chem. 19, 443-54). Formation of iso-oleic acid during the sulfonation can be reduced according to the report of C. Riess (Collegium 775, 566-8), by carrying out the process at lower temperatures and with use of sulfuric acid equal to 40 per cent of the oil. This is important to the leather industry from the point of view of spewing. K. Lindner and A. Russe (Ger. 607,018 and 611,443, Cl. 12o) render the sulfonation action of halohydrins of sulfuric acid milder by treating the oils with benzene and dehydrating agents; this results in better products.

New method of producing sulfonates were patented. K. Ott and G. Mauthe patent (U. S. 2,023,769) relates to sulfiting the unsaturated acids with sulfurous acid and oxidizing to sulfate. A. W. Baldwin and H. A. Pigott (Brit. 435,039) convert aliphatic hydroxy sulfides, into sulfuric esters by reacting them with an addition product of sulfur trioxide and a tertiary amine. The patent of C. Flesch (Ger. 564,759) using acetic and other low molecular weight fat acids in the production of sulfonates of high sulfur content is supplemented by a subsequent patent (Ger. 617,347) so that the inventor can also claim the anhydrides of these acids.

The new apparatus of W. Wenzel (Ger. 608,692) allows more efficient sulfonation of fats and oils at very low temperatures.

The sulfonated esters are separated from the excess sulfuric acid according to the patent of Chemische Fabrik Stackhausen & Cie (Ger. 614,702), by extracting with organic solvents. Sulfonated neats-foot oil which successfully stands cold is prepared, per patent of E. Mezey (Ger. 608,

693), by sulfonating the oil in carbon tetrachloride solution.

The conversion of fat acids to alcohols is being actively investigated as a result of the increasing demand for these raw products. The catalytic autoclave process is described by Sei-ichi Ueno and associates (J. Soc. Chem. Ind. Japan 38, 279-82B, 482-6B). The Imperial Chemical Industries (Brit. 433,549) accomplish this by hydrogenating fat acids. W. H. McAllister (U. S. 2,022,894) obtains the alcohols by electrolysis of the fat acid salts.

Mixing aliphatic alcohols with aromatic phenols or ketones before sulfonation results in creating advantages according to K. Lindner (Ger. 609,456). The production of good sulfonated products from tertiary alcohol is claimed by Henkel and Cie (Brit. 424,891; 429,036 and Fr. 778,373). The sulfonation of cyclohexylcyclohexanol or homologs was novel enough to allow issuance of patent to J. W. Blagden and G. C. H. Clark (Brit. 425,239).

The sulfonic esters of mineral oil fractions are sufficiently important to foster delving into these raw materials by several inventors. A product capable of being sulfonated is produced by W. Schrauth (U. S. 2,000,994) from naphthenic acid by reduction with carbon monoxide or hydrogen in presence of nickel. I. G. Farbenind. (U. S. 2,014,502) and Oranienburger Chem. Fab. (Ger. 616,321) are successful in using mineral oil fractions as a raw material by mixing them with high molecular weight aliphatic alcohols or acids before sulfonation. The Standard Oil Development Co. (Fr. 783,319) improve the paraffin hydrocarbons intended for sulfonation by cracking in a manner to produce unsaturated products of more than six carbon atoms, without appreciable formation of polymers. K. Lindner (Fr. 782,280) and A. Beyer (Fr. 782,612) prepare sulfonates from fat acid esters of phenolic compounds.

Polymerizing oils are capable of being sulfonated by two recent methods. Soc. pour l'ind. Chim. a Bale (Brit. 430,038 and Swiss 166,789; 169,563) treat the oil with resorcinol before reacting with the acid. M. De Groote and B. Keiser (U. S. 2,020,998 and 2,020,999) blow the oils at 150-250° C., followed by heating to 330° before sulfonation. This

is especially applicable to sardine oils.

Several other means of making raw materials more adaptable for sulfonation into satisfactory products have been proposed. H. Bertsch (U. S. 2,007,492) obtains improved results if the unsaturated fat acids are first converted into polybasic acids. C. Flesch (Fr. 782,332) transforms the raw materials into amides and condenses them with disulfonic acid aldehydes. Pine oil is mixed with o-chlorophenol before sulfonation per patent of Soc. pour l'ind. Chim. a Bale (Swiss 169,923). Oranienburger Chem. Fab. (Ger. 616,055) prepare sulfonated compounds from the halogenated fats or fat acids. L. Orthner and H. Keppler (U. S. 2,002,613) prepare the hydroxyalkyl amide of coconut fat acids and treat the resultant product with ethylene oxide before sulfonating. Henkel & Cie's patent (Brit. 428,153) also pertains to sulfonation of acid amides. The Carbide & Carbon Chem. Corp. (Fr. 782,835) condense various raw materials with ketones before sulfonation; on the other hand, H. Flesch, C. Flesch, and L. E. Abelman (Brit. 425,942) sulfonate with ketone di- or poly-sulfonic acids. I. G. Farbenind. A.-G. (Brit. 420,897) react glycide with fat alcohol in presence of sodium hydroxide as a catalyst and sulfonate the product. S. Schrauth and R. Hueter (U. S. 2,014,782) sulfonate alkyl glycols such as may be obtained from sperm oil. C. C. Clark (U. S. 2,006,309) reacts fat acids with one of the free hydroxyl groups of 1, 2 dihydroxypropane sulfonic acid.

Analytical methods for sulfur-containing detergents are reported by R. Hart (Am. Dyestuff Reporter 24, 284-93 and Ind. & Eng. Chem. Anal. Ed. 7, 137-40), C. Reiss (Collegium 1934, 644-7), S. Swindells (Dyer 73, 120-1) and T. M. Biffen and F. D. Snell (Ind. & Eng. Chem. Anal. Ed. 7, 234-7).

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