Solubility of Tin Ricinoleate in Solvents

A. MÉRZ, Plastic Division, Oil and Chemical Works Ltd.,
Hausen near Brugg, Switzerland

LITTLE or no information has been published (1) on the properties of metallic ricinoleates. Contrary to the well known metallic soaps (aluminum, zinc and calcium stearate, lead, cobalt, manganese, and copper naphthenate), the salts of ricinoleic contain an hydroxyl group on the 12th carbon atom of the ricinoleic acid, which may have a considerable influence on the solubility.

In a recent issue of this Journal (2) has been published a paper on the solubility and swelling of metallic ricinoleates in various solvents. It was found that among five soaps examined [aluminum (tri), barium, calcium, magnesium, and zinc] the salt of magnesium shows the best solubility, followed by the salt of calcium. Aluminum (tri) and magnesium ricinoleate give clear mixtures of soap/solvent whereas the other four soaps generally give transparent mixtures only.

In connection with this study we have investigated the solubility of tin ricinoleate in the same manner. Characteristics may be described thus:

> Tin ricinoleate, the salt of bivalent tin, is a viscous liquid of slightly brownish color and with very little odor. Starting from pure ricinoleic fatty acid, theoretically the contents of tin would amount to 16.6%. For a technical product, like that used, the contents of tin was found to be 12-14%. The technical data are as follows:
>
> Specific gravity at 20°C.—about 1.112
> Refractive index at 20°C.—about 1.504
> Viscosity at 20°C.—4,000-7,000 cp.
> Flash point (Marcusson)—165°C.

The suggested field of application for tin ricinoleate is for use as a heat and light stabilizing agent in halogenized polymers (3, 4).

The stabilizing effect is limited to certain special resins. Small additions to plastisols increase noticeably the thixotropic properties. For processing, tin ricinoleate is very useful as a sliding and lubricating agent for calandery.

Summary

Among the salts of ricinoleic acid available [aluminium (tri), barium, calcium, magnesium, zinc, and tin] the salt of tin shows the best solubility, in polar as well as in non-polar solvents (with the exception of glycols).

TABLE I

Solubility of Tin Ricinoleate in Solvents

Solvents Class		Product	Tin-Ricinoleate Weight % 20	40	60	80
Hydro-carbons	Aliphatic	Mineral Spirits	+	+	+	+
		White Spirit	+	+	+	+
	Aromatic	Xylene	+	+	+	+
Terpenes		Turpentine	+	+	+	+
Alcohols		Butanol	+	+	+	+
		Diacetone Alcohol	—t	+	+	+
Glycol		Propylene Glycol	—	—	—	—
Ketones		Acetone	+	+	+	+
		Cyclohexanone	+	+	+	+
Esters		Butyl Acetate	+	+	+	+
		Dioctyl Phthalate	+	+	+	+
		Methyl Acetyl Ricinoleate	+	+	+	+
Ether Alcohol		Methyl Cellosolve	+	+	+	+
Chlorinated Solvents		Carbon Tetrachloride	+c	+c	+c	+c
		Trichloroethylene	+c	+c	+c	+c
Solvent Mixture		80 Toluene/20 Ethanol	+	+	+	+
Vegetable Oils		Castor Oil	+	+	+	+
		Linseed Oil	+	+	+	+
		Dehydrated Castor Oil	+	+	+	+
Varnish		DCO-Pentalyn G	+	+	+	+

Coding: + transparent clear yellow solution.
t translucent yellow.
c cloudy.
— no significant solubility of metallic soap in hot solvent.

In the case of diacetone alcohol the diacetone alcohol is soluble in tin ricinoleate, but not *vice versa.*

All the viscosities of the soap/solvent mixtures are according to the viscosities of the solvents. Normally there are no separations in phases, no swelling or thixotropic phenomena.

REFERENCES

1. Doss, M. P., "Properties of the Principal Fats, Fatty Oils, Waxes, Fatty Acids and Their Salts," The Texas Company, New York, N. Y.
2. Patton, T. C., and Lindlaw, W. J., J. Am. Oil Chemists' Soc., *30,* 331-335 (1953).
3. Chertoff, G. J., Curtiss, G. B., and Caldwell, S. S., U. S. 2,629,700 (1953).
4. Furter, F., Kunststoffe, *43,* 189-191 (1953).

[Received August 9, 1954]

ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
R. L. Broadhead, Abstractor
Sin'itiro Kawamura, Abstractor

Extraction of oil by solvents at elevated temperatures. II. A. G. Antonioli and R. Turriziani (Univ. Rome). *Ann chim.* (Rome) 43, 839-44 (1953). The extraction of oil from olive pulp with ligroine (b. 80-120°) was more efficient at temperatures above 60° than at lower ones.

Refining of black cottonseed oil by an emulsification method. D. M. Bortovoĭ and M. P. Salganskiĭ (Fat Combine, Gorki). *Masloboĭno-Zhirovaya Prom.* 19(3), 34-5 (1954). Description with diagrams of an emulsifier is given for refining black cottonseed oil, utilizing essentially the treatment scheme of Sergeev and Sterlin (*C. A.* 47, 8391). Best results were obtained when the black cottonseed oil was emulsified with 58-67% lye solution. Some batches of oil with high acid no. required as much as 150% excess of alkali, while others were not clarified when even 300% excess was used. (*C. A.* 47, 9719)

Solvents for the extraction of oil from kamala seeds. S. C. Gupta and J. S. Aggarwal(Natl. Chem. Lab. India, Poona). *J. Sci. Ind. Research* 12B, 545-7(1953). Ground kamala kernels were twice extracted in a Soxhlet apparatus, regrinding between the extractions. Et_2O, EtOAc, and C_6H_6 were efficient solvents; petroleum ether, acetone, C_2HCl_3 and CCl_4 were not. The most economically available solvent in India is C_6H_6, but the oil extracted with this solvent has a poor keeping quality. A better-keeping oil is extracted with petroleum ether; this process can be followed by extracting residues with C_6H_6 to recover all the oil. (*C. A.* 48, 7917)

Addition of hydrogen cyanide to unsaturated compounds. P. Arthur, Jr., D. C. England, B. C. Pratt and G. M. Whitman (Chem. Dept., Experimental Station, E. I. du Pont de Nemours, Wilmington, Del.). *J. Am. Chem. Soc.* 76, 5364-67(1954). The addition of hydrogen cyanide to unactivated carbon-carbon double bonds has been accomplished by the use of dicobalt octacarbonyl at 130° in sealed vessels. Best results were obtained with compounds of the type $RCH = CH_2$, where R is hydrogen, phenyl or an alkyl group, with conjugated dienes, and with Diels-Alder adducts of cyclopentadiene.

Electrophoretic movement of higher fatty acids on filter paper. A. J. G. Barnett and D. K. Smith(Div. of Ag. Biochem., Dept. of Biological Chem., Univ. of Aberdeen, Scotland). *Nature* 174, 659-60(1954). The present work deals with the movement of straight-chain acids from C_{10} to C_{18} in ammonia solution, on paper, in a closed vessel under electrophoresis, and it has been shown that the observed rates of movement, under 6 V./cm., for the C_{10}, C_{12}, C_{14}, C_{16}, C_{18} acids were, respectively, 4.5, 1.5, 0.33, 0.07 and 0.0017 cm./hr.

Analysis of high molecular weight alcohols by the mass spectrometer. The wax alcohols of human hair fat. R. A. Brown and W. S. Young(The Atlantic Refining Co., Philadelphia, Pa.) and N. Nicolaides. *Anal. Chem.* 26, 1653-54(1954). High molecular weight alcohols separated from hair oil have been analyzed by high temperature mass spectrometry. Spectra of C_{16} to C_{27} straight-chain alcohols were identified. Alcohols having an even number of carbon atoms were present in significantly greater quantity than the adjacent odd homolog. Pure compounds in the C_{10} to C_{34} range were used as calibration standards.

Deteriorative changes in the oil fraction of stored parboiled rice. D. F. Houston, I. R. Hunter, Elizabeth A. McComb, and E. B. Kester(Western Utilization Res. Branch, Agricultural Res. Service, U.S.D.A., Albany 6, Calif.). *J. Agr. and Food Chem.* 2, 1185-90(1954). Changes in the oil fraction of stored parboiled rice have been followed as criteria of loss in quality. Storage of parboiled rice in the dark at several temperatures permitted a study of rancidification and of nonenzymatic changes in the oil as measured by peroxides, monocarbonyl compounds, and free acids. In open-container storage, values for peroxides, monocarbonyls, and free acids remained low during an induction period, then rose markedly at or just before the time rancid odors appeared. Peroxides and monocarbonyls again decreased to low residual values and rancidity disappeared.

Flavor origins. Review of chemical mechanisms affecting flavor acceptability of dairy products. D. V. Josephson(Penn. State Univ., State College). *J. Agr. and Food Chem.* 2, 1182-85 (1954). Milk is a complex biological fluid which spontaneously undergoes chemical change under a variety of conditions. Heat, light, air, agitation, trace metal contamination, and microorganisms are a continuous threat. Frequently the only measurable manifestation of these chemical reactions is change in flavor or odor. They involved photolysis of methionine in milk, responsible for the ''sunlight'' flavor; heat denaturation of β-lactoglobulin, causing ''cooked'' flavor; decomposition of lactose and formation of furan compounds, associated with ''caramelized'' flavor; and secretion of acetone bodies causing ''cowy'' flavor.

Determination of fat peroxides in the presence of phospholipids. L. Hartman(Fats Research Lab., Dept. Scientific and Industrial Research, Wellington, New Zealand). *J. Sci. Food Agr.* 5, 476-81(1954). Details of a method are given for the determination of peroxides in fats extracted from tissues by a 7:3 mixture of benzene and methanol. Phospholipids do not interfere. Peroxides are reduced with ferrous chloride in benzene-methanol solution and the amount of ferric ion produced is estimated colorimetrically after reaction with 2,6-dichlorophenolindophenol and pyrophosphoric acid. Results of analysis of fats from several meat and fish tissues by this method are compared with results using the ferric thiocyanate method.

Chemical investigation of seed oil of Sesbania aegyptica. M. O. Farooq, M. S. Ahmad and M. A. Malik(Dept. Chemistry, Muslim Univ., Aligarh, India). *J. Sci. Food Agr.* 5, 498-500(1954). *Sesbania aegyptica* seed oil was hydrolyzed and the fatty acid mixture was analyzed by the lead soap, bromination, thiocyanogen, Bertram oxidation and methyl ester fractionation methods. The composition was calculated to be (as per cent): oleic 24.4; linoleic 36.3; linolenic 10.9; palmitic 9.0; stearic 17.5; and lignoceric 1.9.

Review of work on soybean lecithin at the Peoria laboratory. J. C. Cowan(Northern Utilization Research Branch, Peoria, Ill.). *Soybean Digest* 14(12), 14-16(1954). Annual production data for soybean phosphatides over the period from 1947-1953 show a steady increase as a result of decreased cost and improved quality of the phosphatides. Work on the fractionation of these materials is reviewed briefly. Color is due to (1) carotenoids which are decolorized by peroxide treatment, and (2) brown materials which are formed in the miscella, go with the phosphatides on degumming, and are not removed by peroxide treatment. Since the brown color is apparently formed at high temperatures, if a light colored phosphatide is desired, low temperatures during all stages of processing seem advisable.

Surface and interfacial tensions of synthetic glycerides of known composition and configuration. Ruth R. Benerito, W. S. Singleton and R. O. Feuge(Southern Regional Res. Lab., New Orleans, La.). *J. Phys. Chem.* 58, 831-4(1954). Surface tensions against air at various temperatures between 20° and 100° and interfacial tensions against water at 25° and 75° are reported for triacetin, tributyrin, tricaproin, tricaprylin, tripalmitin, tristearin, triolein, trielaidin, trilinolein, 1,2-diaceto-3-olein, 1,2-diaceto-3-stearin, 1,3-dioleo-2-palmitin and tripelargonin. Surface tensions of 1-monostearin, 1-monopalmitin, and 1,3-dipalmitin are also given. Changes in enthalpy and entropy of surface formation are calculated. For the simple triglycerides containing an even number of carbon atoms, the variation of enthalpy and entropy changes with number of carbon atoms is shown graphically; a minimum appears at about six carbon atoms. The effect of unsaturation, *cis-trans* isomerization, and degree of esterification on these properties are discussed.

Suggest specific definitions for raw and acidulated soap stock. *Soybean Digest* 15(1), 18-19(1954). Recommendations of the Association of American Soap and Glycerine Producers, Inc. for additional grades of raw and acidulated soap stocks (particularly, soybean and cottonseed) are discussed. Suggested definitions emphasize analyses for total fatty acids, oxidized fatty acids, iodine value of total fatty acids, and pH.

The component acids and glycerides of areca-nut (Areca Catechu) fat. S. P. Pathak and S. S. Mathur(Dept. Indus. Chem., Banaras Hindu Univ.). *J. Sci. Food Agr.* 5, 461-5 (1954). Fatty acid composition was determined by fractionation of methyl esters. Glyceride structure was studied by crystallizing the neutral fat from acetone and ether; the fractions were then analyzed by the lead salt and methyl ester fractionation methods. Areca-nut fat contains the following percentages of fatty acids: lauric 19.5; myristic 46.2; palmitic 12.7; stearic 1.6; decanoic 0.3; oleic 6.2; linoleic 5.4; dodecenoic 0.3; tetradecenoic 0.6; hexadecenoic 7.2. The fat consists of 56% of fully saturated glycerides, 30% of monounsaturated-disaturated glycerides, and 14% of monosaturated-diunsaturated glycerides which were identified as trimyristin 4.8% dimyristolaurin 21.8; dimyristopalmitin 18.5; lauromyristopalmitin 11.2; hexadecenolauromyristin 23.5; oleomyristopalmitin 3.5; linoleomyristopalmitin 2.0; hexadecenodimyristin 0.9; oleodimyristin 0.1; oleolinoleolaurin 1.9; oleolinoleomyristin 1.9; and oleolinoleopalmitin 9.9.

Metal ion - monolayer interactions. The effect of uranyl nitrate on myristic acid monolayers. J. G. N. Thomas and J. H. Schulman(E. Oppenheimer Lab., Dept. Colloid Science, Univ. Cambridge). *Trans. Faraday Soc.* 50, 1128-30(1954). Force-area curves were determined for monolayers of myristic acid on $M/2000$ uranyl nitrate over the pH range from 3.0 to above 6. No interaction between the monolayer and substrate was apparent at pH 3.0, but above pH 3.2 the transition pressure of the film was raised and was accompanied by a condensation of the liquid-expanded region. Above pH 3.9, the monolayer showed no transition region. In the pH range 3.9 to 4.6, condensed liquid films stable up to pressures about 40 dynes/cm. were obtained. At more alkaline pH values, films were less stable, and above pH 6 dissolved rapidly. The monolayers were liquid at all pH values although at high pressures (40 dynes/cm.) they became gel-like. These effects are shown to be consistent with the formation of monolayer soaps of uranyl ion and its hydrolysis products. Caproic acid and 2-ethyl-hexoic acid at concentrations greater than $10^{-4}M$ gave good flotation of pitchblende over the pH range 2.8 to 6. This result suggests that hydrogen bonding is of secondary importance in attaching the fatty acid to the mineral surface.

Monolayers of sodium cetyl and their interaction with polyvalent metal ions. *Ibid.*, 1131-9. Force-area curves for monolayers of sodium cetyl sulphate were determined on substrates of varying ionic strength and pH, including 0.01-3 N NaCl, 0.001-1.0 N HCl, N NaOH, $M/2000$ $CuSO_4$ at pH 2.0-9, $M/2000$ $FeCl_3$ at pH 2.9-6, $M/2000$ $Al_2(SO_4)_3$ at pH 4-8, and $CaCl_2$ at pH up to 9. Although the usual substrate temperature was 19 ± 0.5°C., effects of temperatures between 13.8 and 19.3°C. were determined for monolayers on $N/100$ NaCl. Raising the temperature caused transition to occur at higher pressure. On ion-free water, the monolayer was very largely soluble. The force-area curves of sodium cetyl sulphate on acid solutions did not show a transition. At the same ionic strength, the monolayer on HCl was less soluble and more expanded than that on NaCl. No hydrolysis of the sulphate occurred in one hr. on N HCl. Monolayers on alkaline solutions gave force-area curves similar to those on neutral NaCl. Substrates containing $FeCl_3$, $Al_2(SO_4)_3$ or $CuSO_4$ induced solidification of sodium cetyl sulphate monolayers over pH ranges which were characteristic for each metal ion. Except near the pH of maximum interaction, the shape of the force-area curve within the pH range of solid film formation was dependent on the time of contact between the monolayer and inorganic sulphate. Successive monolayers spread on the same substrate showed decreasing degrees of interaction. Solidification of the monolayer occurred only in the presence of complex metal ions which could stabilize the monolayer soap by hydrogen bonding, i.e., only on basic ferric or aluminum salt solutions or complex carbonate ions in cupric salt solutions.

The effects of metal ion concentration and buffer salts on fatty acid monolayers. *Ibid.*, 1139-47. Force-area curves at 18°C. were determined for monolayers of myristic acid on various concentrations of $CuSO_4$ and $FeCl_3$ between 5×10^{-3} and $5 \times 10^{-5}M$ and at various pH levels. On sufficiently acidic solutions, polyvalent metal ions have no effect on the force-area curve, but as the pH increases the first effects observed are a condensation of the liquid-expanded region and a lowering of the prsesure at which transition occurs between the expanded and the condensed states. The results show that the metal ion-monolayer interaction is primarily due to the formation of normal or basic soaps. Comparisons of the force-area curves of monolayers on $CaCl_2$ in $NaHCO_3$ and $CuSO_4$ in NaOH or $NaHCO_3$ show that reaction occurs between the monolayer and complex copper carbonate ions to form solid films having areas up to 50 $Å^2$ per molecule. The force-area curves for monolayers of stearic acid on NaCl and myristic acid on $CaCl_2$ at various CO_2 concentrations show that the surface pH of solutions saturated with CO_2 is higher than the bulk solution pH because of evaporation of CO_2 from the surface. Chemical analysis of myristic acid monolayers removed from copper salt solutions confirm the presence of complex copper soaps.

Monomolecular films of mixtures. I. Stearic acid with isostearic acid and with tri-p-cresyl phosphate. Comparison of components with octadecylphosphonic acid and with tri-o-xenyl phosphate. H. E. Ries, Jr. and H. D. Cook (Res. Dept., Standard Oil Co. [Ind.], Whiting, Ind.). *J. Colloid Sci.* 9, 535-46 (1954). Pressure-area isotherms were determined for monolayers of pure compounds whose structures were related to those of lubricant additives. These compounds were stearic acid, isostearic acid, octadecylphosphonic acid, tri-*p*-cresyl phosphate, tri-*o*-xenyl phosphate, and equimolar mixtures of stearic acid with isostearic acid, and stearic acid with tri-*p*-cresyl phosphate. Cross sectional area per molecule, collapse pressure, and compressibility were calculated from the isotherms. The data are discussed in relation to the molecular structures of the compounds. Stearic acid and octadecylphosphonic acids, individually, form strong films. Isostearic acid has a larger molecular area and a lower collapse pressure than stearic acid. Tri-*p*-cresyl phosphate and tri-*o*-xenyl phosphate have much larger areas and lower collapse pressures. An equimolar mixture of stearic acid and isostearic acid has monolayer properties close to the calculated average. However, an equimolar mixture of stearic acid and tri-*p*-cresyl phosphate has film properties approaching those of the phosphate at low pressures. At intermediate pressures expulsion of the phosphate from the monolayer occurred and at high pressures film properties approached those of stearic acid.

Ternary systems of liquid carbon dioxide. A. W. Francis (Socony-Vacuum Labs., Socony-Vacuum Oil Co., Inc., Res. and Dev. Dept., Paulsboro, N. J.). *J. Phys. Chem.* 58, 1099-1114 (1954). Triangular graphs are presented for 464 ternary systems involving liquid carbon dioxide. Data are included for systems containing: butyl stearate, caproic acid, caprylic acid, castor oil, isocaproic acid, lauric acid, monoacetin, oleic acid, olive oil, and triacetin.

The unsaponifiables of palm oil. Simone Argoud. *Oleagineux* 9, 717-723, 789-795 (1954). The composition and methods of analyzing and separating the pigments and other fractions in the unsaponifiables of palm oil are reviewed first. Analyses were conducted on the unsaponifiables from pressed palm oil and from the oil (palm fiber oil) obtained by petroleum ether extraction of the press cakes. The unsaponifiables of the fiber oils from widely varying sources were found to contain variable quantities of lycopene in addition to alpha, beta, and gamma-carotenes. Four compounds of secondary importance (phytocene, phytofluene, zeta-carotene and tetrahydrolycopene) not yet mentioned as being present in fiber oil were detected in a fiber oil rich in lycopene. Only phytofluene and phytocene have been found to date in pressed oil.

Extension of the dichlorethane method for the determination of solid fatty acids in oils and oleins. M. Loury and Monique Frelat. *Revue Francaise des Corps Gras.* 1, 557-561 (1954). The fatty acids of the oil to be studied are dissolved in dichlorethane and the solution held at —20° for 15 hours to precipitate the saturated acids. In order to diminish the ''third-solvent'' effect of the unsaturated acids that are present a very dilute solution (1.0 to 1.5 grams of fatty acids in 300 ml. of solvent must be used. The chilled solution then is filtered to remove the precipitated solids and the resulting filtrate is held at —20° for an additional 15 hours. After filtration to remove a second much smaller crop of solids the solution is evaporated to recover the fluid acids. Results in good agreement with those from the Bertram method are obtained. Under the above conditions it was not possible, however, to separate erucic acid cleanly from saturated fatty acids.

Extraction of carotene from palm oil. M. T. Mellier and M. Servant. *Oleagineux* 9, 873-876 (1954). The methods for separating carotene from palm oil are reviewed.

Preparation of fatty monoamides of ethylene diamine by aminolysis of triglycerides. J. Baldy, M. Naudet and P. Desnuelle. *Revue Francaise des Corps Gras* 1, 552-556 (1954). The direct condensation of ethylene diamine with fatty acids is not a good technique for the formation of the monoamides since considerable quantities of the imidazolines also are formed. Imidazolines are not found in the products obtained by the reaction of ethylene diamine with fatty monoesters, but the reaction is slow. The aminolysis of triglycerides with this amine, however, proceeds rapidly. To prepare the monoamide from the triglyceride it is reacted with ethylene diamine in the presence of a catalytic amount of concentrated hydrochloric acid. A temperature of 118° is maintained for 4 hours. The water and unreacted amine are distilled from the reaction mixture with the temperature not being allowed to exceed 150°. Glycerol is removed by treatment with a concentrated solution of sodium chloride and the monoamide purified by mixing it at 35° with a selective solvent for the monoamides such as methanol or ethanol. After two such treatments the extracts contain the greater part of the monoamides almost completely free of diamides. The monoamides may be converted into the quaternary ammonium compounds of the type known as "Sapamines" by reacting them with formic acid in ethanol solution, subsequent purification and treatment with the required organic halide. Instructions are given for the preparation of N-lauroyl-N^1-dimethylbenzylethylenediamine hydrochloride.

Polarography of the unsaturated fatty acids. Teruzo Asahara and Choichiro Hirai (Univ. Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 392-5 (1954). Acrylic acid, ethyl acrylate, crotonic acid, vinyl caproate, 2-nonenoic acid, ethyl 2-nonenoate, ω-undecenoic acid, oleic acid, linoleic acid, α-eleostearic acid, China tung oil, soybean oil, soybean oil fatty acids, octadecadienoic acid, dodecene-1, and dodecadiene-1,3 were studied polarographically.

The ester condensation about ethyl stearate. Kazuhiro Teramura, Kunio Kitamura, and Ryohei Oda (Kyoto Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 64-5 (1954). Ethyl stearate was condensed with ethyl benzoate in the presence of Na to give ethyl α-benzoylstearate, m.p. 54-5°, which was derived to stearophenone, m.p. 52-3°. Ethyl stearate was condensed with diethyl phthalate in the presence of Na ethoxide to give *n*-hexadecyldiketohydrindene, m.p. 59°. The condensation of ethyl stearate with ethyl acetate gave poor yield of ethyl α-acetylstearate.

The highly unsaturated acids in sardine oil. XX. Ultraviolet absorption spectra of highly conjugated acids obtained by the alkali-isomerization of clupanodonic acid and mixtures of clupanodonic and docosahexanoic acids. Yoshiyuki Toyama and Tsutomu Shimooka(Nagoya Univ.). *J. Oil Chemists' Soc. Japan* **3**, 158-60(1954). Clupanodonic acid (4,8,12,15,19-docosapentaenoic acid) and mixtures of this acid and docosahexaenoic acid were separated from dewaxed sardine oil, and were isomerized under N_2 with 21% KOH-glycol at 180°for 15 min. Solid highly conjugated acids were separated from the isomerized products and their ultraviolet absorption spectra were measured.

Recent advances of grease. Akira Wakana. *J. Oil Chemists' Soc. Japan* **3**, 247-60(1954). A review with 67 references.

Utilization of sperm whale oil. I. The fractionation of fatty alcohols in sperm oil by the urea adducts. Yoshiro Abe and Shoichiro Watanabe(Keio Univ., Tokyo). *J. Oil Chemists' Soc. Japan* **3**, 164-6(1954). Fractionation was made by heating sperm whale fatty alcohols in methyl or ethyl alcohol with urea. Saturated alcohols with the lowest iodine no. were obtained when the ratio of sample : solvent : urea was 2 : 20 : 3. *n*-Propyl alcohol was inferior to lower alcohols in giving heterogeneous reaction mixture. Oleyl alcohol was obtained in a good yield by urea adduct fractionation.

The antistatic agents. I. Noboru Kanô and Mitsuo Kimoto. *J. Oil Chemists' Soc. Japan* **4**, 167-9(1954). The effects of several surface active agents were examined as the antistatic agents (used for preventing the accumulation of static electricity) for nylon cloth by measuring specific surface resistance of the treated cloth with a resistance tester. Excellent results were obtained with the following surface active agents: triethanolamine salts of higher alcohol phosphates, polyoxyethylene glycol alkyl ethers, the same alkyl ester, the same alkylphenol ether, and cationic agents of quaternary ammonium base type.

Determination of dissolved oxygen in fatty oils preserved in the air. Shizo Hirano and Morizi Kurobe (Nagoya Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* **57**, 624-6(1954). Experiments on perilla oil, China tung oil, sesame oil, peanut oil, rapseed oil, Camellia oil, ray liver oil, and cuttle-fish liver oil showed that more oxygen was dissolved in oils with lower iodine no. than in oils with higher iodine no. The dissolved oxygen increased when hydroquinone was added to the oils with higher iodine no. The microdetermination of oxygen in liquid was carried out by the method of Hirano and Kitahara (*J. Chem. Soc. Japan, Ind. Chem. Sect.* **56**, 325(1953), based on the fact that free oxygen dissolves Cu quantitatively in ammoniacal solution containing ammonium chloride.

The rust-preventive additives (for mineral oil). Seimi Sato (Technol. Sta. Aichi Pref., Nagoya). *J. Oil Chemists' Soc. Japan* **3**, 149-54(1954). Experiments were made to examine the rust-preventive properties of maleic anhydride adducts of oleic acid, its methyl, butyl, stearyl, and oleyl esters, triolein, and oleyl alcohol when added to commercial turbine oil by the static water-drop corrosion test at 40°. The maleic adducts were effective at 0.05% or more. Other additives tested include sebacic acid (effective at 0.01%), castor oil fatty acids, naphthenic acid, stearic acid monoglyceride, zinc stearate (all less effective than the maleic adducts), and 3 commercial additives.

Reactions of halogens with the metallic salts of fatty acids. IV. Some experiments on the reaction mechanism. Eturô Maekawa(Nagoya Inst. Technol., Nagoya). *J. Oil Chemists' Soc. Japan* **3**, 154-7(1954). Undecane was formed as a by-product of the reaction of Br_2 with Ag laurate in CCl_4. The velocity of decarboxylation or the formation of bromoundecane was independent of the concentration of Br_2. In the reaction of other halogens with Ag laurate in CCl_4, Cl_2 and I_2 gave the corresponding haloundecane with lower yield in the case of Cl_2. When the equimolecular mixture of 2 halogens in CCl_4 was used, the halogen with larger atomic number was combined with the alkyl radical. The yields of haloalkanes were very low, when Cl_2 or Br_2 gas was used instead of the solution in CCl_4. From these results the reaction of Br_2 with the Ag salt of fatty acid in CCl_4 was concluded to be a monomolecular reaction involving the formation of alkyl anions.

The effect of peroxides upon the rust-preventive property of oils. Seimi Sato(Technol. Sta. Aichi Pref., Nagoya). *J. Chem. Soc. Japan, Ind. Chem. Sect.* **58**, 26-7(1955). The utility as rust preventatives in turbine oil of benzoyl peroxide (peroxide value 8054) and of methyl oleates of peroxide values 185, 205, 333 and 1010 was determined. In general a peroxide concentration in the turbine oil corresponding to a peroxide value of 4.5-9.3 prevented rust formation.

Apparatus for filtering frying fat. J. A. Morton(Frysweet Filter Corp.). *U. S. 2,698,092.* Description is given of an apparatus for the continuous filtration of hot frying fat.

Process of producing conjugated fatty acids. R. T. Arnold (General Mills, Inc.). *U. S. 2,698,857.* To a solution of alkali metal sals of mono-olefinic C_{8-22} fatty acids is added a solution of alkali metal hypochlorite. Carbon dioxide is passed through the mixture in order to form hypochlorous acid. Chlorohydrins of the fatty acids are then formed by holding the mixture at 0 to 35°C. By reaction of the product with alkali metal acetate, acetic anhydride and acetic acid at 170 to 200°C., diacetates of the fatty acids are formed. Pyrolysis of the diacetates at 350 to 475°C. then yields the desired conjugated fatty acids.

Stabilization of glyceridic oils. C. F. Brown and C. M. Gooding (The Best Foods, Inc.). *U. S. 2,699,395.* An edible glyceride oil is stabilized by the addition of an aliphatic tricarboxylic acid dissolved in an ester of a polyhydric alcohol. The tricarboxylic acid contains no more than six carbons, and no functional groups other than hydroxyl or carboxyl. The preferred esters are monoglycerides, diglycerides, mono-fatty acid esters of propylene glycol, and condensation products of such esters with no more than four moles of propylene oxide.

Fractionation of fatty acid glycerides. T. F. Bradley, A. C. Mueller, and E. C. Shokal(Shell Development Co.). *U. S. 2,700,036.* A process is described for separating monoglycerides of soybean oil fatty acids into fraction A, having a relatively low iodine number, and fraction B, having a relatively high iodine number. The crude monoglycerides are mixed with a methanol solution of urea and maintained at 10 to 45°C. for 10 to 300 min. Fraction A forms a crystalline urea complex which may be separated from the soluble fraction B.

• Biology and Nutrition

F. A. Kummerow, Abstractor
Joseph McLaughlin, Jr., Abstractor

Carbon dioxide utilization by rumen organisms. C. N. Huhtanen, F. J. Carleton, and H. R. Roberts(National Dairy Res. Labs., Inc., Oakdale, L. I., N. Y.). *J. Bacteriology* **68**, 749-51(1954). Rumen bacteria, RO-L_1, RO-C1, RO-C8, RO-L_5, RO-CR, *Proteus mirabilis* and *Propionibacterium freudenreichii*, were grown in rich organic media containing $Na_2C^{14}O_3$. Dried cells were fractionated into lipide, nucleic acids, and proteins. Production of acetic, propionic, butyric, and $>C_4$ acids by the lactate utilizers RO-C8 and RO-C1 were determined. Although RO-C8 did not fix carbon dioxide, RO-C1 incorporated carbon dioxide into acetic, propionic and $>C_4$ acids but not into butyric acid.

The fats: a story of nature's art. T. P. Hilditch. *J. Sci. Food Agr.* **5**, 557-66(1954). A review. The very marked regularity in qualitative compositions of fats from wide ranges of biological species of land flora or land fauna or aquatic origin is emphasized. In each group, the fat of a single family or a single species consists largely of an acid which is uniquely different from any of the more characteristic and prevalent acids. Many examples are discussed. Studies of the compositions of mixed glycerides have shown that each acid tends to be distributed as evenly or widely as possible among all the glyceride molecules. Exceptions to this generalization occur only in a very few seed fats, and in certain animal body and milk fats.

Studies on the production of glycolipide by Pseudomonas aeruginosa. G. Hauser and M. L. Karnovsky(Dept. Biological Chem. and Biophysical Lab., Harvard Med. School, Boston, Mass.). *J. Bacteriology* **68**, 645-54(1954). A crystalline glycolipide composed of two moles each of L-rhamnose and 1-β-hydroxydecanoic acid had previously been isolated from *P. aeruginosa* by Jarvis and Johnson [*J. Am. Chem. Soc.* **71**, 4124-6(1949)]. A synthetic medium containing glycerol as the sole carbon source has now been developed for the production of this glycolipide at 31-34°C. Modifications in the method of isolating the crystalline glycolipide are described. Assay procedures based on the determination of methylpentoses are discussed; results were confirmed by the isotope dilution technique. Rate of glycerol disappearance, glycolipide appearance, and bacterial growth were measured on both the glycerol synthetic media and a peptone-containing medium. In all cases, glycolipide formation occurred only in aging bacterial populations after the logarithmic phase of growth had been passed. In the absence of carbon dioxide in the atmosphere, only small amounts of glycolipide were formed in spite of fair growth of organisms. Fructose could act as the carbon source, but glucose, citrate, succinate, acetate, and ethylenediamine tetraacetic acid inhibited glycolipide production.

Phospholipide changes in rat skin after exposure to radiant thermal energy. W. Lee, A. K. Davis, C. Enterman and G. E. Sheline(U. S. Naval Radiological Defense Lab., San Francisco, Calif.). *Arch. Biochem. & Biophys.* **54**, 146(1955). An investigation of the effects of measured amounts of radiant thermal energy on the phospholipide, acid-soluble phosphorus, and water content of rat skin has been made. The appearance of labeled phospholipide and acid-soluble phosphorus in skin at 6 hr. following application of thermal energy and injection of P^{32}-labeled sodium phosphate has been determined. The radiant energy was delivered to the skin in a period of 0.4 sec. The phospholipide and acid-soluble phosphorus contents are not significantly altered in the burned skin. The water content of the heat-damaged skin is elevated over normal when 3.5 cal./sq. cm. was used. The specific activity of acid-soluble phosphorus increases in burned skin. Phospholipide production appears to fall when 6 cal./sq. cm. or more thermal energy is applied.

Modifications in the hydroxamic acid method for the estimation of the esterified fatty acids in small amounts of serum. R. Nailor, F. C. Bauer, Jr., and E. F. Hirsch(Henry Baird Favill Lab., St. Luke's Hospital, Chicago, Ill.). *Arch. Biochem & Biophys.* **54**, 201(1955). Modifications in the published hydroxamic acid method for estimating the total esterified fatty acids in small amounts of serum are described. The mean value of 42 normal fasting human serums is 12.3 meq./l. with a maximum of 20.8 and a minimum of 8.6 meq./l. Various aspects of the modified procedure are discussed.

The occurrence of n-heptadecanoic acid (margaric acid) in hydrogenated mutton fat. R. P. Hansen, F. B. Shorland, and N. June Cooke(Fats Res. Lab., Dept. of Scientific and Ind. Res., Wellington, New Zealand). *Biochem. J.* **58**, 513(1954). Hydrogenated mutton fat has been found to contain approximately 1.2% of *n*-heptadecanoic acid.

The occurrence of n-pentadecanoic acid in hydrogenated mutton fat. R. P. Hansen, F. B. Shorland and N. June Cooke(Fats Res. Lab., Dept. of Scientific and Ind. Res., Wellington, New Zealand). *Biochem J.* **58**, 516-517(1954). Hydrogenated mutton fat has been found to contain approximately 0.15% of *n*-pentadecanoic acid.

The estimation of serum liproproteins. A micromethod based on zone electrophoresis and cholesterol estimations. G. S. Boyd (Dept. of Biochem., Univ. of Edinburgh). *Biochem. J.* **58**, 680(1954). A micromethod for the separation and estimation of the serum lipoproteins is described. The procedure involves filter-paper zone electrophoresis of serum, followed by segmentation of the supporting media, elution of cholesterol and estimation of the latter, by a micromethod. Summation of the cholesterol data permits calculation of the ratio of α- to β-lipoprotein.

Route of absorption and distribution of oleic acid and triolein in the rat. S. Bergström, R. Blomstrand and B. Borgstrom (Dept. Physiological Chem., Univ. of Lund, Sweden). *Biochem. J.* **58**, 600(1954). The intestinal absorption of [1-C^{14}] oleic acid has been studied in rats with cannulated thoracic ducts. It was found that oleic acid was transported via the thoracic-duct lymph and incorporated into triglycerides and phosphatides to the same extent as found for palmitic acid in earlier work. The same results were obtained whether the oleic was fed as free acid or as triolein. The incorporation of the labelled acid into the lipids of the intestinal wall and the appearance of the isotope in the expired carbon dioxide has been followed. The results indicate that there is no detectable difference between the routes followed during absorption of fed free oleic or palmitic acids, or of glycerides containing these acids.

Intestinal absorption and metabolism of 2:2-dimethylstearic acid in the rat. S. Bergstrom, B. Borgstrom, N. Tryding and G. Westoo(Dept. of Physiological Chem., Univ. of Lund, Lund, Sweden). *Biochem. J.* **58**, 604(1954). The [*carboxy*-C^{14}]-2:2-dimethylstearic acid and 2:2-dimethyladipic acid have been synthesized. The former acid was well absorbed when dissolved in olive oil and administered to rats. The absorbed acid was transported via the lymphatics incorporated into glycerides and phospholipids. No isotope was found in the expired carbon dioxide but more than 90% of the absorbed isotope was recovered in the urine as C^{14} dimethyladipic acid. Dimethylstearic acid did not take part in the formation of ester bonds occurring during hydrolysis of olive oil with pancreatic lipase. When the lymph glyceride containing this acid was treated with bile-pancreatic juice, this ester bond appeared virtually resistant to the action of lipase. A discussion of various enzyme behavior is given.

Studies on the volatile fatty acids of sheep blood with special reference to formic acid. E. F. Annison(A. R. C. Inst. of Animal Physiology, Babraham, Cambridge). *Biochem. J.* **58**, 670 (1954). A method has been developed for the complete analysis of the volatile fatty acids present in 10-20 ml. blood, and formic acid is found to be 10-30% of the volatile fatty acids in sheep. Chromatographic evidence was obtained indicating that formic acid was present in human blood and also in blood from goats, cattle, horses, cats, and dogs at concentrations similar to those in sheep blood. Sheep urine was analyzed for formate and acetate. Investigation of the distribution of blood volatile fatty acids between cells and plasma in sheep and cattle indicated that formate is considerably concentrated in cells. Formic, acetic and propionic acids were analyzed in the volatile fatty acid totals.

Isolation, identification, and function of long chain fatty aldehydes affecting the bacterial luciferin-luciferase reaction. B. L. Strehler and M. J. Cormier(Biology Div., Oak Ridge Nat. Lab., Oak Ridge, Tenn.). *J. Biol. Chem.* **211**, 213-25(1954). It has been possible to obtain in pure form a compound from hog kidney cortex powder, called KCF, which will produce a 100- to 200-fold increase in the luminescence of bacterial extracts in the presence of excess $DPNH_2$, FMN, and oxygen. This factor has been identified as palmitic aldehyde by elementary analysis, molecular weight, and mixed melting point of the dinitrophenylhydrazine derivative.

A new and physicochemically well-defined group of tumor-promoting (cocarcinogenic) agents for mouse skin. K. Setala, H. Setala, P. Holsti(Dept. of Pathology, Univ. of Helsinki, Finland). *Science* **120**, 1075-76(1954). The tumor-promoting property of an un-ionic detergent, Span 20 (sorbitan monolaurate), was studied by using Berenblum's technique. Two-month old male white mice were divided into 3 subgroups, 50 mice in each. The skins of the animals in group 1 received a single painting of 0.3% 9,10-dimethyl-1,2-benzanthracene dissolved in paraffin oil. After the application, no tumors developed. The mice in group 2 were painted twice daily with pure Span 20; no tumors have developed in this group either. The animals in group 3 received a single painting of 0.3% 9,10-dimethyl-1,2-benzanthracene in paraffin oil, and then the same area of the skin of the back was painted twice daily with Span 20. In this group local cutaneous tumors began to appear at the end of the fifth week, and after 24 weeks of treatment, 21 of the 50 mice had together 34 tumors.

Effects of a fat-free diet on growing male rats with special reference to the endocrine system. T. C. Panos and J. C. Finerty (Dept. of Pediatrics and Anatomy, University of Texas Medical Branch, Galveston). *J. Nutrition* **54**, 315-29(1954). Thirty male Holtzman rats were fed, from the time of weaning and for a period of 20 weeks, a synthetic diet completely devoid of fat. Eighteen animals maintained under identical conditions were fed Purina Laboratory chow to serve as controls. Constant findings in the rats fed fat-free diets were impaired growth, the body weight attained being 66% that of the controls. Other groups of male rats maintained on the fat-free diet for periods of only 2 and 5 weeks showed similar differences from controls in body weight and weight of brain, liver, heart, kidney, and thyroid, indicating that definite effects of fat deficiency are present long before the appearance of skin lesions.

Dietary fat and liver necrosis. *Nutrition Reviews* 12, 312-13 (1954). Diets low in the sulfur-containing amino acids, methionine and cystine, and in *alpha*-tocopherol led in due time to the development of acute hepatic necrosis. This liver disorder differed from the fatty infiltration and diffuse cirrhosis seen under conditions of choline or other methyl donor deficiency.

Vitamin K deficiency in chickens fed corn-soybean diets. *Nutrition Reviews* 12, 274-75(1954). Considerable interest in vitamin K in practical poultry rations has been evident this past year. A "hemorrhagic syndrome" has been observed in commercial broiler flocks reared under field conditions and there was some evidence that vitamin K deficiency may be involved.

The relation of diet to atherosclerosis. *Nutrition Reviews* 12, 270-71(1954). A. Keys has suggested that the fat rather than the cholesterol content of the diet may be of importance in determining the incidence of atherosclerosis. This interpretation may be hazardous. Much of the force of the argument depended on the accuracy of vital statistics. Granting the validity of the vital statistics, the possibility that variables other than the fat content of the diet, such as total caloric intake, were significant in the production of atherosclerosis cannot be excluded. Moreover, the difference in the means of the serum cholesterol values was small when compared to the wide variation of individual values. Despite these considerations the indictment of dietary fat deserves further careful study in view of the large and increasing proportion of fat in the American diet.

Irradiation effects on linoleate oxidation. *Nutrition Reviews* 12, 286(1954). Ionizing radiations have the property of inducing a chain reaction which in many respects was similar to autoxidation. Such a reaction was reported to occur when linoleic acid was exposed to irradiation.

The metabolism of styrene in the rat. I. Danishefsky and M. Willhite(Dept. of Biochem. and the Inst. of Cancer Res., College of Physicians and Surgeons, Columbia Univ., New York, N. Y.). *J. Biol. Chem.* 211, 549-553(1955). Styrene-β C^{14}, when injected subcutaneously into rats, was distributed in almost all the tissues within an hour. Practically all of the radioactivity was eliminated within 35 hours. The urine was, by far, the major route of excretion; only a minor amount of radioactivity was found in the feces or respiratory CO_2. The radioactive substances in the urine were highly water-soluble and were probably in the form of conjugates. More than 60% of the radioactive metabolites were extractable with ether after hydrolysis.

The D-α-hydroxy fatty acid nutrition of Lactobacillus casei 280-16. M. N. Camien and M. S. Dunn(Chemical Lab., Univ. of Calif., Los Angeles). *J. Biol. Chem.* 211, 593-604(1954). D-α-hydroxy fatty acids of from 3 to 14 carbon chain length were nutritionally active in meeting an essential growth requirement of *Lactobacillus casei* 280-16. Corresponding acids of the L configuration were inactive, as were analogous DL acids containing hydroxyl, carboxyl, and certain other substituent groups (in addition to the α-carboxyl and α-hydroxyl). Hydrolysates of butter fat and wool wax contained nutritionally active substances, presumably D-α-hydroxy fatty acids. It was suggested that the D-α-hydroxy fatty acids serve as metabolic precursors to long chain D-α-hydroxy acid components of essential lipides in *L. casei* and perhaps other species, and that naturally occurring lipide α-hydroxy fatty acids were predominantly of the D series.

Synthesis of phosphatides in isolated mitochondria. III. The enzymatic phosphorylation of glycerol. C. Bublitz and E. P. Kennedy(Dept. of Biochem., Univ. of Chicago, Chicago, Ill.). *J. Biol. Chem.* 211, 951-61(1954). An enzyme from rat liver which catalyzed the phosphorylation of glycerol to form L-α-glycerophosphate has been purified about 170-fold, and its properties have been described. The name glycerokinase was suggested for this enzyme, which also catalyzes the phosphorylation of dihydroxyacetone and L-glyceraldehyde. The importance of glycerokinase for phosphatide synthesis has been discussed.

A note on the asymmetrical metabolism of glycerol. *Ibid.* 211, 963-67(1954). The biologically synthesized, asymmetrically labeled glycerol obtained by Swick and Nakao from *Saccharomyces chevalierei* fermentation has been enzymatically phosphorylated by the purified glycerokinase of rat liver, and the distribution of isotope in the L-α-GP so produced has been determined. About 83% of the total radioactivity was in the carbon atom bearing the unphosphorylated primary hydroxyl. The C^{14} in chemically synthesized glycerol and the L-α-GP derived from it was equally distributed between C-1 and C-3. The implications of these findings for the mechanism by which glycerol was converted to glycogen were discussed.

Utilization of branched chain acids in cholesterol synthesis. K. Bloch, L. C. Clark, and I. Harary(Dept. of Biochem., Univ. of Chicago, Chicago, Ill.). *J. Biol. Chem.* 211, 687-99(1954). The branched chain acids were fed to rats, and C^{14} concentrations in cholesterol and in the fatty acids of liver were determined. The cholesterol isolated from the tissues was partially degraded for the analysis of C_{10} and C_{25} of the steroid molecule. The C^{14} data obtained indicated that the branched chain acids were converted to cholesterol without prior breakdown to acetate or acetoacetate.

• Drying Oils

Raymond Paschke, Abstractor

Thermal polymerization of tung oil. C. Boelhouwer, W. A. Klaassen, and H. I. Waterman(Tech. Univ., Delft). *Research* (Supplement) *Correspondence* 7 (12), S61(1954). Whereas during thermal polymerization of linseed oil (300°C.) the fatty acid groups combine to form bicyclic dimers, the thermal treatment of tung oil at 200°C. produces monocyclic dimeric fatty acid groups. The fact that the Diels-Alder condensation reaction is apparently not followed by a further ring closure in the latter case is due to the relatively low polymerization temperature. Similarly, the tung oil fatty acid groups themselves show little tendency to cyclize at 200°C., the distillates of the several methanolized glycerides being practically noncyclic.

New drying oils for caulking compounds. N. M. Cornell(Archer-Daniels-Midland Co.). *Paint Oil Chem. Rev.* 117 (24), 36 (1954). The primary oils used in glazing and caulking are soy, marine, and segregated marine type oils of a non- or semi-drying type. Each of these oils is used in the crude, refined, or processed form.

Newest development in two container coating system. D. E. Floyd, M. S. Herban and W. S. Mitchell(General Mills, Inc.). *Can. Paint Varnish Mag.* 28 (12), 10(1954). Finishes of epoxy resins and polyamides are discussed. Formulations and properties of films are given. 8 references.

Drying oils. M. R. Mills(British Oil and Cake Mills Ltd.). *Paint Technol.* 18, 87(1954). A brief review with emphasis on (1) solvent segregation, (2) isomerization, (3) drying oil copolymers, (4) epoxy resin esters, (5) polyamides, and (6) analysis by newer methods.

Epikote esters—new raw materials for industrial enamels. H. P. den Otter(Kunstharzfabrik Synthese N. V. Holland.) *Paintindia* 4(7), 34(1954). Three fatty acid esters of epoxy resins are discussed. The dehydrated castor oil fatty acid ester can be used in airdrying as well as ovendrying applications. Outstanding property is unequalled elasticity. The coconut oil fatty acid ester can only be used in ovendrying enamels. Outstanding properties are lasting whiteness even at higher temperatures and high chemical resistance. The linseed oil fatty acid ester is used for airdrying purposes and possesses excellent durability and water-resistance.

The fire hazard of surface coatings. R. W. Pickard. *Paint Manufacture* 24, 426(1954). This paper discusses some of the hazards presented by a painted surface and the tests which are carried out to assess them.

Oleic acid as a film former. I. T. Taranenko. *Zhur. Priklad. Khim.* 27, 794-7(1954). Films prepared from oleic acid by heating on clean plates to 120-60° (with wt. loss of some 30%) do not differ in physical properties from those prepared from linseed oil. In drying of oleic acid and such oils the process is not polymerization but polycondensation with loss of CO_2. The sharp drop of saponification no. is thus explained by addition of O, forming hydroxy derivatives which then lose H_2O intermolecularly forming ether-bound cross links. (*C. A.* 48, 13237)

• Detergents

Lenore Petschaft Africk, Abstractor

Lanolin in powdered hand soaps. R. Bernstein, M. Haftel, and R. Grant(Philadelphia Naval Shipyard, Pa.). *Soap and Chem. Specialties* 30(11), 48-9, 106(1954). A Soxhlet extraction procedure permitted easy and quantitative separation of lanolin from soap and vegetable abrasive and avoided erratic and tedious extraction of lanolin and fatty acid from acidified solutions containing insoluble vegetable abrasive. For soaps containing cornmeal 55%, powdered laundry soap 42%, and lanolin 3% corrections are made for the determined lanolin. These are 0.1% for lanolin from corn cob and 0.3-0.4% from soap.

The effect of organic additives on the rate of surface tension lowering of sodium dodecyl sulfate solutions. E. J. Burcik and R. C. Newman(Penn. State U., State College, Penn.). *J. Colloid Sci.* 9, 498-503(1954). Addition of dodecanol or dodecanoic acid to solutions of sodium dodecyl sulfate lowers the static surface tension of the solution and causes a decrease in the rate of surface tension lowering. Addition of *n*-decane to solutions of sodium dodecyl sulfate does not cause these effects. These results suggest that dodecanol-1 and dodecanoic acid associate with the sodium dodecyl sulfate. These association aggregates behave similarly to acid soaps with regard to their effects on the static and dynamic surface tension.

Sorption of surface active agents from aqueous solution by phosphate rock. E. J. Fox and W. Z. Jackson(U. S. Dept. of Agr., Beltsville, Md.). *J. Agr. Food Chem.* 3, 38-42(1955). The adsorption of surface active agents from aqueous solutions by phosphate rock suspensions has been investigated as a possible clue to previously reported differences between the behaviors of nonfloated and double-floated phosphate rocks during acidulation. Changes in surfactant concentration as measured by differences in relative surface tensions of the solutions before and after contact with the rock indicate that the anionic, nonionic and cationic types of surfactants are adsorbed on the surface of rock particles in varying degrees depending on the type and molecular complexity of the surfactant, the particle size and the degree of surface saturated of the rock, and on the previous treatment of the latter with one or more flotation reagents. The presence of the cationic reagent used in the flotation process doubtlessly explains the enhanced reaction rates observed in the acidulation of double floated rock.

Dichlorofluorescein as an indicator in the determination of anionic detergents. Helene Iwasenko(Bristol-Myers Co., Hillside, N. J.). *J. Assoc Offic. Agr. Chemists* 35, 1165-9(1953). The method described is based on titration of the anionic detergent with a standard quaternary ammonium chloride solution, by using a dichlorofluorescein as the indicator. A collaborative study of the method by 7 analysts shows that the method is satisfactory. (*C. A.* 48, 14257)

Effects of surface active agents on properties of superphosphates and mixed fertilizers. R. Kumagai and J. O. Hardesty (U. S. Dept. of Agr., Beltsville, Md.). *J. Agr. Food Chem.* 3, 34-8(1955). A study has been made of the effects of seven different surfactants (anionic and nonionic types) on densities and ammonia-absorption efficiencies of ordinary and triple superphosphates and on caking tendencies of mixed fertilizers. Nonionics decreased and anionics increased the bulk density of superphosphates by over 13% when added during acidulation of rock. Ammonia-absorption efficiencies of superphosphates prepared with surfactants added during acidulation were 1 to 9% higher than those of the corresponding reference superphosphates. Caking tendencies of mixed fertilizers were decreased by as much as 45% with use of nonionics during acidulation and increased by as much as 37% with use of anionics. Surfactants added during preparation of mixed fertilizer were about half as effective as the same surfactants added during acidulation. In general, maximum effects may be obtained with the addition of proper amounts of nonionic surfactants during superphosphate manufacture and these effects may take the form of lower density of superphosphate, moderate increases in ammonia-absorption capacity, and slightly better physical condition of the bagged fertilizer.

Detection of surface-active phenol ethers with sulfuric acid and formaldehyde. M. J. Rosin(Brooklyn College, Brooklyn, N. Y.). *Anal. Chem.* 27, 111-14(1955). Surface-active agents containing an active benzenoid nucleus, such as O-substituted alkylphenols and monosulfonated diphenyls, may be detected by the dark red color which they produce when treated with concentrated sulfuric acid and formaldehyde. Other functional groups present in surfactants produce no interfering colors. Reactions of various commercial products are listed.

Detection of beta-hydroxyethylamines by pyrolysis with sodium chloroacetate. M. J. Rosin(Brooklyn College, Brooklyn. N. Y.). *Anal. Chem.* 27, 114-16(1955). β-Hydroxyethylamines, upon pyrolysis with sodium chloroacetate, decompose to yield acetaldehyde. The acetaldehyde, when led into a solution of sodium nitroprusside containing diethanolamine, produces a blue color which may be used as a qualitative test for these amines. Reactions of various commercial products are listed.

New method for the determination of lathering power. J. P. Sisley and M. Loury. *Rev. franc. corps gras* 1, 390-5(1954). A common electric household mixer was adapted to the measuring of lather by replacing the usual glass bowl by a tube graduated from 1 to 1000, and with whipping conditions of 30-sec. periods at 1200 r.p.m. For 5 minutes the upper and the lower levels of the froths of 21 commercial detergents at concentrations of 0.05, 0.1, and 0.15% dissolved, respectively, in distilled and tap water, were determined and tabulated. The results are generally comparable with those obtained with the less practical and cumbersome apparatus of Ross and Miles. (*C. A.* 49, 647)

Syndet manufacture from petrochemicals. Cornelia T. Snell and F. D. Snell(Foster D. Snell, Inc. N. Y.). *Petroleum Eng.* 26 (13), C-7 to C-10(1954). The production of synthetic detergents, alkyl aryl sulfonates and nonionics from petroleum sources is reviewed.

Alkylolamides in detergent formulation. A. Taylor(Marchon Products Ltd., Whitehaven, Engl.). *Manuf. Chemist* 25, 530-2 (1954). Alkylolamides are condensates of alkylolamines and fatty acids and are generally referred to as foam boosters or additives. Their use in detergent formulation aids the problems of stabilization, improvement and creaming of lather. They can be used as detergents in their own right, but their main outlet is as ingredients in shampoo and liquid and powder detergents. Their chemistry and uses are reviewed.

Interpretation of the conductivity of soap solutions. D. Stigter. *Rec. Trav. chim.* 73, 611-25(1954). The relation between specific conductivity and concentration for micellar solutions changes sharply near the critical micellar concentration. The change is more clearly demonstrated if differentials are plotted, leading to a stepped graph. The departure of the shape of the graph from the ideal case is a sensitive test for the size distribution of the micelles. In a number of cases the micelles are found to be practically uniform in size. From the data in the region of the critical micellar concentration the molecular weight of the micelle may be calculated. Anomalous conductivity curves may be explained in terms of a wide range of size distribution of the micelles.

Spray drying of detergents. H. Stupel and A. V. Segesser. *Seifen, Ole, Fette, Wachse* 80, 545(1954). The many factors involved in spray drying of detergents are reviewed. Methods of spray drying may be classified according to end products. Powders resulting from finest possible dispersion have a relatively large contact surface which insures a favorable ratio between heat expenditure and drying yield. Hollow beads have a smaller contact surface than do powders and therefore more energy is required to dry them. Agglomerates such as are formed by the lumping of beads have high bulk density, but dissolve even less readily in water than do the beads. Spray drying may be performed by a spray plate, spray disc or spray nozzle. Particle size of the dried product is determined by the slurry and the spray conditions. The product should be as uniform as possible, non-dusting, and have large size beads. The effect of various of the detergent additives on the spray drying of the product is discussed.

Preparation of surface active agents from ricinoleic acid and its esters by the use of sulfamic acid. Saburo Komori, Seizaburo Sakakibara, and Takeshi Takahashi(Osaka Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 83-4(1954). Excellent results were obtained in the presence of urea as the catalyst. Ricinoleic acid and methyl ricinoleate were derived to the ammonium salts of the corresponding sulfuric acid esters which were high in solubility in organic solvents, relatively high in surface tension, low in foaming capacity, but high in emulsifying power.

The relation between the molecular structure and surface activity of alkyl benzene sulfonates. Hideo Amatsu, Masatsugu Shimoyamada, and Masamichi Motose(Nissan Chem. Ind. Co., Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 379-82 (1954). Pure alkyl benzenes [*n*-hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecylbenzenes and dodecylbenzene-(2), -(4), and -(6) (i.e. 2-phenyldodecane, 4-phenyldodecane, and 6-phenyldodecane)] were sulfonated, neutralized, and purified. Their surface tension, specific interfacial tension, penetrating power, and detergency power were compared.

Sweating of soap. Mititarô Kawaguti and Hiroso Nobori(Kaoo Soap Co., Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 573-5(1954). Free alkali retained in soap was considered to be related with sweating, since it influences the vapor pressure of the soap. The alkali soap and neutral soap with the same composition were compared in respect to the velocity of water evaporation, vapor pressure, sweating, and absorption of water.

Properties of guanidine soaps. Oyobu Inoue, Jiro Mikumo, and Toru Kusano(Nagoya Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 330-2(1954). The guanidine soaps of lauric, palmitic, stearic, and oleic acids had lower melting points (57°, 87°, 95°, —, respectively), relatively high solubilities in water and organic solvents, and similar properties with Na and K soaps in respect to pH, hydrolyzability, critical micelle concentration, electric conductivity, and surface tension. Guanidine laurate was bacteriostatic.

Hydrolysis of butyl acetate with hydrochloric acid and another reaction in the presence of surface active agents. Eturô Maekawa and Jirô Mikumo (Nagoya Inst. Technol.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* **58**, 19-21 (1955). Two reactions were studied as typical fundamental ones of chemical reactions with emulsions. Polyoxyethylene glycol monododecyl ethers with average polymerization degrees 5.2, 7.0, 12.6, 14.5, and 17.5 were prepared and tested for surface tension in *N* HCl. The optimum concentration was about 0.01% of the agent tested. Another reaction examined was transsulfonation, i.e. the reaction of hexadecyl bromide with Na_2SO_3.

Promotion of efficiency in sulfur refining with surface active agents. Go Okamoto, Takeshi Ookura, and Masahura Kitahama (Hokkaido Univ., Sapporo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* **57**, 24-6 (1954). The use of surface active agents (Skoarol, Emulgen, Emal paste, Emal, Binzol, Neoperex paste, and lignin; the first 3 were good) increased the yield of sulfur in the steam refining from inferior sulfur ores.

Improvements in or relating to foam-producing compositions. Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij. *Brit. 717,536.* Compositions having improved foaming properties in aqueous media consist of a water-soluble surface active salt of at least 8 carbon atoms and a sulfone free from sulfonic acid groups, and containing in the molecule at least one hydrophobic radical of from 8 to 18 carbon atoms, at least one imido carbonyl group —NR.CO—, and at least one sulfone-containing group $\rightarrow CSO_2C \leftarrow$.

Detergent composition. L. McDonald. *U. S. 2,697,695.* A substantially foamless and nonsudsing detergent for use in washing machines consists of a composition comprising by weight 20 parts of the fatty acid (C_9 to C_{20}) ester of an ethylene oxide condensation product of a hexitol, 80 parts of sodium stearate and ½ part of emulsified ethyl cellulose having between 2 and 4 ethoxy groups per glucose residue.

Antiseptic detergent composition. R. S. Shumard (Monsanto Chem. Co.). *U. S. 2,698,301.* An effective antiseptic detergent composition comprises a detergent soap and 0.5 to 5% by weight, based upon the weight of the detergent soap, of a pentahalogenated phenol.

Detergent compositions containing metal discoloration inhibitors. H. S. Sylvester (Colgate-Palmolive Co.). *U. S. 2,698,302.* A detergent composition is claimed which consists of about 10 to 50% of a water soluble non-soap synthetic detergent such as an anionic organic sulfated or sulfonated detergent, about 10 to 80% of a water-soluble inorganic polyphosphate, and about 1% of monophenyl thiourea as a tarnishing inhibitor. This composition in water solution will reduce tarnishing of a copper base alloy.

Heats of solution of some alkyl sulfates in water. E. Hutchinson, K. E. Manchester and L. Winslow (Stanford U., Stanford, Calif.). *J. Phys. Chem.* **58**, 1124-7 (1954). The heats of solution of three alkyl sulfates in water have been obtained by direct calorimetry and from solubility measurements. A relationship is deduced between the turbidity of the solution and the factor required to convert the apparent heats of solution obtained from solubility measurements made above the Krafft point.

Launderometric determination of CMC in detergents. J. V. Karabinos and G. E. Kappella (Blockson Chem. Co., Joliet, Ill.). *Soap Chem. Specialties* **30**(12), 48-9, 113 (1954). A launderometric procedure is described for assaying carboxymethylcellulose for its detergent activity, particularly with respect to the prevention of soil redeposition.

Micellar molecular weights of selected surface active agents. A. M. Mankowich (Aberdeen Proving Ground, Md.). *J. Phys. Chem.* **58**, 1027-30 (1954). Using light scattering methods, the micellar molecular weights of six anionic and non-ionic surface-active agents were determined in unbuilt aqueous solution in the concentration range of 0.2 to 1.0%. The effects of one alkaline and two neutral builders on the micellar size of an alkyl aryl sulfonate surfactant were found to be considerable. While practically no dissymmetry was found for unbuilt solutions, the reverse was generally true of built surfactants. The possibility of a continuous change in micellar size with increase of concentration for some unbuilt surfactants is indicated.

Artificial surface dirts for detergency studies with painted surfaces. W. E. Shelberg, J. L. Mackin, and R. K. Fuller (U. S. Naval Radiological Defense Lab., San Francisco, Calif.). *Ind. Eng. Chem.* **46**, 2572-9 (1954). Surface dirts and their standardized simulation on painted surfaces were studied in order to devise a simple immersion test to compare the ability of mildly agitated solutions to remove outdoor urban and shipboard surface dirts. This paper describes the formation, properties, and analysis of some outdoor surface dirts; the preparation of synthetic urban and shipboard dirts and their conversion to realistic artificial surface dirts on painted test surfaces; and a laboratory detergency test which employs the test surfaces and quantitatively measures by weighing the percentage of artificial surface dirt removed when a test surface is immersed in a cleansing solution.

The effect of alcohols on the critical micelle concentrations of fatty acid soaps and the critical micelle concentration of soap mixtures. K. Shinoda (Yokohama National Univ., Minamiku, Yokohama, Japan). *J. Phys. Chem.* **58**, 1136-41 (1954). The effect of various alcohols on the critical micelle concentrations (CMC) of potassium octanoate, decanoate, dodecanoate and tetradecanoate was determined by the change in color of pinacyanol chloride. It was found that (a) the CMC of fatty acid soaps is a linear function of the alcohol concentration, (b) the logarithm of the rate of change of CMC with alcohol concentration is a linear function of the number of carbon atoms in the alcohol molecule, and (c) the logarithm of the rate of change of CMC with the concentration of a given alcohol is a linear function of the number of carbon atoms in the soap molecule. The CMC of several ternary soap mixtures were determined and a theoretical equation derived for the CMC of multi-component soap mixtures; the experimental results are in good agreement with the calculated values.

Absorptiometric determination of a nonionic detergent. D. G. Stevenson (At. Weapons Research Establishment, Aldermaston, Berks, Engl.). *Analyst* **79**, 504-7 (1954). The nonionic detergent Lissapol N which is used in the anhydrous form Lissapol NXA, gives a clear red color when a trace of it is added to concentrated H_2SO_4. The color persists when the acid is diluted with 3-4 parts of water. The detergent gives a more sensitive color, violet to rose pink, when a little phosphomolybdic acid is added to the detergent in H_2SO_4. Two procedures are given, based on these colorations, which will detect 10 γ of the detergent in 10 ml. of solution. (*C. A.* **48**, 13243)

Determination of the ionic type of synthetic surface-active compounds. A. S. Weatherburn (National Research Labs., Ottawa). *Can. Textile J.* **71**(16), 45-6 (1954). A 2-phase solution of methylene blue (I) in water and an anionic complex of I in $CHCl_3$ adjusted to equal color depth in both phases, shows deepening of color in water if catinoic agent is added and lightening in water with an anionic agent. Soap acts as a nonionic agent under these conditions, but is distinguished by acidification. (*C. A.* **48**, 13351)

Frictional properties of soaps at high pressures. J. R. White (Socony-Vacuum Laboratories, Paulsboro, N. J.). *Lubrication Eng.* **10**, 340-4 (1954). The resistance to shear of lubricant soap films has been measured under normal pressures ranging from 30,000 psi to 250,000 psi. For sodium soaps at pressures below 70,000 psi, the shear strength (coefficient of friction) becomes less as the chain length of the fatty acid component increases from C_4 to C_{18}. At high pressures the reverse is true and shear strength increases slightly with increased chain length. In regard to temperature, shear strength is less at 100° than at 27°. Above 100°, the soap films fail to separate the surfaces and shear strength measurements cannot be made.