

filtration-extraction tests and to Marco L. Paredes for the analyses reported.

REFERENCES

1. Burnett, R. S., and Fontaine, T. D., *Ind. Eng. Chem.*, **36**, 284-288 (1944).
2. Dunning, J. W., *Oil Mill Gaz.*, **56** (1), 64-68 (1951).
3. Deckbar, F. A. Jr., Persell, R. M., Pollard, E. F., and Gastrock, E. A., *Cotton Gin and Oil Mill Press*, **53** (15), 13-15, 17, 48, 50-51, 54-56, 58-62 (1952).
4. Gastrock, E. A., and D'Aquin, E. L., *Oil Mill Gaz.*, **53** (4), 13-21 (1948).
5. Graci, A. V. Jr., Spadaro, J. J., Paredes, Marco L., D'Aquin, E. L., and Vix, H. L. E., *J. Am. Oil Chemists' Soc.*, **32**, 129-131 (1955).
6. Persell, R. M., Pollard, E. F., and Gastrock, E. A. *Cotton Gin and Oil Mill Press*, **51** (26), 9-11, 24-25, 30-32 (1950).
7. Pominski, J., Knoepfler, N. B., Graci, A. V. Jr., Molaison, L. J., Kulkarni, B. S., and Vix, H. L. E., *J. Am. Oil Chemists' Soc.*, **37**, 361-364 (1955).
8. Rose, Downs, and Thompson, Ltd. (Old Foundry Hull, Eng.), *Oil Mill Gaz.*, **56** (12), 13-15, 17-18 (1952).
9. Pack, F. C., Southern Utilization Research Laboratory unpublished data.

[Received June 13, 1955]

ABSTRACTS

R. A. Reiners, Editor

• Oils and Fats

S. S. Chang, Abstractor
Sini'tiro Kawamura, Abstractor
Dorothy M. Rathmann, Abstractor

For top-quality fried foods curb these six trouble factors. W. A. Quammen (Res. and Dev. Dept., Procter and Gamble Co., Cincinnati, Ohio). *Food Eng.*, **27**, 76-77 (1955). The tendency of a bland stable frying fat to darken, foam, smoke, develop poorer flavor and produce gum on equipment is accelerated by (1) excessive heat, (2) metallic contamination, (3) soap and caustic residues left on equipment after cleaning operation, (4) burnt food particles, (5) inadequate filtering and (6) insufficient turnover. For most efficient operation complete turnover of fat in about 10 hours is required.

Separation of triglycerides by countercurrent distribution. J. J. Taber (University of Pittsburgh, Pittsburgh, Pa.). *Univ. Microfilms* (Ann Arbor, Michigan), Publ. No. 11609, 176 pp. *Dissertation Abstr.* **15**, 727-8 (1955). (*C. A.* **49**, 11,301)

Preparation of tasty vegetable products by deep fat frying. E. G. Kelley and R. R. Baum (Eastern Reg. Res. Lab., Philadelphia, Pa.). *Food Tech.* **9**, 388-92 (1955). Beet, carrot and parsnip slices have been cooked in deep fat to yield tasty and attractive vegetable chips. Peas and lima beans have been prepared as crunchy pieces having a nut-like flavor and appearance. When cooked in a stabilized oil, the fried vegetables are stable over 6-12 months at room temperature.

Catalysts. X. Rate and selectivity of hydrogenation of sunflower oil in the presence of nickel formate catalyst. Z. Csuros, I. Géczy and D. Szabó (Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.* **2**, 33-56 (1952). A catalyst consisting of 50% Ni in hydrogenated sunflower oil was prepared. The rate of hydrogenation of sunflower oil with 0.4% catalyst was increased by raising the temperature from 160° to 200° and declined above 200°. An induction period was present at 120-40°. By controlling the rate of hydrogenation, sunflower oil could be selectively reduced so that only one double bond in the linoleic acid became saturated. Selectivity increased with larger quantities of the catalyst up to 0.6% and with a rise in temperature up to 220°; above this temperature and concentration selectivity declined. (*C. A.* **49**, 11,300)

Component fatty acids of the oil from the seeds of Benincasa cerifera. S. C. Sethi and J. S. Aggarwal (National Chem. Lab. India, Poona). *J. Sci. Ind. Research* **13B**, 853-4 (1954). Extractions of the seed kernels with petroleum ether gives a yellow oil n_D^{20} 1.4739, d_4^{20} 0.9196, and unsaponifiable matter 1.47% (identified as stosterol; acetate, m. 130°). The fatty acid content of the yellow oil is linolenic 1.02, linoleic 62.36, oleic 20.03, palmitic 10.56, stearic 5.76, and arachidonic 0.27%. (*C. A.* **49**, 11,299)

Studies on the oxidation mechanism in emulsified fat or oil. I. The influence of milk constituents on oxidation in margarine. Y. Ozawa, H. Kembo and K. Naito. *Bull. Natl. Inst. Agr. Sci., Jap.*, Ser. G, **28**, 67-74 (1953). Of several milk constituents tested for antioxidant properties in margarine enriched with vitamin A, the most effective were skim milk, buttermilk, and sodium caseinate, and their action was equal to that of propyl gallate. The seat of this activity was the protein, probably the casein, and since the antioxidant properties were not affected by heating, no correlation with oxidation-reduction potential was indicated. (*C. A.* **49**, 11,199)

II. The influence of milk and egg constituents on the catalytic oxidation under the existence of copper ions. *Ibid.* 75-81. The

rate of oxidation increased when 1-4 p.p.m. of Cu were added to margarine. The fats were protected by colloidal protein solutions (e.g., egg white, egg yolk, sodium caseinate, skim milk, etc.), their antioxidant activity increasing with increased emulsifying powers. Egg yolk and sodium caseinate were the most effective. (*C. A.* **49**, 11,199)

Antioxidants and their detection. H. Janecke (Univ. Frankfurt/Main, Ger.). *Deut. Lebensm.-Rundschau* **51**, 121-4 (1955). The means for detecting the four most frequently used antioxidants, i.e. dihydronorguaiaretic acid, butoxyanisole, some gallates and mixtures of tocopherol are discussed. (*C. A.* **49**, 11,195)

The detection and quantitative determination of coloring materials in butter and margarine. H. M. Espoy and H. M. Barnett (Barnett Lab., Long Beach, California). *Food Tech.* **9**, 367-72 (1955). A method has been developed for the detection and quantitative estimation of the principal pigments found or used in commercial butters and margarines. Mixtures of carotene, annatto extract, and coal tar colors can be separated and analyzed individually without the necessity of saponifying and extracting the oil carrier. A number of samples of butter and margarine were analyzed by these methods for type and strength of coloring materials.

Multicolumn continuous distillation. R. Dobrowolski. *Przemysl Chem.* **9**, 419-26 (1953). Multicolumn apparatus was applied to distillation of crude fatty acids. Five small columns were used; in each one only one fraction was fractionated. The most corrosive acids (C_7-C_8) were distilled in the first column made of porcelain, and the least corrosive acid, C_{22} , was distilled in the fifth column made of chrome steel. The advantages of this distillation are: (1) differentiation of column according to variables as temperature and vacuum, (2) differentiation of the material used in producing the columns, and thus saving of the acid-proof materials, (3) lesser use of thermal energy, (4) better quality of the products, and (5) saving of steel. (*C. A.* **49**, 10,671)

The branched-chain fatty acids of ox fat. 2. The isolation of 15-methylhexadecanoic acid. R. P. Hansen, F. B. Shorland, and N. June Cooke (Fats Research Lab., Dept. of Scientific and Ind. Res., Wellington, New Zealand). *Biochem. J.* **61**, 141-143 (1955). The C_{17} branched-chain fatty acid 15-methylhexadecanoic acid has been isolated in trace quantities (approximately 0.06% of total fatty acids) from hydrogenated ox perinephric fat.

Determination of carboxylic acid anhydrides by reaction with morpholine. J. B. Johnson and G. L. Funk (Chemical & Physical Methods Lab., Carbide & Carbon Chemicals Co., South Charleston, W. Va.). *Anal. Chem.* **27**, 1464-5 (1955). A titrimetric method employing an indicator was sought for the direct determination of carboxylic acid anhydrides in the presence of and to the exclusion of the corresponding acids. A satisfactory method was developed, based on the reaction of the anhydride with morpholine and titration of the excess reagent with methanolic hydrochloric acid. Data are presented on the determination of the purity of eight anhydrides and the determination of low concentrations of acetic anhydride in glacial acetic acid. The procedure is rapid, generally applicable to a variety of acid anhydrides, and accurate and precise over a wide range of concentrations.

The component fatty acids of the fat of *Aspergillus nidulans*. J. Singh, T. K. Walker, and M. L. Meara (College of Technology, Univ. of Manchester, England). *Biochem. J.* **61**, 85-88 (1955). The fat elaborated by *A. nidulans* grown on a sucrose medium is remarkably low in free acidity. The component acids

of the fat have been shown to be: myristic, 0.7; palmitic, 20.9; stearic, 15.9; higher saturated acid, 1.4; hexadecenoic, 1.2; oleic, 40.3; linoleic, 0.2; C₂₀₋₂₂ unsaturated, 2.4%. The fat appears to be somewhat anomalous compared with the fats of other micro-organisms by virtue of its relatively high stearic acid content.

Gas-liquid partition chromatography: the separation and micro-estimation of volatile fatty acids from formic acid to dodecanoic acid. J. H. Van de Kamer, K. W. Gerritsma and E. J. Wansink (Central Inst. for Nutrition Res. T.N.O., Utrecht, The Netherlands). *Biochem. J.* 61, 174-176 (1955). The gas-liquid partition chromatography of volatile fatty acids is modified in such a way that the lower fatty acids, including formic acid, and higher volatile fatty acids up to dodecanoic acid can be separated and quantitatively determined by one column analysis. The effect of adsorbed water on active clay and acid clay upon the decoloration of oils. Taketoshi Yamada and Zenko Komatsu (Mizusawa Chem. Ind. Co., Yamagata-ken). *J. Japan Oil Chemists' Soc.* 4, 191-3 (1955). For animal fats and fish oils the maximum decoloration occurred when active clay contained 15-18% adsorbed water or acid clay contained 10-12% adsorbed water. For vegetable oils it occurred when active clay contained 12-15% or acid clay contained 8-10% adsorbed water. Excessive drying of clays lowered the effect of decoloration.

The lipide of a fish, Xenogramma carinatum. Taro Matsumoto, Hiroshi Sone, and Isao Niiya (Nihon Univ., Tokyo). *J. Japan Oil Chemists' Soc.* 4, 131-3 (1955). Body lipide of this fish, extracted with ether, showed acid no. 2.6, saponification no. 107.4, iodine no. (Wijs) 90.6, \bar{d}_4^{20} 0.8703, n_D^{20} 1.4617, unsaponifiable matter 46.6%. The unsaponifiable matter consisted of about 60% cetyl alcohol and 35% oleyl alcohol, and the fatty acids consisted of about 60% oleic acid and unsaturated acids with 2, 3, 4, 5, and 6 double bonds. Viscera and liver lipides contained, respectively, 24.5, 11.0% unsaponifiable matter and 2840, 5120 i.u. of vitamin A.

The methods of examination of fats and fat products. Committee reports. Tomotaro Tsuchiya, et al. *J. Japan Oil Chemists' Soc.* 4, 219-23 (1955). Experimental data are presented which led to the selection of the methods described previously for moisture, fat content, acid no. of extracted oil, purification loss, and phosphatides.

Tall oils. IV. Properties and components of Japanese tall oils. Taro Matsumoto, Choichiro Hirai, and Toshitake Tamura (Nihon Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 58, 291-3 (1955). Eleven samples were analyzed especially by ultraviolet absorption spectroscopy. Most oils were derived from *Pinus densiflora*. These tall oils consisted of 32.6-47.1% fatty acids, 24.0-52.3% resin acids, and 12.0-28.9% unsaponifiable matter. The fatty acids consisted of 1.1-9.8% saturated, 42.1-54.3% oleic, 36.8-52.5% linoleic, 0.7-1.9% linolenic, and 4.9-12.0% conjugated dienoic acids. The resin acids consisted of 20-53% abietic acid type; 30-57% of the resin acids were converted to abietic acid type by isomerization. The unsaponifiable matter contained 0.7-7.9% volatile terpenes.

Survey of fats and oils industry of Japan and some of her undeveloped oil resources. Toshiro Takei (Lion Yushi Co., Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 58, 235-8 (1955). A review. Cuttle-fish oil and rice oil are mentioned as undeveloped resources.

The unsaponifiable matter of the seed oil from Impatiens balsamina. Taro Matsumoto, Satoshi Ueyama, and Choichiro Hirai (Nihon Univ., Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.* 75, 346-7 (1954). This seed oil (21% of seed) showed \bar{d}_4^{20} 0.9514, n_D^{20} 1.5070, acid no. 1.9, saponification no. 182.5, iodine no. 203.0. From the unsaponifiable matter were isolated α -spinasterol and β -amyirin.

The seed oils of Bombax sessile and of Lupinus termis. D. N. Grindley and A. A. Akour (Wellcome Chem. Labs., Med. Services, Ministry of Health, Khartoum, Sudan). *J. Sci. Food Agr.* 6, 461-5 (1955). Plants of *Bombax sessile* and *Lupinus termis*, and the characteristics and possible use of their seed oils are described. *B. sessile* oil contained little free acidity or unsaponifiable matter and may be an excellent edible oil. The unsaponifiables from *L. termis* oil contained alkaloids and may be a useful source of carotenoids. Fatty acids were isolated and characterized by iodine values, thiocyanogen values, bromination, oxidation with potassium permanganate or by the Bertram method. *B. sessile* and *L. termis* oils had the following fatty acid compositions (as %): linolenic, ..., 6.80; linoleic, 8.54, 23.40; oleic, 40.80, 52.59; saturated C₁₆₋₁₈, 50.66, 11.33; and saturated C₂₀₋₂₄, ..., 5.88. *B. sessile* has a composition similar to palm oil; *L. termis* oil resembles other members of the Papilionaceae family.

Vegetable oils. IV. A new method of determining the component acids of oils containing epoxy- and/or hydroxy-acids. K. E. Bharucha and F. D. Gunstone (The Univ., Glasgow). *J. Sci. Food Agr.* 6, 373-80 (1955). Seed oils of *Vernonia anthelmintica* and *Strophanthus hispidus* were found to contain 74% 12:13-epoxyoctadec-9-enoic and 15% 9-hydroxy-octadec-12-enoic acid, respectively. The analytical method included the following stages: conversion of epoxy- to dihydroxy-acids by refluxing the oil with 5 volumes of acetic acid for 5 to 7 hrs.; hydrolysis of the products with alcoholic potassium hydroxide and removal of unsaponifiables in the usual manner; partition of the acids between petroleum ether (b.p. 40-60°) and 4:1 methyl alcohol-water; and finally fractionation of the nonhydroxy acids by crystallization from methyl alcohol at -20° or by the lead salt method. Iodine values, saponification equivalents and spectral absorptions were determined for all fractions and used in calculating compositions. The limitations of the usual periodate reagents for the determination of dihydroxy acids are discussed. The most satisfactory reagent seems to be potassium periodate in acetic acid. However, its accuracy was only ± 1.5 to 2%; reactions with triglycerides showed lower errors than reactions with free fatty acids or simple alkyl esters. The method could not be used if the mixture contained epoxy compounds. The following derivatives were prepared: 9-hydroxyoctadec-trans-12-enoic acid; 9:12:13-trihydroxystearic acid; and the *p*-bromophenacyl esters of 9-hydroxyoctadec-cis-12-enoic, 9-hydroxystearic and 12-hydroxystearic acids.

Distillation of tall oil. W. J. A. Spangenberg and K. H. W. Culemeyer (W. Spangenberg Co.). *U. S.* 2,716,630. A two-stage process for the separation of tall oil fatty acids and resin acids is described. Fatty acids are removed in the first stage by distillation under vacuum (less than 20 mm. Hg) and with the aid of wet steam at 230 to 240°. Resin acids are separated from the residue by a similar distillation at 290 to 310°.

Method of obtaining concentrates of carotene. M. C. de Witte. *U. S.* 2,717,210. The oil is mixed with a hydrocarbon which later may be removed from the carotene concentrate at temperatures below 70°. The solution is cooled rapidly (5°/min.) to 10°, and then more slowly (0.5 to 1.5°/min.) until the temperature is -25°. Solids are removed by filtration and the solvent is removed from the filtrate.

Installation for the extraction and treatment of fatty vegetable materials. J. Carpentier (Soc. d'Etudes et de Recherches Industrielles et Chimiques). *U. S.* 2,717,768. Into the walls of the tube receiving the oily material are set electrically insulated windows of thin plates of quartz parallel to the axis of the tube. These quartz plates are excited by a high frequency current. Material is carried through the tube by an Archimedean screw.

Tall oil separation by urea extraction. E. K. Drechsel (American Cyanamid Co.). *U. S.* 2,717,890. A concentrated aqueous solution of urea is added to tall oil until the crystalline complex of urea and fatty acids separates. The precipitate is removed and washed thoroughly with water. Fatty acids, containing no unsaponifiable matter, are obtained by steam distillation of the urea complex under acid conditions. Both the color and color stability of the fatty acids is good.

Process for degreasing wool and the recovery of wool grease. D. P. Norman (Pacific Mills). *U. S.* 2,717,901. Raw wool is extracted with tetrachlorethylene. The extract is removed from the fibers and allowed to separate into two phases, one of which is rich in wool grease.

Oleaginous spread. E. P. Jones, H. J. Dutton and J. C. Cowan (U.S.A., Secy. Agr.). *U. S.* 2,718,468. The spread is prepared from an edible glyceride oil and mono- and diglycerides of fatty acids which are mixed at a temperature at which the additive is soluble in the oil. The mixture is chilled rapidly so microcrystals of the additive form. Preferred mixtures consist of 80 to 90 parts by weight of edible oil, 10 to 20 parts of mono- and diglycerides and 0.5 to 2.0 parts of polyalkyleneglycol esters of fatty acids.

Continuous hydrogenation of fatty oils and acids. Bamag Ltd. and Bernard Bregman. *Brit.* 723,887. A method is described for the continuous hydrogenation of fatty materials by means of intimate and vigorous contact with a catalyst and hydrogen. A mixture of the fatty material and catalyst is caused to flow in a laterally confined stream. Hydrogen is injected throughout the length of the stream transverse to the stream to agitate continuously the stream and to maintain the distribution of the catalyst in the fatty material. Agitation is also by rotary mechanical means. Excess hydrogen is withdrawn from the whole area of the upper surface of the stream. (*C. A.* 49, 11,302)

Separation of fatty acid mixtures. Henkel & Cie. G. m. b. H. *Brit. 724,222*. A method is provided for the separation of a fatty acid mixture with components having different melting points. The mixture is dispersed in an aqueous solution of a capillary-active substance, such as alkylphenol polyglycol ethers, fatty alcohol sulfates, or alkylbenzenesulfonates. Two phases are separated in a centrifuge at a temperature at which part of the fatty acid particles occur as a liquid and part as solid. The two phases are separately removed, and the aqueous solution is removed from the suspended solid fatty acid. The aqueous suspension is heated to separate the solid fatty acid out as a separate layer. Each component thus separated can again be separated at an elevated or lower temperature into a liquid phase and a solid phase. (*C. A. 49, 11,302*)

Practically neutral unsaturated fatty acid esters from sperm oil. E. Grünthal and L. Mannes (Henkel & Cie. G. m. b. H.). *Ger. 871,148*. Sperm oil composed essentially of unsaturated fatty acid esters of fatty alcohols besides a lower amount of triglycerides is treated with water at an elevated temperature and pressure (possibly in the presence of fat-splitting agents and/or solvents) to split the triglycerides without affecting the esters of fatty alcohols. The fission product is then separated from the esters of fatty alcohols and any free fatty acid left in the esters is esterified with fatty alcohols. (*C. A. 49, 10,643*)

Elaidinization of unsaturated fatty acids. H. Wittka (Vereingte Oelfabriken Hubbe & Fahrenholtz). *Ger. 894,559*. The known process of elaidinizing unsaturated fatty acids by heating in the presence of aqueous solutions of bisulfites or sulfurous acid is improved by heating unsaturated fatty acids in the presence of solid anhydride alkali or alkaline earth metal metabisulfites (0.5–2.5%) at an elevated temperature, possibly under pressure. (*C. A. 49, 10,642*)

Treatment for oil containing a large amount of carotenoid. Katsuhiko Miyaji. *Japan 4431('54)*. A mixture of 100 parts palm oil and 2 parts SiO_2 gel-activated C (9:1) is heated in nitrogen for 15 minutes at 100–5° and filtered to obtain a greenish yellow oil. The oil is heated with 1% acid clay for 15 minutes at 100–10° while passing in air, and filtered to obtain a colorless oil. (*C. A. 49, 10,644*)

Catalytic hydrogenation of fats and fatty acids. Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes. *Span. 212,632*. A mixture of the oxides of Cu and Cr, with Cu chromite, is an effective hydrogenation catalyst for use at 150–350° and at 200–350 atm. A similar catalyst may be prepared containing Zn, Cd, and Cu chromite and oxides of these metals. (*C. A. 49, 11,302*)

Catalytic hydrogenation of fats. Empresa Nacional "Calvo Sotelo" de Combustibles Liquidos y Lubricantes. *Span. 215,121*. An improved hydrogenation catalyst, composed of 25–40% Ni, 25–40% Cu, and 20–50% Kieselguhr is used for hydrogenation at 6 atm. and 200°. (*C. A. 49, 11,302*)

FATTY ACID DERIVATIVES

Dibasic fatty acids. II. Synthesis of 1,7-octadiene-2,7-dicarboxylic acid. S. Ouchi. *J. Pharm. Soc. Japan 74, 980–3* (1954). α -Methylsuberic acid was synthesized from ethyl suberate. This dibasic acid when recrystallized from petroleum ether had a m.p. 86–7°. (*C. A. 49, 10,854*)

Preparation, characterization and polarographic behavior of long chain aliphatic peracids. W. E. Parker, C. Ricciuti, C. L. Ogg, and D. Swern (Eastern Reg. Res. Lab.). *J. Am. Chem. Soc. 77, 4037–4041* (1955). A new procedure for the preparation of aliphatic peracids is described. This consists in the reaction of a fatty acid with 0.5–2.0 moles of 50–65% hydrogen peroxide in concentrated sulfuric acid solution. The reaction is an excellent example of the nucleophilic character of hydrogen peroxide. Yields of C_7 - to C_{18} -peracids range from 61–99%, the reactions are rapid at 10° to 30° and product isolation is readily accomplished. The C_7 - to C_{18} -peracids are new compounds and, with the exception of perstearic acid, have been characterized by melting point, ultimate analysis, and chemical and polarographic behavior.

The relationship of charge density, antibacterial activity and micelle formation of quaternary ammonium salts. J. A. Cella, L. A. Harriman, D. N. Eggenberger, and H. J. Harwood (Research Div., Armour and Co.). *J. Am. Chem. Soc. 77, 4264–4266* (1955). An earlier hypothesis that the antibacterial activity of quaternary ammonium salts is influenced by the charge density on the nitrogen atom has not been confirmed. An inverse relationship between antibacterial activity and critical micelle concentration has been shown in the series of compounds studied. It is suggested that steric effects are a major factor

in determining the tendency toward micelle formation and the biological activity of cationic surface active agents.

Plasticizers from fatty oils. III. Plasticizers from oleic, rosin, hydroxy, and fatty acids, and fatty alcohols. Koichi Murai and Giichi Akazome (Nihon Yushi Co., Osaka). *J. Japan Oil Chemists' Soc. 4, 125–7* (1955). Among oleic acid esters synthesized, tetrahydrofurfuryl oleate was the most suitable, and methoxyethyl oleate, phenoxyethyl oleate, and oleoyl diacetyl glyceride were suitable plasticizers for vinyl chloride resin as examined by the methods described previously. The oleic acid esters such as 3,5,5-trimethylhexyl oleate, ethoxyethyl oleate, methoxypropyl oleate, butoxypropyl oleate, methoxypolyethylene glycol oleate, and polyethyleneglycol oleate were immiscible; cyclohexyl oleate was partly miscible. Methyl, butyl, ethoxyethyl, and tetrahydrofurfuryl esters of rosin acid were remarkably hard and should be considered as fillers rather than plasticizers. Oleyl acetyl glycolate, butyl lauroyl glycolate, 2-ethylhexyl lauroyl glycolate, and methyl oleoyl glycolate were miscible, ethyl stearoyl lactate was partly miscible, and methyl stearoyl glycolate was immiscible; even the miscible ones were not good plasticizers.

Manufacture of fatty alcohols by continuous hydrogenation of fatty acids. Sumio Matsuda and Ryoichi Toyoda (Osaka Univ.). *J. Chem. Soc. Japan, Ind. Chem. Sect. 58, 523–8* (1955). An industrially feasible method was devised for preparing Cu-Cr-O catalyst. The activity of the catalyst was remarkably influenced by the conditions of heating. An industrial plant was devised for continuous hydrogenation. Coconut oil and lower boiling coconut fatty acids were successfully converted to the corresponding alcohols.

The derivatives of fatty acids. VI. The surface activity and germicidal property of N-(acyloxyethyl)-pyridinium chlorides. Shin-ichiro Takase (Osaka Univ.). *J. Chem. Soc. Japan, Pure Chem. Sect. 75, 166–8* (1954). These are effective as cationic detergents and germicides. The surface activity was high in lauryl, myristyl, and palmityl compounds. The germicidal property against *Bac. coli* was in the order of myristyl (highest), palmityl, lauryl, caprianyl, stearyl, and capryl compounds.

Antistatic treatment of fibrous materials. L. A. Fluck and A. L. Logan (American Cyanamid Co.). *U. S. 2,718,478*. The fibers are treated with a solution of a water soluble condensation product made from 1 mole of a lower alkylolamide of a dimerized unsaturated higher fatty acid and at least 8 moles of a lower alkylene oxide.

Anticorrosion agents consisting of the monamides of dimerized fatty acids. A. G. Rocchini (Gulf Res. and Dev. Co.). *U. S. 2,718,503*. To the mineral oil is added a small amount of a monoamide of a primary or secondary amine having at least 6 carbons and a dimer of a C_{8-22} di- or tri-ethenoid fatty acid.

• Biology and Nutrition

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

The role of overheated fats in the formation of harmful substances. A. I. Shtenberg and L. P. Naumova (Inst. Nutrition, Acad. Med. Sci. U.S.S.R., Moscow). *Voprosy Pitaniya 13, (2), 41–5* (1954). A critical review is given of non-Soviet scientific literature concerning the role of overheated fats and cholesterol on the formation of harmful substances during the preparation of fat-containing foods. (*C. A. 49, 11,203*)

Lack of effect of a high-fat intake on serum lipid levels. G. V. Mann. *Am. J. Clin. Nutrition 3, 230–3* (1955). Experiments on 2 young male subjects showed no significant increase of serum cholesterol or various β -lipoprotein fractions during 15 days of a diet consisting of 57% fat. (*C. A. 49, 10,455*)

Effects of feeding on the oxidized flavor in milk. I. Effects of cod-liver oil and herring oil. H. Hvidsten, J. Mehlum and H. Simonsen. *Meieriposten 41, 145–51, 170–3, 186–90* (1952); *Biol. Abstr. 27, 3083* (1953). Addition of cod-liver oil to feed for cows produced milk with higher iodine number and vitamin A content in the fat, but lower content of tocopherol and a decreased resistance to development of oxidized flavor. Herring meal added to the ration had no significant effect on the development of oxidized flavor. Considerable individual variations were found between cows as regards the stability and the tocopherol content of the milk. No relation could be detected between the individual variations in the tocopherol content and the resistance of the milk to development of oxidized flavor. (*C. A. 49, 10,457*)

Fat metabolism in three forms of experimental obesity. IV. Instantaneous rates of lipogenesis in vivo. Margaret W. Bates, Claire Zomzely and J. Mayer (Harvard School of Public Health, Boston, Mass.). *Am. J. Physiol.* 181, 187-90 (1955). The retention of C^{14} in carcass and liver lipides 30 minutes after an intraperitoneal injection of C^{14} -carboxyl labeled acetate was measured in 3 types of obese animals: animals with the hereditary obeshyperglycemic syndrome, mice obese with an L.D.₅₀ injection of gold thioglucose, and rats with hypothalamic lesions. The bulk of synthesis appeared to occur in the adipose tissue. In the control mice this was 60-70% of the total synthesis; in the rats it was 80%. In fasted animals, lipogenesis was more markedly affected in the liver than in the peripheral tissues, being decreased to about 15% of the fed values in the liver of the control animals, while peripheral synthesis is decreased only to about 70% of the fed value. When all animals were fed *ad libitum*, the 3 types of obese animals synthesized more fat both in liver and carcass than did their controls. Under fasting conditions the obese-hyperglycemic mice still synthesized more fat than their controls, while the gold thioglucose obese mice and the hypothalamic rats did not synthesize more fat than their controls. (*C. A.* 49, 11,146)

The absorption of short-chain fats by premature infants. S. E. Synderman, S. Morales and L. E. Holt, Jr. (Bellevue Hosp., New York, N. Y.). *Arch. Disease Childhood* 30, 83-4 (1955). The defective fat retention characteristic of premature infants was not observed when tributyrin and triacetin were fed. The nearly complete absorption of these fats suggested that the portal absorption mechanism is unimpaired, and that the defect is in the lacteal mechanism. The superior absorption of these fats is, however, counterbalanced by their inferior caloric yield. Body weight gains from these fats were more than twice those from butter, but less than from corn oil. (*C. A.* 49, 11,110)

Digestion of neutral fats by human subjects. R. S. Harris, J. W. Chamberlain and J. H. Benedict (Mass. Inst. Tech., Cambridge). *J. Clin. Invest.* 34, 685-9 (1955). Liquids recovered from the lumen of the intestine of 11 healthy young men were analyzed for content of free fatty acids, total monoglycerides, and 1-monoglycerides. The level of total monoglyceride ranged up to 13% of the total lipides, and $\frac{1}{2}$ to $\frac{2}{3}$ of this was present as 2-monoglyceride. The free fatty acid content was 2 to 3 times the total monoglyceride content. There was no significant difference in the proportion of fat-digestion products recovered when fat was fed alone and when incorporated into a meal. (*C. A.* 49, 11,111)

Vitamin A, carotenoid, tocopherol and cholesterol contents of blood serum of aged people. F. Curcio (Osp. S. Camillo de Lellis, Rome). *Giorn. Gerontol.* 2, 258-6 (1954). In 21 men and women, 61-96 years old, lower vitamin A, normal vitamin E, and higher cholesterol and carotenoid values were found in the blood serum. (*C. A.* 49, 11,139)

Body lipides in small mammals following prolonged exposures to high and low temperatures. D. R. Young and S. F. Cook (Univ. of California, Berkeley). *Am. J. Physiol.* 181, 72-4 (1955). The group of male Swiss mice exposed to 4° temperature for 30-36 days continuously consumed more food than the 24° controls, showed no growth, and deposited less total lipides than the control group. The mice exposed to the 35° temperature consumed less food than the controls, grew as well as the control group, and deposited similar quantities of lipides. The group of Long-Evans strain rats exposed to a low temperature, although consuming a substantially greater quantity of food than the 24° controls, showed a decrease in growth and deposited less lipides. Those exposed to 35° temperature consumed less food but grew as well as the control group, and deposited similar quantities of lipides. The melting point of the carcass fatty acids of rats shows a tendency to rise with increasing environmental temperature whereas the skin fatty acids retain the same approximate melting point regardless of environmental temperature. (*C. A.* 49, 11,143)

Yellow fat deposition in growing rats. Rosemarie Müller (Anstalt Vitaminforsch. u. Vitaminprüfung, Potsdam-Rehbrücke, Ger.). *Vitamine u. Hormone* 6, 303-17 (1954). The yellow fat deposition is caused by the feeding of large amounts of unsaturated fatty acids in the presence of a vitamin E deficiency. (*C. A.* 49, 11,109)

Human utilization of carotenoids as provitamin A. A. Ciusa and G. Nebbia (Univ. Bologna, Italy). *Acta Vitaminol* 8, 257-62 (1954). A review of the literature leads to the conclusion that carotene probably does not have provitamin A activity for man, or at best acts as such only under special conditions. (*C. A.* 49, 11,108)

Action of vitamin E on sugar balance and on gastric secretion. L. Benacchio (Osp. civile, Lonigo, Italy). *Il Polichinico (Rome) Sez. prat.* 62, 486-90 (1955). In 17 of 20 patients blood sugar was reduced after administration of 200 mg. of vitamin E per day for 8 days. The reduction was noted especially in diabetic patients. Increase in acid values of gastric juice was more evident in cases of low acid content. There was enough correlation in the two groups of data to suggest a causal relation. (*C. A.* 49, 11,106)

The role of lipides in the preparation of hemoglobin and its derivatives. A. Hamsik (Charles Univ., Prague). *Rospravy české akad.* 61(21), 1-17 (1951); *Bull. intern. acad. tchèque* 52, 567-71 (1951). The presence of lipides in the blood brings about a better yield of the derivatives of the coloring matter of blood and of native globin as well. In the presence of lipides, there are formed crystals of blood and of the hemins, in which lipides are complexly bound and difficult to remove. Thus lipides influence the shape and properties of the crystals of blood and of the hemins. Furthermore, the presence of lipides effects a prolonged maintenance of activity of the hemins of which they are the constituents. (*C. A.* 49, 10,415)

Microdetermination of cholesterol and of the cholesterol-protein complex in the blood serum of the cow. N. V. Okunev and S. S. Kruglova (Med. Inst., Stalingrad). *Ukrain. Biokhim. Zhur.* 27, 108-12 (1955). The method used is a slight modification of the one described by Engel'gardt and Smirnova [cf. *Zhur. Eksptl. Meditsiny* 7, 168 (1926)]. Accurate determinations can be made with 0.2 ml. of serum and duplicate results are within the limits of permissible deviation. No special apparatus nor unusual reagents are required. (*C. A.* 49, 10,410)

Lipide constituents of normal bile. B. Isaksson. *Acta Soc. Med. Upsaliensis* 56, 177-95 (1951); *Biol. Abstr.* 27, 2995 (1953). A new procedure for fractional extraction and quantitative determination of bile lipides is presented. Bladder bile samples from 17 patients with normal bile ducts and liver were analyzed by this method. Total lipides were about 25% of the solids. Of the lipides about 80% was lecithin, the rest mainly cholesterol. Neutral fat and free fatty acids occurred only in inconsiderable quantities. Soaps were not found. Analytical data on bladder bile from dog, cow and calf are also given. (*C. A.* 49, 10,473)

Presence of volatile fatty acids in bovine semen. (21835). R. J. Flippe and F. E. Potter (Dairy Breeding Res. Center, Dept. Dairy Science, Penn. State Univ., University Park). *Proc. Soc. Exp. Biol. and Med.* 89, 432-3 (1955). Concentrations of 0.79-2.50 meq. of volatile fatty acids per 100 ml. were found in pooled ejaculates of bovine semen. Acetic and formic acids were identified as the major volatile fatty acid constituents by column chromatography, paper chromatography and selective oxidation.

Unsaturated fatty acids of blood serum from pigs with and without parakeratosis. H. Hvidsten, W. G. Hoekstra, R. H. Grummer, and P. H. Phillips (Dept. Biochem., College of Agr., Univ. of Wisconsin, Madison). *Proc. Soc. Exp. Biol. and Med.* 89, 454-5 (1955). As a part of nutritional studies on parakeratosis in swine, the content of essential fatty acids in blood serum of pigs with and without parakeratosis was determined. It is concluded that low levels of the essential fatty acids in the blood are not associated with the development of parakeratosis.

Hydrolysis of lecithin by plant plastid enzymes. M. Kates (National Research Labs., Ottawa, Canada). *Can. J. Biochem. & Physiol.* 33, 575-589 (1955). Enzymatic liberation of choline from egg lecithin by plastid fractions from sugar beet, spinach, and cabbage leaves, and from carrot root was a rapid, first order reaction (up to 70% hydrolysis), and was not preceded by a lag phase. None of the choline-containing products of lecithin degradation (lysolecithin, glycerylphosphorylcholine, or phosphorylcholine) lost choline on incubation with spinach chloroplasts. Inorganic phosphate liberation from lecithin by the plastids was preceded by a lag phase and was much slower than choline liberation. The L- α -structure for egg lecithin was confirmed.

Capacity of the rat intestine to absorb cholesterol. (21832). T. M. Lin, E. Karvinen, and A. C. Ivy (Dept. of Clinical Science, Univ. of Illinois College of Med., Chicago). *Proc. Soc. Exp. Biol. and Med.* 89, 422-3 (1955). The existence of a limited capacity for cholesterol absorption in the rat has been demonstrated. At dietary levels of from 50 to 288 mg. per 250-g. rat per day the percentage of cholesterol absorption decreased as a linear function. The amount of cholesterol absorbed reached a plateau when the dietary cholesterol intake was 192 mg. per 250-g. rat per day. Under the conditions

specified, the capacity of the intestinal mechanism for the absorption of cholesterol in a 250-g. rat is 90 mg. or approximately 360 mg. per kilo body weight per day.

Paper electrophoretic study of C¹⁴ fat emulsion cleared from post-heparin rat plasma. (21838). R. A. McDaniel and M. I. Grossman (U. S. Army Nutrition Lab., Fitzsimons Army Hospital, Denver, Colo.). *Proc. Soc. Exp. Biol. and Med.* **89**, 442-3 (1955). C¹⁴-labeled fat emulsion was incubated with post-heparin plasma and the mixture was then subjected to filter paper electrophoresis. Some of the C¹⁴ activity was found to migrate with the albumin fraction.

A histochemical study of normal and cirrhotic livers. P. O'B. Montgomery (Dept. of Pathology, Univ. of Texas, Southwest-Med. School, Dallas, Texas). *Proc. Soc. Exp. Biol. and Med.* **89**, 355-357 (1955). Liver cells contain lipids, potassium, free aldehyde groups, sulfuric acid esters of mucopolysaccharide origin, protein bound sulfhydryl groups, mucoproteins, calcium, non-specific esterase, ribonucleic acid and vitamin C. The lipids of the liver cell showing fatty metamorphosis is histochemically different than normal liver cell lipid. The non-specific esterase activity is increased and clumped in the fatty liver. Fatty liver appears to contain more vitamin C than the normal liver.

The effect of cholesterol feeding on the distensibility of the isolated thoracic aorta of the rabbit. J. T. Nichol (Univ. of Western Ontario, London, Canada). *Can. J. Biochem. & Physiol.* **33**, 507-516 (1955). The descending thoracic aortas of control and cholesterol fed rabbits were dissected out. These aortas were used to prepare tension-length diagrams. Cholesterol feeding increased the distensibility at pressures up to 70 mm. Hg, but at pressures above this value no significant change is produced. Cholesterol feeding increases the resistance of the aorta to collapse, i.e., the longer the cholesterol feeding continued, the greater the magnitude of the negative pressure required to make the vessel segment collapse.

Filament induction in Escherichia coli by ricinoleic acid. (21817). Virginia Whiteside-Carlson, B. F. Feaster, and W. W. Carlson (Dept. Biochem. and Cancer Res. Labs., Univ. of Alabama Med. Center, Birmingham). *Proc. Soc. Exp. Biol. and Med.* **89**, 382-385 (1955). Sodium ricinoleate interferes with cell division in *E. coli* causing the organisms to develop as filaments. The effect appears to be specific and dependent upon the 9:10 unsaturation and the 12-hydroxy group as well as the *cis*-configuration around the double bond, present in this fatty acid. A variety of metabolites, as well as other organic and inorganic compounds, were tested for an ability to induce cell division in filamentous forms of the organisms. Of the substances evaluated, only inorganic phosphate consistently and rapidly caused such an effect.

Aggravating effect of cholesterol on cardiovascular changes in choline deficient rats. (21850). G. F. Wilgram, C. H. Best, and J. Blumenstein (Banting and Best Dept. of Med. Res., Univ. of Toronto, Canada). *Proc. Soc. Exp. Biol. and Med.*, **89**, 476-9 (1955). Cholesterol supplements (4%, 2% and 1% in decreasing order of effect), increase the rate of occurrence of cardiovascular lesions in choline-deficient female and male rats which are resistant to the effects of choline-deficiency alone. The significance of kidney damage in the production of these cardiovascular lesions is discussed. The aggravating effect of cholesterol on choline-deficient tissues occurs in the presence of decreased serum cholesterol levels. The significance of choline in the production of experimental arteriosclerosis depends upon the procedures used.

Improved substrate for study of clearing factor. (21796). I. Zuckerman and H. O. Singher (Dept. of Biochemistry, Ortho Res. Found., Raritan, N. J.). *Proc. Soc. Exp. Biol. and Med.* **89**, 315-317 (1955). A commercially available 50% coconut oil emulsion (Ediol) diluted one hundred fold with physiological saline and mixed with 5 volumes of normal plasma or of 3% albumin is a good substrate for the study of clearing factor in heparinized plasma. Albumin is only one of the cofactors for the clearing factor.

The lipoxidase activity of wheat. J. A. Blain and J. P. Todd (Food Sci. Section, Royal Tech. College, Glasgow, C. I.). *J. Sci. Food Agr.* **6**, 471-9 (1955). A method for estimating the lipoxidase activity of extracts from various wheat fractions is described. Wheat embryo was carefully cleaned and defatted with pentane-trichloroethylene mixtures. Enzyme extracts were prepared by grinding embryo, endosperm or whole wheat with sand and 0.1 N acetate buffer at pH 4.5 and then centrifuging. Lipoxidase activity was determined by measuring the rate of decoloration of linoleate-carotene suspensions. Some characteristics of the reaction were studied. One unit of

lipoxidase activity is defined as the quantity which will destroy 0.015 mg. of carotene in 5 mins. at 20° under the assay conditions. Lipoxidase activities were determined in fractions from various types of wheat. Activities in dry, fat-free embryo ranged from 40.4 to 94.9, and in dry endosperm from 0.9 to 2.0 units/g. Scutellum had an activity similar to embryo.

Studies on the aerobic oxidation of fatty acids by bacteria.
V. Caprate oxidation by cell-free extracts of Pseudomonas fluorescens. D. Ivler, J. B. Wolfe and S. C. Rittenberg (Dept. Bacteriology, Univ. S. Cal., Los Angeles). *J. Bacteriology* **70**, 99-103 (1955). *Pseudomonas fluorescens* was cultured in a liquid mineral salts medium with 0.4% disodium malonate as the carbon source. Cell-free extracts were obtained by grinding the dried cells with 0.05 M phosphate buffer at pH 6.1, and centrifuging. The extract oxidized caprate, consuming one micromole of oxygen per micromole of substrate. Adenosine triphosphate and coenzyme A were required for the oxidation; acetate was found at the end of the reaction. After partial fractionation of the extract with ammonium sulfate, only ½ micromole of oxygen was consumed per micromole of caprate oxidized. Mg⁺⁺ temporarily inhibited oxidation. An unidentified compound accumulated, having an R_f on paper chromatograms similar to those of β-hydroxy and α,β-unsaturated caprates. It is concluded that the mechanism involves β-oxidation of an activated caprate.

Biochemical studies on the fat of sardine body. I. The seasonal variation of fat, unsaponifiable matter, and cholesterol contents in several tissues of sardine body. Masafuto Wada (Nagasaki Univ.). *J. Agr. Chem. Soc. Japan* **29**, 339-42 (1955). The deposition of fat was found in every part examined (muscle, liver, and fatty tissue) and was especially remarkable in the fatty tissue. The fat content became maximal in August, and decreased extremely in December immediately before the spawning season. Both unsaponifiable matter and cholesterol in the liver was much higher than in any other part of the fish. The change of these contents was inversely proportional to the change of fat content, and both of them were markedly stored up immediately before the spawning season.

II. The seasonal variation in fat and lecithin contents of the sardine liver. *Ibid.*, 342-3 (1955). Lecithin was stored up in the liver together with the increase in fat from the spring to the autumn, and both lecithin and fat decreased toward the winter. Lecithin increased and kept up a high constant value, while fat decreased gradually, immediately before the spawning season.

III. The seasonal variation in the fat content in different tissues of male and female sardines. *Ibid.*, 465-71 (1955). After the spawning season fat is deposited rapidly, and its highest value came in July-August. The deposition of fat took place not only in the fatty tissue, but also in the liver, muscle, gonad, head, and even gills of the fish. In the winter simultaneously with maturing of the gonad the depot fat in every tissue decreased to the spring level. The fatty tissue nearly disappeared and fat was utilized also in the liver. In the spring, the deposition of fat was slightly greater in the female than in the male. However, the fat deposition of the male exceeded that of the female from the autumn to the winter. Immediately after the spawning much larger amount of fat was found in the female than in the male.

IV. The relation between the character of fat and the fish conditions. *Ibid.*, 471-3 (1955). The characteristics of fatty oil from the muscle were scarcely influenced by the degree of corpulency, sex, or age of the fish, when they were captured at the same time.

V. Fatty acids and unsaponifiable matter contents in the sardine gonad of different maturity. *Ibid.*, 473-5 (1955). In the spawning season a sudden change occurred in the content of fat constituents in the gonad. Simultaneously with the maturation of the gonad, fatty acids and unsaponifiable matter contents increased remarkably and they were spent extremely in spawning. The degree of this variation was more remarkable in the female than in the male.

The nutritive value of aliphatic alcohols. I. The nutritive value of C₁-C₈ saturated alcohols. Motoyoshi Miyazaki (Food Research Inst., Tokyo). *J. Agr. Chem. Soc. Japan* **29**, 497-501 (1955); *Rept. Food Research Inst.* (Tokyo) **10**, 185-92 (1955). The nutritive value was measured by the gain (or loss) of the weight of albino rats maintained on a standard restricted diet before the test. Methyl alcohol showed a slight toxicity. Ethyl, propyl, butyl, isobutyl, and isoamyl alcohols were utilized by rats, but their nutritive values were lower than those of soybean oil and glucose. Isopropyl alcohol was hardly utilized and tert-butyl alcohol retarded the growth of rats.

II. The nutritive value and toxicity of C₆-C₁₈ saturated alcohols. *Ibid.*, 501-5(1955); *Rept. Food Research Inst.* (Tokyo) 10, 193-9(1955). Hexyl alcohol was utilized slightly by rats, while octyl, decyl, dodecyl, and tetradecyl alcohols gave toxic effects. Cetyl alcohol had weak toxicity and octadecyl alcohol gave no effect on rats because of low absorption.

The $\Delta^{5,7}$ -sterols in some kinds of Japanese fresh-water shell-fish. Taro Matsumoto, Toshitake Tamura, and Shunsuke Ito (Nihon Univ., Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.* 76, 953-6(1955). Ultraviolet absorption spectroscopy of the digitonides of the sterol fraction revealed the presence of $\Delta^{5,7}$ -sterol at 6-13% (of sterol) in *Viviparus malleatus*, *V. japonicus*, *Corbicula japonica*, *C. leana*, *Cristalia spatiosa*, *Anodonata woodiana*, and *A. woodiana lauta*. There seemed to be at least 2 kinds of this sterol with different solubilities in acetone-methanol.

The sterols of *Viviparus japonicus*. Taro Matsumoto and Toshitake Tamura (Nihon Univ., Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.* 76, 951-3(1955). The ether extract (64 g. from 4.5 kg. air-dried sample of this rolled shell-fish) had n_D^{20} 1.675, acid no. 30.2, saponification no. 106.3, iodine no. 112.2 (Wijs). By repeated fractional crystallization as acetate bromides, the sterols of this lipid were identified as brassicasterol, poliferasterol, cholesterol, and α -sitosterol. By ultraviolet absorption spectrum the presence was proved of $\Delta^{5,7}$ -sterol, though not isolated.

Chemical and biochemical studies on cardiolipin. I. Isolation of cardiolipin from bacteria and other sources. Ichiro Hara (Univ. Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.* 76, 910-14(1955). Antisyphilitic phospholipid was isolated from *Corynebacterium diphtheriae*, human brain, black muscle of tuna, sheep testis, and human placenta by the method of M. C. Pagborn [*J. Biol. Chem.* 161, 71(1954)]. This was presumed to be similar in structure to cardiolipin from ox heart because of P content (4.0-4.7%), iodine no. (80-114), and serological activity. The cardiolipin from ox heart was changed in solubility but not changed in serological property after hydrogenation from iodine no. 119 to 10.

II. Cardiolipin-clupein complex. *Ibid.*, 914-19(1955). Cardiolipin and cephalin combined with clupein in all pH ranges to form lipoprotein soluble only in organic solvents. Lecithin combined with clupein only on the alkaline side. Cardiolipin-clupein reacted with syphilitic serum similarly with cardiolipin. Cardiolipin-clupein had no blood-coagulating action.

Concentration of vitamin A by the solvent method. V. By the use of urea adduct. Yoshiro Abe and Toyoko Ihara (Keio Univ., Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 58, 511-14(1955). The liver oil of the fish, *Theragra chalcogramma*, was subjected to methanolysis with alkaline catalyst such as NaOH, KOH, or metallic Na. Vitamin A was concentrated by removing saturated and monoethenoid fatty acids as urea adduct. Na at 1.5% lowered the yield of vitamin A. The vitamin A concentrated by this method was very unstable. Further concentration could be obtained by applying this method after molecular distillation.

Gossypol-cephalin compound from fresh eggs of hens fed cottonseed meal. C. L. Woronick, C. R. Grau (Dept. of Poultry Husbandry, U. of Calif., Davis, Calif.). *J. of Ag. and Food Chem.* 3, 706-707(1955). The cephalin fraction of egg yolks from hens fed gossypol is yellow in color and possesses an absorption spectrum with maxima at 380 and 400 m μ . Gossypol was identified in the cephalin fraction after oxalic acid hydrolysis. The reaction of gossypol with ethanolamine and with ethylamine resulted in products having absorption spectra that were almost identical with the absorption spectrum of gossypol egg cephalin. It is concluded that the aldehyde groups of gossypol condense with the primary amino groups of phosphatidylethanolamine to form a Schiff base which is present in the egg.

The separation of sphingosine and related compounds by reversed phase partition chromatography. J. B. Wittenberg (Dept. of Biochem., School of Med., Western Reserve U., Cleveland, Ohio). *J. of Biol. Chem.* 216, 376-390(1955). Sphingosine and related compounds have been separated by reversed phase partition chromatography on silicized diatomaceous earth. Prior to chromatography these compounds are converted to their N-succinyl derivatives by reaction with succinic anhydride. Compounds differing in the number of their hydroxyl groups, in methylation of one hydroxyl group, and in degree of unsaturation have been separated. A new assay for sphingosine is proposed. Sphingosine and related compounds are converted to the N-succinyl derivative, and the carboxylic acid group thus introduced is titrated with alkali. Quantities of from 3 to 100 m μ moles are determined with an accuracy of 5%.

The value of animal fat for different strains and crosses of broilers. S. J. Slinger, J. D. McConachie and W. F. Pepper (Dept. of Poultry Husbandry, Ontario Ag. College, Guelph, Canada). *Poultry Science* 34, 789-794(1955). One hundred chicks from each of ten different strains and crosses were fed practical broiler diets and a like number received these same diets modified to contain 5% of stabilized animal fat. Efficiency of feed utilization was enhanced in the case of every strain and cross by the inclusion of animal fat. This difference proved to be highly significant statistically.

Studies on vitamin E poultry nutrition. M. L. Scott, F. W. Hill, L. C. Norris, D. C. Dobson and T. S. Nelson (Cornell U., Ithaca, N. Y.). *J. Nutrition* 56, 387-402(1955). A basal diet has been developed which appears to be suitable for use in the study of uncomplicated vitamin E deficiency in the chick. The occurrence of vitamin E-deficiency symptoms in chicks receiving the basal diet was not influenced to a measurable extent by the presence or absence of pro-oxidants or antioxidants in the diet.

Chemistry of vitamin A. XXIV. The synthesis of geometric isomers of vitamin A via methyl β -methylglutaconate. C. D. Robeson, J. D. Cawley, L. Weisler, M. H. Stern, C. C. Eddinger and A. J. Chechak (Research Lab. of Distillation Products Ind., Div. of Eastman Kodak Co.). *J. Am. Chem. Soc.* 77, 4111-4119(1955). A method is described for the synthesis in pure crystalline form of four geometric isomers of vitamin A for the *cis*- and *trans*- β -ionylideneacetaldehydes via the intermediate 4-carboxyvitamin A acids. On the basis of certain described properties of these isomers, assignments of their stereochemical configurations have been made. Three isomers, the all-*trans*, the 2-*cis* and the 6-*cis* appear to be identical with those already reported, while the fourth, the 2,6-*di-cis*, had not been described previously. The preparation and properties of " α -vitamin A," the structural isomer in which the ring double bond has the same position as in α -ionone, are also described.

Chemistry of vitamin A. XXV. Geometrical isomers of vitamin A aldehyde and an isomer of its α -ionone analog. C. D. Robeson, W. P. Blum, J. M. Dieterle, J. D. Cawley and J. G. Baxter (Research lab. of Distillation Products Industries of Eastman Kodak Co.). *J. Am. Chem. Soc.* 77, 4120-4125(1955). The preparation of four synthetic geometrical isomers of vitamin A aldehyde (identified as all-*trans*, 2-*cis*, 2,6-*di-cis*, 6-*cis*) is described. Their ultraviolet absorption spectra, infrared spectra and other physical and chemical properties are given. The configuration of a fifth isomer of vitamin A aldehyde, neoretinene-b, was also studied. A 2,4-*di-cis* structure was preferred for it over a possible 2-*trans*, 4-*cis* configuration. An all-*trans* " α -vitamin A aldehyde" was synthesized from α -ionone. Its properties were different from those of the 6-*cis* and 2,6-*di-cis* isomers which excluded the possibility that the latter two compounds might be geometrical isomers of α -vitamin A aldehyde.

Dietary fat and life span. *Nutrition Reviews* 13, 278-279(1955). It would seem from these data that short-term feeding (five months) of a diet moderately high in fat can somewhat prolong the life of an animal, providing the diet is fed early in life. On the other hand, long-term feeding of such a diet can reduce the animal's life span. While the mechanisms underlying this duality of action are quite unknown, these observations emphasize again the uniqueness of dietary fat as such.

The metabolism of n-butyrate-C¹⁴ by mammalian heart muscle. V. Lorber and Margaret Cook (Dept. of Physiology, U. of Minn. School of Med. Minneapolis, Minn.) *J. of Biol. Chem.* 215, 823-832(1955). Acetoacetate, β -hydroxybutyrate, crotonate, vinyl acetate, lactate, pyruvate, and fumarate have been isolated from the perfused, sliced, or minced mammalian heart metabolizing n-butyrate-3-C¹⁴, and their isotope distribution patterns determined. The results are consistent with the reaction sequence postulated for butyrate oxidation on the basis of enzymatic studies and with the reactions of Krebs cycle as the main route of interconversion of the products of butyrate oxidation to carbohydrate precursors. In the absence of added carrier, acetoacetate and β -hydroxybutyrate have been found to accumulate to a slight extent during butyrate oxidation in the heart.

Marine sterols. I. Isolation of 24-methylenecholesterol from molluscs. D. R. Idler, U. H. M. Fagerlund (The Pacific Fisheries Exp. Sta.). *J. Am. Chem. Soc.* 77, 4142-4144(1955). A new sterol, 24-methylenecholesterol, has been isolated by a chromatographic separation of the azoyl esters prepared from the sterols of the oyster (*Ostrea gigas*) and the clam (*Saxidomus giganteus*). Oyster and clam sterols contain 36 and 53%, respectively, of this sterol.

Metabolism of epicholesterol-4-C¹⁴ in the rat. F. M. Harold, M. E. Jayko, I. L. Chaikoff (Dept. of Physiology, U. Calif.

School of Med., Berkeley, Calif). *J. Biol. Chem.* **216**, 439-447 (1955). The elimination of the C^{14} of intravenously injected epicholesterol-4- C^{14} from the bodies of rats with cannulated bile ducts has been studied. In the course of 48 hours, approximately 50% of the injected C^{14} was excreted via the bile. In that period, only 0.6% was excreted via the feces. Ninety per cent of the biliary C^{14} was in the form of bile acids and the rest in non-saponifiable steroids. The C^{14} bile acids formed resembled taurochenodeoxycholic acid and taurocholic acid, but were not identical with them. It is concluded that epicholesterol is not an intermediate in the conversion of cholesterol to bile acids. Dihydrocholesterol has been shown to be a product of epicholesterol metabolism in the rat. The conversion of epicholesterol to cholesterol could not be demonstrated.

Some factors affecting the quantity of water-insoluble fatty acids in cream. L. K. Crowe (Dairy Husbandry Dept., Univ. of Neb., Lincoln, Neb.). *J. Dairy Science* **38**, 969-980 (1955). Holding cream at low temperatures did not assure a low water insoluble acid content. Reduction in water insoluble acid levels during the holding of cream at 40°-50°F. and 55°-60°F. were obtained. Extraction of fatty acids by the Hillig procedure from cream acidified with lactic acid was incomplete. High water insoluble acid values in cream resulted from excessive agitation of milk during cooling. The accuracy of identification of cream with a high water insoluble acid content by direct titration of the fat has been shown.

Chemistry of vitamin A. XXVI. The condensation of aldehydes with methyl β -methylglutaconate. J. D. Cawley (Research Lab. of Distillation Products Ind.). *J. Am. Chem. Soc.* **77**, 4125-4129 (1955). The condensation of a variety of aldehydes with methyl β -methylglutaconate to yield alkylidene- β -methylglutaconic acids is described. The ultraviolet absorption spectra of these are consistent only with their having a *cis* relationship of the R and C(CH₃)=CH-CO₂H groups about the newly created double bond. Certain of the compounds differ in chemical and physical properties from those previously reported by Petrow and Stephenson.

Biochemical studies on vitamin A. XIV. Biopotencies of geometric isomers of vitamin A acetate in the rat. S. R. Ames, W. J. Swanson, P. L. Harris (Research Lab. Distillation Products Ind., Div. of Eastman Kodak Co.). *J. Am. Chem. Soc.* **77**, 4134-4136 (1955). The physiological potencies of three new isomers, 6-mono-*cis*, 2,6-di-*cis*, of vitamin A acetate as well as of neo (2-mono-*cis*) vitamin A acetate have been determined using standard vitamin A bioassay procedures. Neovitamin A acetate (2-mono-*cis*) has a biopotency of 2,190,000 units/gram. The 6-mono-*cis*-vitamin A acetate has a biopotency of 634,000 units/gram; the 2,6-di-*cis* isomeric acetate has a biopotency of 688,000 units/gram; and the 2,4-di-*cis* isomeric acetate has a biopotency of 679,000 units/gram.

XV. Biopotencies of geometric isomers of vitamin A aldehyde in the rat. *Ibid.* 4136-4138 (1955). The physiological potencies of five geometric isomers [all-*trans*, neo-(2-mono-*cis*), 6-mono-*cis*, 2,6-di-*cis*, and 2,4-di-*cis*] of vitamin A aldehyde and of α -vitamin A aldehyde have been determined. All-*trans* and neo-(2-mono-*cis*)-vitamin A aldehydes have the same biopotency of 3,070,000 μ /g., about 91% the molar bioactivity of all-*trans*-vitamin A acetate. The 6-mono-*cis*- and 2,6-di-*cis*-vitamin A aldehydes have the relatively low biopotencies of 637,000 and 581,000 μ /g., respectively about 18% the molar bioactivity of all-*trans*-vitamin A acetate. The 2,4-di-*cis*-vitamin A aldehyde has a biopotency of 1,610,000 μ /g., about 48% the molar bioactivity of all-*trans*-vitamin A acetate. The α -ionone analog of vitamin A aldehyde has less than 2% the potency of vitamin A acetate and during metabolism it is converted to the corresponding α -vitamin A alcohol which is stored in the liver.

Method of accelerating the growth of chicks. C. M. Ely and S. Schott (National Distillers Products Corp.). *U. S. 2,717,809*. Improved growth of chicks is obtained when 0.05 to 0.50% of sodium soaps of C₈₋₁₈ fatty acids is added to the solid feeds.

• Drying Oils and Paints

Raymond Paschke, Abstractor

New shape for paints. Anon. *Chem. Eng. News* **33**, 4108 (1955). The thixotropic gellation of alkyds with polyamide resins is discussed. The Washburn process is outlined. These vehicles are now being used by 120 paint formulators.

Drying oil oxidation mechanism, film formation, and degradation. S. B. Crecelius, R. E. Kagarise, and A. L. Alexander (Na-

val Res. Lab., Washington, D. C.). *Ind. Eng. Chem.* **47**, 1643 (1955). The work on the autoxidation of drying oils was instituted in order to gain more insight in regard to the mechanism of oxidation and decomposition of oil-modified film coatings, particularly when exposed to ultraviolet light. Strong evidence was found that under artificial lighting conditions certain definite chemical reactions take place in films of linseed and dehydrated castor oil, such as formation of OH groups, probably hydroperoxide groups, increase in carboxyl groups, shift toward conjugation of double bond systems, and changes involving *cis-trans* isomerism. There is also evidence that vinyl polymerization may be one of the chief mechanisms of film solidification. Exposure of dried films to intense ultraviolet light results in rapid decomposition and weight loss of the oil films, the infrared spectra indicating that there is a loss in OH groups, CH₂ groups, and carboxyl group which correlates quite closely with the weight losses. This work has practical significance as a basis for predicting in advance, the behavior of oil modified air drying films on exposure to ultraviolet light.

Casting of free paint films on press polished polyethylene. J. S. Heckles (Armstrong Cork Co., Lancaster, Pa.). *Off. Dig. Federation Paint Varnish Production Clubs* **27**, 519 (1955). The advantages of polyethylene over mercury are noted. Paint films pigmented or clear can be cast on press polished polyethylene, cured and removed by lifting one edge with a spatula and pulling the entire film off intact. The polyethylene sheets can be reused by cleaning with paint solvents or alkalis until they become too scratched for further film casting. Paints based on alkyds, styrenated oils, and linseed oil have released well.

Evaluation of dehydrated castor oil in exterior white house paints. T. C. Patton (Baker Castor Oil Co.). *Off. Dig. Federation Paint Varnish Production Clubs* **27**, 627 (1955). On long range performance, 100% DCO white house paints appear fully equivalent to linseed oil paints and in the important case of self-primed paint systems (applied over the most commonly used woods) DCO appears to contribute better durability.

Atmospheric pollution control. D. C. Sayles (Sayles Chemical Consultants, Dayton, Ohio). *Off. Dig. Federation Paint Varnish Production Clubs* **27**, 566 (1955). It is an inescapable fact that the surface coating producers are notoriously guilty of releasing large quantities of pollutants into the atmosphere. Cost of gas cleaning can easily be offset through an effective by-product reclamation program. This paper discusses the problems and their solutions.

Styrenation of alkyds with controlled maleic functionalities. L. Schechter and J. Wynstra (Bakelite Company, Bloomfield, N. J.). *Ind. Eng. Chem.* **47**, 1602 (1955). Polyesters and oil-modified alkyds containing a small amount of an α,β -unsaturated dibasic acid such as maleic, along with a major proportion of a nonreactive dibasic acid, such as phthalic, can be copolymerized with vinyl monomers to yield soluble, homogeneous products. The alkyd must be carefully selected, however, to yield useful copolymers. Several alkyd composition factors—maleic content, degree of esterification, type of polyalcohol, and extent of oil modification—which are interdependent on one another were combined in one parameter, maleic functionality, which was then used to define the operable alkyd composition range for copolymer formation under a given set of conditions. A mathematical formula to calculate this functionality was derived and found very useful in predicting whether a given polyester composition can be expected to yield a gelled or soluble, a heterogeneous or homogeneous product on styrenation. Although empirical and of no exact physical meaning, these functionality values did provide a valuable screening tool in a systematic survey of styrenated maleic-based alkyds.

Paints. F. Schofield (Nat. Paint Varnish Lacquer Assoc., Washington, D. C.). *Ind. Eng. Chem.* **47**, 2007 (1955). A resumé of the year's advances in the paint industry. Discussed are (1) anticorrosive paints and other coatings for metals, (2) house paints, moisture, and the painting of wood, (3) newer materials such as the epoxy resins, and (4) special use paints such as those for retarding fire, preventing mildew, retaining insecticides, etc.

Analysis of lacquers containing nitrocellulose, alkyd resins, and phthalate-type plasticizers. M. H. Swann, M. L. Adams, and G. G. Esposito (Paint and Chem. Lab., Aberdeen Proving Ground, Md.). *Anal. Chem.* **27**, 1426 (1955). Lacquers containing nitrocellulose, alkyd resins, and plasticizers such as esters of phthalic or phosphoric acid are used as protective coatings for automotive equipment and other ordnance applications. New methods have been developed for solvent separation of

nitrocellulose, direct spectrophotometric determination of total phthalate, separation and analysis of phthalate ester plasticizers by charcoal adsorption, and nonvolatile and phosphate ester determinations.

Liquid oiticica oil (cicoil) and its industrial use. L. Huffman (Brasil Oiticica S. A., Rio de Janeiro). *Vernici* 7, No. 3, 31-43 (1951). The following data are reported for cicoil: viscosity (Gardner-Holdt, 25°) W-Y, color value (Gardner) 9-11, heat test (ASTM) max. 17 min., d_{20}^{20} 0.9770-0.9880, n_D^{25} 1.5090-1.5130, free fatty acid max. 4%, saponification no. 186-93, nonsaponifiable matter max. 1.5%. Cicoil and the stand oil prepared from it are useful for the preparation of oil varnishes, oil alkyls, styrolized oils, mixed vinyl polymers, and printing inks. (*C. A.* 49, 11,300)

Paint industry (in Japan). Saburo Toyota. *J. Japan Oil Chemists' Soc.* 4, 194-8 (1955). Production records (1953-54), production planning (1955), development of synthetic resin paints, raw materials, imports and exports, and standards for paints are discussed.

Drying property of fish oils and its improvement. V. Thermal polymerization of maleic acid-treated cuttle-fish oil and its drying property. Hideo Marumo, Akira Nakajima, and Shin-ichi Tomiyama (Lion Yushi Co., Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.* 58, 424-9 (1955). Cuttle-fish oil with low saturated fatty acid content fractionated by low-temperature interesterification and dewaxing was treated with maleic acid. Heat polymerization occurred even at 230° and was considered to be intermolecular polymerization which was unaffected by temperature. The activation heat was 12.8 kcal./mol., i.e. much lower than for linseed oil. Polymerized oils had excellent drying property. The product could be utilized for various varnishes in place of linseed oil.

VI. Thermal polymerization of phthalic acid-treated cuttle-fish oil and its drying property. *Ibid.*, 430-2 (1955). Results similar to those in Part 5 were obtained. The activation heat was 18.3 kcal./mol.

VII. Thermal polymerization of fractionated cuttle-fish oil and its drying property. *Ibid.*, 432-6 (1955). Fractionated cuttle-fish oil with low saturated acid content was polymerized even at 230°. The activation heat was 18.3 kcal./mol. The treatment with phthalic acid did not affect the polymerization velocity. The presence of saturated acid residue and mono- and diglycerides affected the drying property of polymerized fish oils.

• Detergents

Lenore Petschaft Africk, Abstractor

Unilever's new process of household soap manufacture. Anon. *Soap, Perfumery, Cosmetics* 29, 1010-13 (1955). The new Unilever process of manufacture of "Sunlight" and other household soaps is described. The installation consists of several units, comprising chilling drums, 5-roll mills with chilled iron rolls, vacuum refiner plodders, automatic cutting tables, conditioning towers, and scrap refiners. The output of each unit is approximately 2½ tons per hour.

The role of colloidal electrolytes in decontamination studies. R. C. Chandler and W. E. Shelberg (U. S. Naval Radiological Defense Lab., San Francisco, Calif.). *J. Colloid Sci.* 10, 393-401 (1955). The removal of radioactive particulate matter from surfaces by immersion in colloidal electrolytes began with the formation of micelles and increased rapidly with micellar concentration up to 2- to 3-fold the CMC. The decontamination was independent of surface tension. The relation between micellar concentration and decontamination suggested that adsorption of the particulate matter occurred on the micellar interface competing with the original surface. In very dilute solutions at concentrations below the CMC the surface tension, conductance, and turbidity data suggested that small concentrations of secondary colloids were formed in that region.

Synthetic detergents. F. C. Cooke (Coconut Research Inst., Lunuwila). *Ceylon Coconut-Quart.* 5, 131-3 (1954). The replacement of coconut oil-base soaps with synthetic detergents is discussed. (*C. A.* 49, 12,020)

A study of the oleophilic properties of sodium soap of the saturated fatty acids by heat of wetting method. P. A. Demchenko and L. G. Demchenko. *Dopovid Akad. Nauk Ukr. RSR.* 1952, 284-7. Heat liberated by wetting of Na soap of the saturated fatty acids is a result of the formation of addition compounds. Heat of wetting per g. of soap decreases about 0.06 calories per C atom from the C chain of the soap. One molecule of Na ste-

arate binds about one mole of saturated hydrocarbon or styrene. Na soaps of the higher fatty acids have 2-3 times more heat of wetting than cellulose wetted by the same hydrocarbon. The structural elements in lubricant greases is probably a compound of soap, H₂O, and hydrocarbon in about stoichiometric proportions. (*C. A.* 49, 10,642)

Techniques for evaluating low-foaming detergents. M. N. Fine-man, H. L. Greenwald and C. G. Gebelein (Rohm & Haas Co., Bridesburg, Pa.). *Soap Chem. Specialties* 31 (8), 43-6, 183, (9), 50-2 (1955). Techniques which have been used in the development of new low-foaming surfactants, and low-foaming detergent formulations in applications where foam is undesirable, are described. These techniques include: a novel laboratory apparatus (the Foameter) which simulates the action of a mechanical dishwasher and permits evaluation of foam under controlled conditions of temperature and spray pressure; adaptation of a standard home dishwashing machine as a test instrument and evaluation of detergency efficiency by means of a dynamic hard surface detergency test using a Launder-Ometer. The correlation of foaming behavior in practice with that observed in the Foameter was excellent. It was also found that evaluation of foam of a surfactant in absence of inorganic salts, and over a range of temperatures, provides a more sensitive indication of differences observable in the field, than evaluation of foam of the built formulation. Temperature is the major factor in determining the foam of nonionics, higher foams being produced at the lower temperatures.

Optical bleaching—white magic. S. N. Glarum (Ciba Co., Inc., New York). *Am. Dyestuff Repr.* 44, 625-30 (1955). The optical mechanism by which optical bleaches produce whitening effects and the advantages over bluing agents are illustrated. The versatility of the optical bleaching agents for use on textiles is discussed, as well as the factors that must be considered in selecting the best product for a particular job.

Visual observations of the behavior of soil particles in dilute aqueous soap systems. C. W. Hoek (Hercules Powder Co., Wilmington, Del.). *Textile Research J.* 25, 682-5 (1955). The nature of one type of detergent action was demonstrated visually upon the addition of graphite to sodium oleate solutions of laundry strength. The graphite became coated with elongated soap particles and superficially bore a resemblance to pieces of candy covered with shredded coconut. The soap particles, which may bear some relation to micelles, measured 100 to 150 Å wide and from 500 to 1500 Å long. This exploratory study involved an electron microscopical examination of specimens from which the water had been removed while in the frozen state. This study does not indicate how the soap, with the aid of mechanical work, accomplishes removal of soil in the first place, but it does suggest that by surrounding the soil, the soap particles prevent its redeposition on cloth. This may be brought about by equivalence of charges between the soil-soap complex and the substrate-soap complex, thereby leading to repulsion.

Viscosity behavior of nonionic detergents upon dilution. J. V. Karabinos and A. T. Ballum (Blockson Chem. Co., Joliet, Ill.). *Euchides* (Madrid) 15, (167), 8-11 (1955). The viscosity of most, but not all, polyoxyethylene-type nonionic detergents examined was first increased and then decreased by the addition of progressive amounts of water from 40 to 300 ml./g. of detergent. A polyoxyethylene derivative of the resin acids of tall oil showed no increase, derivatives of decyl alcohol showed only a small increase, while those of dodecyl and octadecyl alcohol showed very large increases. It is concluded that the viscosity behavior is related to the structure of the hydrophobic group. (*C. A.* 49, 11,301)

Viscoelastic properties of aqueous soap gels. N. Pilpel (King's Coll., London). *Trans. Faraday Soc.* 50, 1369-78 (1954). The mechanical properties of some aqueous viscoelastic soap gels were investigated by the following methods: laminar-flow viscosities by capillary flow, elasticities by measurements of the pressure distribution set up during continuous shearing in the rheogoniometer. The mechanical properties of different gels were compared in terms of 3 quantities: a viscosity coefficient, a relaxation time, and a recoverable shear. The variation of these quantities with soap concentration, and on the addition of small amounts of other materials, were investigated. Gel formation took place as a result of interlinking throughout the material of long, threadlike soap micelles. (*C. A.* 49, 10,009)

Improvements in soap compositions. Unilever Ltd. *Brit.* 733, 416. Toilet soap tablets for use in hard water are prepared by milling soap, a non-soapy anionic organic detergent and about 5% of a seum-reducing aid consisting of alkyl or acyl phenols or their ether derivatives, drying the resulting compound, and then plodding and stamping.