

any unsaponified fat present in the soap. The chloroform sometimes tends to spread or emulsify, in which case a little amyl alcohol with chloroform has been found satisfactory. The whole is filtered through a moist filter paper which retains all of the chloroform. At the end of the filtration the chloroform is transferred from the filter paper by puncturing the apex and finally washing the cone of the filter paper with a little alcohol. The free fatty acid can be checked by titration of this chloroform-alcohol solution with alcoholic potash and the total fatty matter by actual weighing after evaporation of the chloroform on a water-bath. It might be noted that by using chloroform, as described above, the tedious process of repeatedly extracting with ether can be avoided even if this direct titration method is not applied. This is easier and quicker and dispenses altogether with the use of a separatory funnel.

In order to investigate how far the usual substances present in commercial soap may introduce complications due to their solubility in the solvent medium, we have determined the solubility of these salts in the mixed solvent. These are given in Table I.

TABLE I.
The Solubility at 25° of Salts in a Mixed Solvent Containing Equal Volumes of Propylene Glycol and Isopropyl Alcohol.

	NaCl	Na ₂ CO ₃	Na ₂ B ₄ O ₇ , 10H ₂ O	Na ₃ PO ₄ , 12H ₂ O	Na silicate
g. anhydrous salt per 100 g. solvent.....	0.898	0.143	9.05	traces	traces

It is seen that with the exception of borates and possibly to some extent carbonates, none of the salts is soluble enough or basic enough to affect the results appreciably. The soap may be separated from borates and carbonates by extracting it with hot alcohol. However, the method is primarily applicable to the analysis of pure soaps for which purpose it was developed, and extension of it to commercial soaps could be done only after finding a suitable method to separate the soap from the extraneous matter. Appre-

ciable amounts of water affect the accuracy of the titration but by using 1 gm. of soap per 10 to 15 ml. of solvent no special drying is necessary since the presence of water to the extent of as much as 30% of the weight of soap will not noticeably affect the result. Commercial samples of the solvents have been used throughout without any purification or dehydration as they generally contain less than 1% water.

In a comparative study of the present method with the standard method (2), the results obtained by analysis of a sample of commercial toilet soap are compiled below in Table II. The proposed method is simpler and quicker and gives equally accurate results.

TABLE II.
Comparison of the Analysis of Toilet Soap by Scott's Method and by the Present Method of Direct Titration.

	Wt. of soap used (gms.)	Per cent free alkali	Per cent Na ₂ O	Per cent fatty acid	Per cent soap
Standard method.....	5.0821	0.00	10.76	83.12	90.86
Direct titration.....	1.1910	0.00	10.80	82.23	90.90

Summary

Glycol, or preferably its mixture with a solvent for hydrocarbons, such as isopropyl alcohol or chloroform, possesses high solvent power for soaps, which may be directly titrated with strong acids, either potentiometrically or with the use of methyl red or methyl orange. The ionization of the organic acid is suppressed so that salts of weak acids can be directly titrated by this method. The colors of the indicators are brighter and the end-point sharper than those in alcohol or water.

Acknowledgment

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REFERENCE

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2. Furman, N. H., "Scott's Standard Method of Chemical Analysis," D. Van Nostrand Co., 5th ed., Vol. II, p. 2029 (1939).

Abstracts

Oils and Fats

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VISCOSITIES AND DENSITIES OF SOLVENT-VEGETABLE OIL MIXTURES. F. C. Magne and E. L. Skau. *Ind. Eng. Chem.* **37**, 1097-1101 (1945). A pycnometer and a viscometer suitable for use with volatile mixtures and for low-temperature determinations are described. Density and viscosity measurements are made from incipient crystallization to a temperature near the boiling point of the solvent for the complete binary systems cottonseed oil-Skellysolve B (commercial hexane), cottonseed oil-acetone, cottonseed oil-2-butanone, peanut oil-Skellysolve B, and soybean oil-Skellysolve B. From these data it is possible to construct soybean oil-Skellysolve B. From these data it is possible to construct for any of these systems the density-composition and viscosity-composition curves for any temperature as well as the density-temperature and viscosity-temperature curves for any composition. The various systems are compared and their

idealities discussed. The density-composition curves for the binary systems of Skellysolve B with the 3 oils practically coincide. The viscosity-composition curves for these systems almost coincide up to about 60% by weight of oil and then diverge to the values of 100% oil. The same is true of the binary systems of cottonseed oil with the 3 solvents, except that the curves start to converge again at about 90% to meet at the 100% oil value. The applicability of these data to other random samples of these vegetable oils is discussed.

THE SYNTHESIS AND CONFIGURATION OF D-14-METHYLPALMITIC ACID AND ITS IDENTITY WITH THE NATURAL ACID FROM WOOL FAT. S. F. Velick and J. English, Jr. *J. Biol. Chem.* **160**, 473-80 (1945). *d*-14-Methylpalmitic acid has been synthesized, starting from the *d*-2-methylbutanol-1 of fusel oil. The synthetic acid is identical with the natural acid isolated from wool.

The proposed structure and configuration of the so-called anteiso acids of wool fat are thus confirmed.

LARD AS PROTECTIVE MATERIAL FOR MEATS. R. L. Hiner. *Quick Frozen Foods* 8, No. 4, 126, 131, 150 (1945). The lard used in these tests consisted of a mixture of leaf, back, plate, and trimming fats. During storage it was noted that weight losses of samples stored at +18°F. unprotected were about twice as much as those stored at 0°F., both in still air. Among samples stored with a lard coating, only those stored at +18°F. showed any weight loss and it was small. At +18°F. storage both protected and unprotected samples decreased in palatability and showed undesirable chemical changes at 12-, 24-, and 36-week intervals. The rate at which these changes took place was greater for the unprotected samples between 24 and 36 weeks than that of the protected samples. In the samples stored at 0°F. little difference was found between protected and unprotected samples at any of the 3 storage intervals. However, these samples were all more palatable and showed less chemical changes after 36 weeks' storage than those stored at +18°F. for only 12 weeks. Lard will remain in good condition for a considerable length of time when held at a temperature of 0°F. However, if the temperature of storage is too high or the time too long the lard may impart a slightly rancid flavor to the meat. It would appear that this could be overcome by the use of a suitable antioxidant.

SPECTROPHOTOMETRIC AND FLUOROMETRIC MEASUREMENT OF CHANGES IN LIPIDES. H. J. Dutton and B. G. Edwards. *Ind. Eng. Chem.* 37, 1123-6 (1945). Changes that occur in the lipide fraction of dehydrated eggs during storage have been studied by spectrophotometric and fluorometric techniques. The reaction of lipide amines with aldehydes, the destruction of carotenoids, and a process that has been interpreted as polymerization of the unsaturated fatty acids were found to proceed faster at 98° than at 70°F.; little change was detected at 15°F. The fluorescing substance that develops in the fat of dehydrated eggs during storage has been tentatively identified as the reaction product of lipide amines with aldehydes.

RANCIDITY OF BACON. EFFECTS OF ANTIOXIDANTS. F. H. Smith, D. E. Brady, and R. E. Comstock. *Ind. Eng. Chem.* 37, 1206-9 (1945). The effects of antioxidants—(1) nordihydroguaiaretic acid (NDGA), (2) *d*-isoascorbyl palmitate, soybean lecithin, and mixed tocopherols, and (3) gossypol in 5 different concentrations—in retarding the development of peroxides in slices of unsmoked and smoked bacon were studied and compared with corresponding slices receiving no treatment. The antioxidants dissolved in vegetable oils were applied to the surface of the slices. This study showed that all of the antioxidants were effective in retarding the development of peroxides, the effectiveness of the gossypol varying with the concentration used. The induction or keeping period for the treated slices was 3-5 times longer than for those receiving no antioxidants. Smoking retards the development of rancidity in bacon.

ANTIOXIDANTS FOR FISH OILS. Dorris L. Bucher. *Fishery Market News* 7, No. 7, 17-19 (1945). Fish oils are variable in natural antioxidant content and are often afforded little protection by seed extracts, gum guaiac, citric acid, tartaric acid, wheat-germ oil,

etc., which inhibit oxidation of other oils. Hydroquinone (I) in 0.1% concentration in fish oil gave a protection factor of 12; α -naphthol (II) acted similarly but imparted an off-flavor. Nordihydroguaiaretic acid (III) gave the following protection factors in salmon body oil exposed in open Petri dishes in a 37° oven: 3.5 at 0.05%, 6.0 at 0.10%, 9.0 at 0.15%, 12.0 at 0.20%. In the 2 latter cases, a slight bitter taste was observed after the natural oil flavor disappeared and tended to confuse the organoleptic tests for rancidity. In herring oil tested in a bubbling tube at 100°, 0.10% of III gave a protection factor of 4. The efficiency of III seems equal whether it is dissolved or suspended. Gallic acid in 0.1% concentration gave protection factors of 6 in salmon oil and 4 in herring oil. A graph compares peroxide formation with time, for exposure to air bubbling at 100° of salmon body oil samples containing I, II, III, resorcinol, or β -naphthol. Preliminary reports indicate that gallic acid esters (Me, Et, Pr, Am, hexyl, octyl, decyl, or cetyl) or the pure acid give protection factors of 2.5 to 20 when the gallate radical is present in 0.1% concentration in oils from dogfish livers, shark livers, menhaden, salmon, pilchards, and seals. These gallates did not appear to be toxic to rats. (*Chem. Abs.* 39, 4767.)

CONTROL OF RANCIDITY IN STORED FISH. H. L. A. Tarr. *Prog. Repts. Pacific Coast Stas.* No. 64, 57-61 (1945). Dipping fillets of pink salmon for one minute in 0.5% Et and Pr gallate solutions prior to storing at 14°F., considerably delayed the subsequent onset of rancidity. With salmon and herring flesh stored at -4°F., Et gallate, Pr gallate and ascorbic acid considerably retarded rancidity, while cysteine conferred only a slight protection and lauryl thiodipropionate and thiourea gave no protection or actually accelerated fat oxidation. Peroxide value was used as a criterion for spoilage; duration of the storage test periods were up to 176 days and the storage temperatures were 14, -4 and -18°F.

THE UNION OF GASEOUS OXYGEN WITH METHYL OLEATE, LINOLEATE AND LINOLENATE. F. D. Gunstone and T. P. Hilditch. *J. Chem. Soc.* 1945, 836-41. The autoxidation of Me oleate in diffused daylight at temperatures between 20 and 130° has been followed by the changes in its peroxide and I values and some of the autoxidized products have been further examined. The process is very slow at 20° and somewhat faster at 50°, but from 80° onwards it becomes very rapid and apparently differs in character from the oxidation at lower temperatures. At the higher temperatures there is development of considerable free acidity, which was shown to be due mainly to oxidative breakdown at the unsaturated group and consequent production of mono- and di-carboxylic acids (including those of the C₃ as well as of the C₉ series). Autoxidation of Me linoleate at 20°, 50° and 80° proceeds with increasing rapidity, but the temperature-coefficient appears to be more constant in this case than with Me oleate. The relative rates of autoxidation of Me oleate, linoleate, and linolenate at 20° were 1:12: ca. 25, the presence of the system —CH:CH·CH₂·CH:CH— causing a marked increase in ease of union with O₂.

INFLUENCE OF SOME FATS AND PROTEINS ON THE THYROID. W. Bergfeld. *Verhandl. deut. Ges. inn. Med.* 52, 412-13 (1940). In rats, feeding large amounts of

fibrinogen or lard caused increased I excretion and decreases in the wt. and the I content of the thyroid. Feeding large amts. of casein or coconut oil did not produce these effects. (*Chem. Abs.* 39, 4358.)

THE INFLUENCE OF AGE AND DIET ON THE LIPID COMPOSITION OF THE RAT. H. H. Williams, H. Galbraith, M. Kaucher and I. G. Macy. *J. Biol. Chem.* 161, 463-74 (1945). The lipid distribution was determined in the whole bodies of new born rats and animals 15, 45, and 70 days old, and in the whole bodies of control rats and litter mates after each had ingested 3,000 calories of an adequate, high fat, or high carbohydrate diet. The essential lipid pattern is altered significantly during growth and development. The concentrations of phospholipid and free cholesterol decrease, whereas those of cerebrosides and cholesterol esters increase, probably not only as the result of changes in the composition of individual tissues but also because of the changes in the relative proportions of the various tissues present in the body. Although diets in which 40-70% of the calories were derived from fat had no influence on the essential lipid composition of the body, a diet in which less than 10% of the calories was furnished by fat produced an apparently significant alteration. On the latter diet the rats contained less cerebrosides and free cholesterol and more esterified cholesterol.

VITAMIN A POTENCY OF OHIO BUTTER. W. E. Krauss, L. Skinner, J. W. Hibbs, T. V. Armstrong and W. L. Slatter. *Bimonthly Bull.* 30, 157-63 (1945). The average vitamin A potency of these butters showed considerable seasonal variation—from a low of 8,800 I.U. per pound in March, 1943, to a high of between 16,500 and 17,000 I.U. per pound in May and Sept. of 1944. The average vitamin A potency for summer-produced butter (May through Nov.) was 15,500 and for winter-produced butter (Dec. through April) was 10,400 I.U. per pound. The mean annual potency, weighted for production, was a little less than 14,000 I.U. per pound. This value compares favorably with the national average. It was found that butter loses little of its original vitamin A potency while in storage at 0°F. for as long as 12 months. Butter produced in northwestern Ohio was higher in vitamin A potency during the drier months of the pasture season, while that produced in southeastern Ohio reached a high peak in potency earlier in the spring. These variations are presumed to be related to the kind of pastures predominating in those areas and to seasonal differences.

PATENTS

METHOD OF TREATING RAW ANIMAL FATS. E. Ratner. *U. S.* 2,388,284. Oleo oil is expressed from fresh suet in a hydraulic press at 20-25°. The oil is said to have better taste and odor than that commonly produced at 28-32°.

PROCESS OF PRODUCING FAT-SOLUBLE VITAMIN CONCENTRATES. L. O. Buxton (National Oil Products Co.). *U. S.* 2,389,955. A process of producing fat-soluble vitamin concentrates comprises admixing an antioxidant for vitamins A and D with a fat-soluble vitamin-containing marine oil, saponifying the marine

oil by means of an alkali and separating the unsaponified fraction from the saponified mass, the antioxidant added to the oil prior to saponification serving to inhibit destruction of the vitamins during and after the saponification reaction.

PRODUCING UNSATURATED COMPOUNDS. H. G. Kirschenbauer (Colgate-Palmolive-Peet Co.). *U. S.* 2,389,260. Unsaturated fats containing unconjugated acids are saponified with a slight excess of alkali at 235-50° (below polymerization temperature), at which temperature the unsaturated constituents are conjugated, the product is then acidified, the acids are recovered and esterified with alcohol.

FAT ACID SEPARATION PROCESS. J. D. Fitzpatrick and L. D. Myers (Emery Industries, Inc.). *U. S.* 2,389,191. A process of separating azelaic acid pelargonic acid and by-product acids from one another in oxidized unsaturated fat mixtures comprises first removing the pelargonic acid content by distillation, adding water to the mixture of azelaic acid and by-products acids thereby forming 2 layers, one containing a solution of azelaic acid and the other consisting essentially of by-product acids, removing the by-product acids from the aqueous solution of azelaic acid and evaporating the water from the solution of azelaic acid.

CONDENSED HALOGENATED TALL OIL PRODUCTS AND METHOD FOR MAKING THE SAME. E. Lieber (Standard Oil Development Co.). *U. S.* 2,389,203. An improved wax modifier comprises a Friedel-Crafts condensation product of about one part by weight of halogenated "tall oil" and about 3-4 parts by weight of an aromatic organic compound.

SELECTIVELY HYDROGENATED TALL OIL. J. A. Turck, Jr. and J. Ross (Colgate-Palmolive-Peet Co.). *U. S.* 2,389,284. The process of saturating olefinic bonds of unsaturated fatty acids in tall oil comprises treating tall oil with H₂ at a pressure of at least 50 pounds per square inch in the presence of a Ni catalyst and at a temperature about 50° but below 135°.

FRACTIONATION OF TALL OIL. A. W. Hixson and R. Miller (Chemical Foundation, Inc.). *U. S.* 2,388,412. Tall oil is separated into a rosin oil and a fatty acid fraction by countercurrent liquid-liquid extraction with propane at a temperature of 90°. The upper fraction consists of fat acids dissolved in propane and the liquid from the lower end of the system comprises liquid rosin containing some dissolved propane.

LUBRICANTS FOR COLD REDUCTION OF STEEL. R. W. Kingerley, Jr. (E. I. du Pont de Nemours & Co.). *U. S.* 2,391,631. A lubricant for use in the cold rolling of steel comprises a major amount of mineral oil, 0.2-0.5 sulfonated castor oil, 0.5-2.0 tricresyl phosphate, and 0.05-0.3% of lorol phosphate.

BARIUM CALCIUM MAGNESIUM STEARATE GREASE. F. A. Leyda (California Research Corp.). *U. S.* 2,389,523. A mixed-base, anhydrous grease consists of mineral oil and stearates and palmitates of Ba, Ca, and Mg; the Mg stearates and palmitates being present in such proportions as to produce a thermally reversible grease.