

was noticed. The solid was more reddish in color. A Lovibond color analysis gave the following results: 15 yellow and 1.4 red for the original oil and for the supernatant fraction; and 20 yellow and 2.3 red for the solid fraction.

Discussion

Under the conditions of these laboratory experiments hexane does not show promise as a practical solvent for use in the solvent winterization of cottonseed oil. A very close control of both the temperature and the oil-solvent ratio would be necessary in order to regulate the amount of solid separating in a 3-hour chilling period. At a given chilling temperature the initial rate of crystallization is very low up to a certain oil-solvent ratio. An increase beyond this ratio results in a sharp increase in the amount of solid separating. A high degree of supersaturation seems to be necessary before the initial rate of crystallization is appreciable. A longer holding-time results in more solid separating with a less sharp break in the curve. However a holding-time longer than 3 hours would probably be impractical for a continuous process. Gentle agitation does not result in any appreciable improvement. Another disadvantage of hexane as compared to acetone is the fact that a much lower chilling temperature would be required to produce a winterized oil, the difference being from 10° to 15°C. and, at oil concentrations less than 40%, even greater.

The use of acetone as a solvent has the advantage of a much more favorable chilling temperature and a definite improvement in the settling qualities of the crystals which form. It has the distinct disadvantage that the presence of a small percentage of moisture may cause the formation of two liquid phases in addition to the solid phase at the chilling temperatures required for adequate winterization, thus causing complications in the subsequent isolation of the solid.

The use of a mixture of acetone and hexane eliminates the major disadvantages experienced with either solvent alone. The mixture containing 15 parts by weight of hexane prevents the formation of two liquid layers at the temperatures required for adequate winterization, using acetone having a water content as high as 1.4% by weight, and it still does not cause

the tendency toward supercooling exhibited when hexane alone is used. Compared with the acetone system the chilling temperature necessary to attain a specified degree of winterization is from 2° to 7°C. lower. The difference is greatest at low oil-solvent ratios. A slightly more rigid control of concentration is required to regulate the yield, but the temperature control is of the same order of magnitude for the mixed solvent as with acetone. If the moisture content of the acetone used is greater than 1.4% by weight, a larger proportion of hexane in the mixed solvent would be necessary.

The ability of the solid to pack out on centrifuging depends upon the oil-solvent ratio, the chilling temperature, and the solvent used, being very low at a given temperature for a small percentage of solid removed, increasing to a maximum, and then decreasing as the percentage increases. These maxima appear at different percentages of solid removed, calculated on the basis of the original oil present in any given solution. However they all correspond to the same number of grams of solid removed from 100 grams of solution.

Summary

Systematic phase relation data pertaining to the solvent winterization behavior of a refined cottonseed oil have been obtained for two additional solvents; namely, commercial hexane and a mixed solvent consisting of 85% by weight of acetone and 15% of hexane. Graphs have been constructed to show the effect of oil-solvent ratio, chilling temperature, holding-time, and agitation on the percentage of solid removed, the degree of winterization and the settling qualities of the solid separating.

These data, with those previously reported for acetone (1), afford a basis for the selection of the optimum conditions and procedures in the application of solvent winterization to cottonseed oil and bring out the relative advantages, disadvantages, and limitations of the three solvents. The acetone-hexane mixture seems to combine the advantages and eliminate the disadvantages of either of these solvents alone.

REFERENCES

1. Skau, E. L., Dopp, W. N., Burleigh, E. G., and Banowetz, L. F. *J. Am. Oil Chem. Soc.*, 27, 556-564 (1950).

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ABSTRACTS

Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

Report on crude fat or ether extract. H. H. Hoffman (Florida Dept. of Agr., Tallahassee). *J. Assoc. Off. Agr. Chem.* 34, 558(1951). A possible alternate AOAC method was investigated in which the extraction time was reduced to 4 hours and the solvent flow increased. Insufficient collaborative data have been reported to judge the method.

Report on fat in fish meal. M. E. Stansby (U. S. Dept. Interior, Seattle, Wash.). *J. Assoc. Off. Agr. Chem.* 34, 549(1951). Preliminary results obtained on extraction of fish meal by boiling in acetone indicate that the oil is extracted rapidly by this method. Further work is planned.

The edible oil industry, a challenge to chemical engineering. W. H. Goss (Pillsbury Mills, Inc.). *Chem. Eng. Prog.* 47, 489 (1951). The limitations imposed upon processing conditions by requirements peculiar to human foods, i.e., flavor, appearance, and nutritional value, have slowed down application of principles learned in other fields to the edible oil industry.

Avocado oil from Kenya. E. Brown and M. W. Jarvis. *Colonial Plant and Animal Products* 1, 318(1951). Avocado oil obtained from the pulp of the Fuerte variety grown in Kenya was found to be very similar to that obtained from California fruit as shown by the following constants: sp. gr., 0.9155; n_D^{20} , 1.4688; acid value, 1.1; saponification value, 191.8; unsaponifiable matter, 0.7%; iodine number (Wijs), 82.6; acetyl value, 6.3.

Chemical engineering in the meat-packing industry. M. D. Sanders, A. W. DeVout, P. Bradford and W. F. Bollens (Swift &

Co.). *Chem. Eng. Prog.* **47**, 441(1951). A brief description is given of unit operations in the meat-packing industry, such as rendering, fat splitting, saponification, and solvent extraction.

Crocodile oil from Tanganyika. H. Bennett, E. Brown, T. J. Coomes, D. Morton and W. D. Raymond. *Colonial Plant and Animal Products* **1**, 315(1951). Crocodile oil prepared from the whole carcass had the following characteristics: specific gravity, 0.9231; n_D^{20} , 1.4629; saponification value, 201.4; iodine number (Wijs), 91.3; unsaponifiable matter, 1.1%. The oil had a fishy odor and was cloudy at room temperature.

The polymorphism of 2-acetyl-, 2-butyryl- and 2-caproyl-distearin and -dipalmitin. F. L. Jackson, R. L. Willie and E. S. Lutton (Procter & Gamble Co.). *J. Am. Chem. Soc.* **73**, 4280 (1951). A study of polymorphism by thermal and diffraction methods is reported for 6 symmetrical diacid triglycerides in which the 2-position is occupied by a very short chain. The polymorphism of these compounds shows several hitherto unreported features—specifically the sub- α -1, α -1, and super α -1 forms and the multiplicity of beta-type forms for the caproyl glycerides. Such abnormalities in behavior presumably result from the relatively large role played by the carbonyl portions of the short acyl groups.

Application of spray drying principles to the desolventization of miscella. C. J. Barr (Iowa State Coll., Ames). *Iowa St. Col. J. Sci.* **25**, 153(1951). Soybean oil-trichloroethylene miscellas were desolventized in a spray dryer using steam at 357° as desiccant. Preliminary results indicate that oil quality is good and steam requirements are roughly half of those of a conventional desolventizer.

Estimation of antioxidants in lard and shortening. J. H. Mahon and R. A. Chapman (Dept. Nat. Health and Welfare, Ottawa, Canada). *Anal. Chem.* **23**, 1116(1951). Procedures have been developed for the extraction and colorimetric determination of propyl gallate, butylated hydroxyanisole, nordihydroguaiaric acid, and tocopherol in lard and shortening. The procedure permits the determination of all combinations of these 4 antioxidants except when propyl gallate and NDGA are present in the same samples. The lower limits of the determinations, with high accuracy, are propyl gallate 0.003%, BHA 0.005%, NDGA 0.005%, and tocopherol 0.015%. However, satisfactory results have been obtained at much lower levels. These procedures permit study of relative rates of destruction of individual antioxidants in mixtures of lard and shortening.

Butylated hydroxyanisole in lard and shortening. *Ibid.* 1120. Because butylated hydroxyanisole is usually present in relatively large amounts, its rapid and accurate determination in the range of 0.01 to 0.02% is of interest. The average standard deviation for a single determination by this method is 1.1% of the amount present.

The constitution of mycolipenic acid—I. N. Polgar and R. Robinson (Oxford Univ.). *Chem. Ind.* 1951, 685. Preliminary work on the constitution of this acid isolated from the lipids of tubercle bacilli indicates that it may have the formula $CH_3(CH_2)_{11}CH(CH_2)CH(CH_2)CH: C(CH_3)CO_2H$.

The distillation, extraction, and chromatographic separation of the C₂-C₈ fatty acids. D. Fairbairn and R. H. Harpur (McGill Univ., Montreal). *Can. J. Chem.* **29**, 633(1951). Thirty-five ml. of an aqueous solution containing 5-70 micromoles of C₂-C₈ acids was distilled to constant volume without refluxing. The distillate was titrated, made alkaline, and evaporated to dryness at 110°. The free acids were regenerated with 10 N H₂SO₄, absorbed on filter paper and extracted with 3 ml. chloroform-butanol (99:1). Acids present in the extract were separated on a silica gel column and, after elution, were determined by titration.

A rapid and exact method for determination of the fat content in foods and fodders, especially in fish meals. Th. Seeler and R. Dietrich (Handelslab. Dr. Th. Seeler, Bremerhaven, Ger.). *Landw. Forsch.* **3**, 43-6(1951). The determination of fat in fish meals by Soxhlet extraction proved to be unsuitable, as was shown by comparison with the method by Stoldt (HCl-treatment), by which much higher values were obtained. Exact results were obtained with a combined method by Stoldt and Gottlieb-Rose and the procedure is more feasible with less cost of time and material. (*Chem. Abs.* **45**, 7271)

Optimum conditions for the manufacture of blown rape oil. T. R. Sharma, Om Prakash and D. Y. Athawale (H. B. Technol. Inst., Cawnpore). *Proc. Ann. Convention Oil Technol. Assoc. India* **2**, 6-9(1945). Preparation of blown rape oil for admix-

ing with mineral oil lubricants was investigated. The oil should be steamed and filtered to remove mucilaginous and suspended matter. The most suitable temperature consistent with the quality of the product as well as the period of blowing was about 125°. Detailed data (viscosity, acid value, iodine no., and color) are tabulated for temperatures of 125, 150, 175, and 200°, and blowing times of 7 and 14 hrs. (*Chem. Abs.* **45**, 7804)

Characteristics of papri oil (Haloptela integrifolia). S. N. Chatterjee and R. K. Gobhil (H. B. Technol. Inst., Cawnpore). *Proc. Ann. Convention Oil Technol. Assoc. India* **2**, 43-4(1945). *Haloptela integrifolia* is a large deciduous tree of the lower ranges of the Himalayas. The seed comprises: husk 27.5, kernel 72.5, moisture 3.2, oil in dry kernel 53.2, and oil in whole seed 37.4%. The oil is yellow, is similar to ghee, has d_4^{20} 0.9001, n_D^{20} 1.4580, acid no. 1.6, saponification no. 203, iodine no. (Wijs) 52, Reichert-Meißl no. 0.27, Polenske no. 0.25, unsaponifiable 3.2%, and solidifies at 13.5°. (*Chem. Abs.* **45**, 7803)

Paper chromatography in the fat field. V. Radiometric determination of the iodine number. H. P. Kaufmann and J. Budwig (Chem. Landesuntersuchungsamt Nordrhein-Westfalen, Munster, Ger.). *Fette u. Seifen* **53**, 253-9(1951). The Hanus method for the determination of the iodine no. has been adapted to paper chromatography. The reagent was I¹³¹Br in methanol saturated with NaBr. Samples of the order of 20 γ are used. The sample (in heptane) is deposited on the paper, the solvent is allowed to evaporate, reagent is added until there is no further fading of the color, the paper is washed, and the radiation is measured. (*Chem. Abs.* **45**, 7801)

Alkali refining of cottonseed oil. A. P. Sharma and J. B. Lal (H. B. Technol. Inst., Cawnpore). *Proc. Ann. Convention Oil Technol. Assoc. India* **2**, 30-2(1945). Refining tests on cottonseed oils were made with solutions containing 9.27, 14.25, 19.15, and 20.49% NaOH. In single-stage refining 9.27% NaOH effected the greatest removal of color at 30° and at 40°. In two-stage alkali refining with 100% of the theoretical amount of alkali in the 1st stage and 10% in the 2nd stage, better decolorization was obtained at 40° than at 30° provided a higher concentration of refining agent is used. (*Chem. Abs.* **45**, 7803)

Fractionation and composition of some lipid fractions of diphtheria bacteria. E. M. Gubarev, E. K. Lubenets, A. A. Kanchukh and Yu. V. Galaev (Med. Inst., Rostov). *Biokhimiya* **16**, 139-45(1951). Extraction of dry *Corynebacterium diphtheriae* PW No. 8 with benzene for 84 hrs. in a stream of CO₂ yields 4.9% lipids. The fraction of the benzene extract that was soluble in ethyl ether and insoluble in acetone gave on hydrolysis the sugar trehalose and the following fatty acids: α -hydroxycorinnic acid, m. 70°, neutralization no. 106.4, acetyl no. 86.6; β -hydroxycorinnic acid, m. 59°, neutralization no. 106.4, acetyl no. 96.7; α -corinnic acid, C₂₆H₅₀O₂, m. 64°, neutralization no. 106.4, iodine no. 5.67; β -corinnic acid, C₂₆H₅₀O₂, m. 44-45°, neutralization no. 109.9, iodine no. 21.2. After the benzene extraction, a second extraction was made with chloroform. An additional 1.8% lipids was obtained. This also consisted of trehalosides of higher fatty acids. (*Chem. Abs.* **45**, 7637)

The low-frequency dielectric properties of some symmetrical mixed triglycerides in the solid state. R. W. Crowe and C. P. Smith (Princeton Univ., Princeton, N. J.). *J. Am. Chem. Soc.* **73**, 2040-5(1951). The dielectric properties at frequencies from 0.5 to 50 kilocycles for 2-palmitodistearin, 2-stearodipalmitin, 2-laurodistearin, 2-oleodipalmitin, and 2-oleodistearin of various thermal histories were measured over a wide temperature range in the solid state and correlated with existing x-ray diffraction and thermal data. The dielectric properties and dispersion characteristics of the α -forms of 2-palmitodistearin, 2-oleodipalmitin, and 2-oleodistearin are very similar to those of tripalmitin and tristearin, for which it was suggested that the dipole orientation was that of molecular segments rather than of the entire molecule, a process that could easily account for the observed distribution of relaxation rates. Although α -forms were found for 2-stearodipalmitin and 2-laurodistearin, they are not of sufficient stability to be isolated in the pure state. Like the simple triglycerides, the thermodynamically stable forms of these substances (usually β) showed slight variation of m.p. with thermal history. (*Chem. Abs.* **45**, 7399)

Vegetable oils. W. H. Shearon, Jr. *Chem. Eng. News* **29**, 4065 (1951). A review giving the properties, quantities available, and yields per acre of the various vegetable oils.

Branched-chain fatty acids. XVIII. Ultraviolet absorption spectra of saturated branched-chain acids. J. Cason and G.

Sumrell (Univ. Calif.). *J. Org. Chem.* 16, 1177(1951). It is shown that substituent alkyl groups in fatty acids exert an influence on the ultraviolet absorption band of carboxyl, even when these groups are as remote from carboxyl as the δ -position. The data may be correlated on the assumption that fatty acids exist to some extent in the form of a quasi ring. Substituents in the α - and β -positions increase the amounts of acid present as a quasi ring.

Branched-chain fatty acids. XVII. Synthesis of two trimethyl-akanoic acids. Certain relationships of boiling point and index of refraction to structure. J. Cason, N. L. Allinger, G. Sumrell and D. E. Williams (Univ. Calif.). *J. Org. Chem.* 16, 1170 (1951). The boiling points of methyl esters of branched-chain fatty acids are lower than that of the normal isomer; a branching methyl lowers the boiling point about 5°, a branching hexyl lowers the boiling point by 7°, a quaternary carbon lowers the boiling point about 22°. The only large effect on refractive index is caused by the presence of a quaternary carbon atom.

Contributions to the study of marine products. XXX. Component acids of lipids of sponges. I. W. Bergmann and A. N. Swift (Yale Univ.). *J. Org. Chem.* 16, 1206(1951). The component acid mixtures of the lipids from the sponges, *Spherospongia vesparia* and *Suberites compacta* have been investigated. Their most characteristic features are their great complexity and the preponderance of C_{28} and C_{29} acids. The component acids of the lipids from *Spherospongia* and their weight per cent are myristic, 1.7; palmitic, 9.1; stearic, 0.7; tetradecenoic, 0.4; hexadecenoic, 3.1; octadecenoic, 15.9; C_{20} (> -2H), 6.5; C_{22} (> -2H), 4.5; C_{24} (> -2H), 4.5; C_{26} (> -2H), 38.8; C_{28} (> -2H), 14.9. The component acids of the lipids of *Suberites* and their weight per cent are myristic, 0.3; palmitic, 6.6; stearic, 1.0; arachidic, 1.1; behenic, 0.6; tetradecenoic, 0.2; hexadecenoic, 3.1; C_{18} (-2.3H), 11.1; C_{20} (-2.3H), 7.8; C_{22} (-6.3H), 17.8; C_{24} (-7.3H), 11.6; C_{26} (-2.9H), 9.4; C_{28} (-xH), 12.2; C_{29} (-4.5H), 17.0. α -Hydroxytetraacosanoic acid is also present in acids from *Suberites*.

Animal fats and oils as industrial raw materials. W. C. Ault (Eastern Reg. Res. Lab., Philadelphia, Penna.). *Chemurgic Digest* 10(9), 4(1951). A review in which the need for finding new uses for inedible animal fats is stressed.

Estimation of volatile fatty acids and ammonia in silage by means of paper chromatography. A. I. Virtanen and J. K. Miettinen (Biochemical Institute, Helsinki). *Nature* 168, 294 (1951). Butyric acid and ammonia can be rapidly determined with reasonable accuracy by chromatographic techniques.

Viscosity of glycerol and its aqueous solutions. J. B. Segur and Helen E. Oberstar (Miner Labs., Chicago, Ill.). *Ind. Eng. Chem.* 43, 2117(1951). Viscosity data are reported over the range of 0 to 100° and 0 to 100% glycerol concentration.

Reversed phase partition chromatography of steroids on silicon-treated paper. T. H. Kritechevsky and A. Tiselius (Biokemiska Inst., Uppsala, Sweden). *Science* 114, 299(1951). Sterols were separated on a paper which had been treated with a cyclohexane solution of a silicone. The strip was developed with an alcohol-water solution saturated with chloroform. The method at present is only qualitative.

PATENTS

Continuous saponification of fats. R. V. Owen (Lever Brothers Co.). *U. S.* 2,566,359.

Hardening and decolorizing glyceride oils with nickel-alumina-silica catalysts. W. J. Paterson (Lever Brothers Co.). *U. S.* 2,566,362. The oil is treated at 100-200° with H_2 at 1-3 atmospheres in the presence of a particulate nickel-alumina-silica catalyst containing 15 to 50% Ni. The remainder of the catalyst consists of Al_2O_3 and SiO_2 in the ratio of 4-16 formula weights Al_2O_3 per 45 SiO_2 formula weights.

Continuous processes for solvent extraction of oil from oil-bearing materials and refinement of the residual solid product. M. Bonotto. *U. S.* 2,567,179. The process for solvent extraction is disclosed which consists of extracting the raw material with a liquid solvent having a boiling point less than the condensation point of steam by continuously moving the raw material through an extraction column. The residual product is fed in an operation continuous with the extraction from the lower end of the extraction column into a direct dryer, and the temperature of the meal product is elevated to a point approximating the condensation temperature of steam by blowing hot vapors of a solvent similar to that employed in the subjection of material to oil extraction directly into the residual product. Then

steam is blown into the vapor-heated product to eliminate the solvent by steam distillation.

Stabilizing fatty material. J. Ross (Colgate-Palmolive-Peet Co.). *U. S.* 2,567,404. Fatty materials containing minor amounts of polyolefinic compounds are treated at an elevated temperature under substantially anhydrous conditions with sufficient acid anhydride having an alpha-beta-enal group to react with said polyolefinic compounds. The reaction is continued until the polyolefinic compounds have reacted with the anhydride, and discontinued before the anhydride reacts with a substantial amount of mono-olefinic constituents of the fatty material.

High molecular weight fatty acids. W. R. Trent (Colgate-Palmolive-Peet Co.). *U. S.* 2,567,409. A method of stabilizing fatty acids is claimed which comprises treating fatty acids containing minor amounts of polyolefinic compounds at elevated temperature with an acid anhydride having an alpha-beta-enal group in sufficient amount to react with the polyolefinic compounds and in the presence of a catalyst for the reaction, and terminating the treatment when the polyolefinic compounds have reacted with the anhydride and before a substantial amount of mono-olefinic acids have reacted therewith.

Fines separation. M. W. Smith and F. W. Weigel (The V. D. Anderson Co.). *U. S.* 2,567,450. Apparatus for separating fines from miscella is described which consists of a number of vertically placed baffles mounted on top of the extractor which retard turbulence, thus permitting rapid settling of the fines.

Countercurrent solvent extractor. G. R. Fitts and F. G. Low (Read Standard Corp.). *U. S.* 2,567,474. An improved Kennedy extractor is described.

Continuous dehydration process. I. M. Colbeth (The Baker Castor Oil Co.). *U. S.* 2,567,925. A continuous stepwise method for dehydrating an ester of a hydroxyl-containing fatty acid having more than six carbon atoms is claimed which comprises passing the ester at an elevated temperature in the substantial absence of oxygen through a plurality of reaction vessels in the presence of a dehydration catalyst distributed throughout the reaction vessels, and introducing the catalyst into more than one of the reaction vessels in controlled amounts during the course of the dehydration reaction.

Process for recovering sterols from mixtures thereof. J. Overhoff and J. T. Hackmann (N. V. Veenendaalse Sajat-en Vijfschachtfabriek voorheen Wed. D. S. van Schuppen & Zoon, Veenendaal, Netherlands). *U. S.* 2,568,202. The mixture of sterols and other unsaponifiable material, is heated under substantially anhydrous conditions with a metal salt selected from a class consisting of the halides, nitrates, sulfates, acetates, benzoates, salicylates and sulfonates of the alkali metals, the alkaline earth metals, magnesium, aluminum, iron, tin, chromium, zinc, manganese, cobalt, and cadmium, thereby forming a sterol-metal salt addition product, separating said addition product from the reaction mixture, decomposing the addition product to produce the free sterol and recovering the latter.

Bleaching oils in the presence of steam. R. M. Christenson and R. E. Harpt (Pitts. Plate Glass Co.). *U. S.* 2,569,124. A process is disclosed for treating glyceride oils containing less than 0.3% break constituents which comprises preheating the oil to 215 to 242° F., blowing it with live steam in the presence of 0.2 to 5% of an adsorbent earth, drying the oil by blowing with an inert gas, and removing the adsorbent earth.

11-bromohendecanoic acid. Societe Organico (M. Genas and Kastner, inventors). *French* 951,932. The amount of 10-bromohendecanoic acid obtained in treating 10-hendecenoic acid with HBr is reduced so as to obtain the 11-Br isomer in 80% yield by carrying out the reaction in an inert solvent, such as benzene, toluene, or a chlorinated hydrocarbon, at a low temperature, e.g. -10 to 40°, in the presence of oxygen, excess of HBr being present, and the presence of Fe, Cu, Al, and their compounds being avoided. (*Chem. Abs.* 45, 7586)

Pyrolysis of ricinoleic esters. Societe Organico (P. F. C. Gregory, M. Genas and O. Kostelity, inventors). *French* 952,985. Good yields of heptanol and hendecenoic esters are obtained by bringing ricinoleates into contact with a surface heated to 400-650°, and quickly condensing the vapors of the compounds formed. The heated surface may be molten metals, except Hg, the alkali metals, and alkaline earth metals, or a fused salt. The preferred ricinoleates are those of monohydric alcohols containing less than 6 C atoms. Single passage of a kg. of methyl ricinoleate over a molten lead surface held at 550-60° yielded 170 g. heptanol and 300 g. methyl hendecenoate. (*Chem. Abs.* 45, 7586)

• Biology and Nutrition

R. A. Reiners, Abstractor

The nutritive value of conophor cake-meal for young dairy stock and fattening pigs. S. Bartlett, E. S. Baxter, R. Braude and K. G. Mitchell (Natl. Inst. Research in Dairying, Shinfield, Engl.). *Empire J. Exptl. Agr.* 19, No. 73, 51-4(1951). The residue from the oil extraction of kernels of *Tetracarpidium conophorum* from Nigeria is called conophor cake. It contains 45.9% crude protein and 25.9% soluble carbohydrates, and is palatable, nontoxic, and high in food value. (*Chem. Abs.* 45, 7720)

The tuberculostatic actions of various organic compounds. II. Fatty acids and their derivatives. Y. Miura (Tokyo Univ.). *J. Biochem. (Japan)* 37, 387-95(1950). With avian type of tubercle bacteria, the antibacterial actions of 64 fatty acids and their derivatives were examined. With straight-chain fatty acids the activity varies with the no. of C; the maximum activity is found between C₈ and C₁₄, generally in the vicinity of C₁₁ acid. With branched-chain fatty acids the maximum effect is found in C₁₄ acid, whenever the methyl, ethyl, or phenyl group is attached as the branch at α , β , γ , or ϵ ; the ethyl group is the most favorable one as a branched-chain. (*Chem. Abs.* 45, 7627)

Fat resorption. H. Kirehmair (Univ. Kinderklinik, Wurzburg, Ger.). *Klin. Wochschr.* 27, 588-9(1949). Fat absorption was studied in the rabbit by determination of the iodine content of urine following administration of iodinated fat containing 20% iodine. A single dose of 5 cc. of an emulsion of the fat was followed by excretion of 439 mg. iodine over 5 days. Addition to the fat of 5 cc. of a finely dispersed 4% sol of cholesteryl oleate caused iodine excretion to total 792-824 mg. The saponification no. of the ethyl ether-soluble fraction of the feces was then lower than the control value. After addition of 50% bile to the fat administered, an average of 526 mg. iodine was excreted, and the saponification no. was low. (*Chem. Abs.* 45, 7203)

The carcinogenic action of heated fats and lipoids. P. R. Peacock (Glasgow Roy. Cancer Hosp., Scot.). *Brit. Med. Bull.* 4, 364-7(1951). A review. (*Chem. Abs.* 45, 7225)

Observations of the spectrophotometric assay of vitamin A by geometric correction of absorption curves. N. T. Gridgeman (Lever Bros. & Unilever Ltd., Sharnbrook, Bedford). *Analyst* 76, 449(1951). The application of the method to cod-liver oil, as originally proposed, appears to be more firmly based than its application to richer oils.

Chemical method for the determination of vitamin D in fish oils. I. N. Garkina and V. N. Bukin (Bakh Biochem. Inst., Moscow). *Biokhimiya* 16, 176-85(1951). Vitamin A is removed by bentonite, and the sterols by digitonin. Vitamin D is then determined with SbCl₅. The accuracy is $\pm 25\%$, compared to an accuracy of $\pm 20\%$ for the biological method. In irradiated fish oils, the tachysterol (which is not precipitated by digitonin) is bound in a complex by treatment with maleic anhydride, previous to the SbCl₅ reaction. (*Chem. Abs.* 45, 7186)

Lipids in normal feces and the determination of fat. P. Muller (Univ. Clinic, Utrecht, Netherlands). *Proc. Koninkl. Nederland. Akad.* 54C, 153-7(1951). Titration, rather than weighing of the free and bound fatty acids, is the correct way to determine fat in feces. The free fatty acids were first determined by acidifying, extracting, and then titrating. The total fatty acids were then determined by saponifying the feces, acidifying, extracting, and titrating. The greater part of the bound fatty acids were not bound to glycerol, but to some undetermined substances and therefore is not fat. The following values were obtained for dog feces: volatile soluble free fatty acid, 6.55%; volatile insoluble free fatty acid, 10.2%; volatile soluble bound fatty acid, 4.7%; and volatile insoluble bound fatty acid, 9.0%. (*Chem. Abs.* 45, 7624)

The precision of the 3-point correction method of spectrophotometric assay of vitamin A. D. C. M. Adamson, W. F. Elvidge, N. T. Gridgeman, E. H. Hopkins, R. E. Stuekey and R. J. Taylor (Glaxo Labs., Ltd., Greenford, Middlesex). *Analyst* 76, 445(1951). A 7-laboratory determination of E_{1%^{1cm}} at 328 m μ , geometrically corrected for absorption irrelevant to vitamin A, was carried out on each of 5 oils containing vitamin A. From a statistical analysis of the results it is concluded that the limits of error of a determination in duplicate for any one laboratory are about $\pm 15\%$ for P = 0.05. The corresponding figure for uncorrected E values is about $\pm 2\%$.

• Waxes

E. H. McMullen, Abstractor

Adulteration of Carnauba. Leon Kresser (Cornelius Products Co.). *Soap Sanit. Chemicals* 27, No. 9, 139, 159(1951). Adulteration of Carnauba wax by paraffin or microcrystalline waxes, hydrocarbon resins or ester gum can be determined by a rapid, reliable procedure.

Detecting wax additives. Charles J. Marsel, Cyril S. Treacy, and Rino L. Godino (New York Univ., N. Y.). *Soap Sanit. Chemicals* 27, No. 7, 122-3, 125-6, 135, 161(1951). Possible methods for detecting additives in vegetable waxes are discussed. The technique of solvent leaching, followed by specific tests on the extracted residue, is simple and useful. Thus 10 g. of pulverized wax is agitated 2 hrs. with 100 ml. of CHCl₃ at 25° in a flask, which is then immersed in an ice bath for 1 hr. with occasional manual stirring. The sample is filtered and the solvent evaporated from the filtrate, a vacuum oven being used near the end to remove last traces of solvent and prevent charring. This residue is compared to normal residue as to (1) wt., (2) acid no., (3) saponification no., and (4) special tests as concerned H₂SO₄ extraction to indicate paraffins. Data are given on the soly. and chem. const. of a number of possible wax additives or extenders. (*Chem. Abs.* 45, 8276)

New sources of Montan wax. E. Peter. *Fette u. Seifen* 53, 280-3(1951). American and Russian work on bituminous coal extraction is discussed. Peter's experiments yielded a yellow wax of acid no. 76 and ester no. 4. (*Chem. Abs.* 45, 8275)

La joboba. Benavides, Gustavo Aguirre. *Bol. Soc. Bot. Mexico* 10, 26-32(1950). Seeds of the jujube, *Bursera chinensis* Link (*Simmondsia californica* Nutt.), have a high wax content (50%). Indigenous to xeric areas, it should be a profitable crop in areas too dry for other species. (*Biol. Abs.* 25, 8, 25300)

Infrared spectrometry in graphic arts. T. U. Marron and T. S. Chambers (A. B. Dick Co., Chicago). *Anal. Chem.* 23, 548-50(1951). Infrared spectrometry can be effectively applied to complex, as well as simple materials. Examples are the specification, purification, and manufacturing control of such complex products as petroleum oils, plasticizers, natural waxes, inks, etc. Sometimes exact chemical composition of a specified material is unknown but infrared comparison with satisfactory and unsatisfactory materials is still possible. The presence of undesirable aldehyde in alcohols, EtOH in ethyl acetate, and hydrolysis in other esters is readily revealed. The curves of the unsaponifiable residues of many natural products are characteristic enough to furnish identification. Spectra of 7 commercial waxes are diagrammed. The instrument used was a specially adapted portable Perkin-Elmer Model 12AB spectrometer. (*Chem. Abs.* 45, 8265)

PATENTS

Waxes: N-acylated piperazines. Arthur L. Jacoby (to National Aluminate Corp.). *U. S.* 2,541,584. High molecular weight diacylated piperazines, such as dioctanoyl-, N-acetyl-N-lauryl-, and N-lauryl-N-benzoyl-piperazine, can be used as substitutes for natural waxes and as constituents for coatings. (*N.P.V.L.A. Abstract Review*, 172, 188)

Waterproofing paper textile fabrics. John J. Petroske (to Pathogue-Plymouth Mills Corp.). *U. S.* 2,536,656. Fabrics woven from twisted colored paper strands are coated on one side with a wax emulsion containing Al(OAc)₃, brushed, and dried before complete impregnation takes place; the fabrics are then sprayed with lacquer on the untreated side. (*Chem. Abs.* 45, 8264)

• Drying Oils

Stuart A. Harrison, Abstractor

Recent developments in drying oil research. R. L. Terrill. *Official Digest Federation Paint and Varnish Production Clubs* No. 320, 573(1951). Reviews recent work done on relation of composition and structure of oils to their drying rate. Discusses modern theories of the role of oxygen in drying of oils (23 references).

Pentaerythritol alkyds. A. G. North. *Paint Technol.* 16, 333(1951). Discusses the chemistry of pentaerythritol, especially in regard to esterification. The theoretical considerations of

functionability of polyhydric alcohols and relation to cross linking are reviewed. Modifications of the theoretical formulae must be made in order that they have practical utility. In the case of air drying materials the rate of oxidative air drying is best predicted on the basis of the number of unsaturated groups per molecule, rather than oil length and iodine value.

Urethane oils. E. B. Robinson and R. B. Waters. *J. Oil & Color Chemists' Assoc.* 34, No. 3/4, 361(1951). Urethane oils were prepared from linseed mixed with mono- and diglycerides by heating with diisocyanate such as hexamethylene diisocyanate or chlorophenylene diisocyanate. The urethane oils obtained in this way were tested as clear and pigmented coatings and compared with long and medium oil length alkyds. The urethane oils were found to dry rapidly (tack free in two hours) to hard, water resistant films. The main defects were poor color, inferior flow, and inferior durability. In these respects they were decidedly inferior to a first class pentacrythritol alkyd.

Grapeseed oil. A. Müller. *Farbe u. Lack* 57, 240(1951). The potential sources, production, and composition of grapeseed oil are reviewed. Grapeseed oil heat polymerizes more slowly than linseed oil; its stand oils are more acid and dry more slowly than linseed oil. Dehydrated grapeseed oil is inferior to dehydrated castor oil. Combinations of grapeseed oil and linseed oil give excellent results. Grapeseed oil makes excellent alkyds. (*Chem. Abs.* 45, 7800)

Tobaccoseed oil in varnishes. M. N. Rao, C. E. McGrew, and A. J. Lewis. *Paint Technol.* 16, No. 188, 337(1951). Tobaccoseed oil was compared with linseed oil in ester gum varnishes, phenolic varnishes, and alkyd varnishes. The varnishes were made by conventional procedures. The drying time, cold and hot water resistance, alkali, acids and solvent resistance, and durability under accelerated weathering conditions were compared for all varnishes. It was concluded that tobaccoseed oil can be successfully used as a substitute for linseed oil in the phenolic and alkyd type varnishes. In the ester gum varnishes the tobaccoseed oil did not dry to as hard tack free coatings as linseed oil-ester gum varnishes.

The composition of poppy seed oils. R. E. Bridges, M. M. Chakrabarty, and T. P. Hilditch. *J. Oil & Colour Chemists' Assoc.* 34, No. 374, 354(1951). The oil from poppy seeds grown in England and in India were found to be quite similar in composition. This indicates that in this instance the differences in climate have had little effect on composition of the oils from seeds. The poppy seed oil has an iodine value of 139, and a free acid content of 3.4%. The component fatty acids are palmitic (9%), stearic (2%), oleic (16%), and linoleic (72%). This puts it in the class of non-yellowing drying oils such as sunflower and safflower seed oil.

The preparation of economical alkyd resins for varnishes modified with neutralization olein. S. Zaccarini. *Ind. vernice* 5, 51(1951). The acid neutralization of soapstock from the alkaline refining of grapeseed oils gives fatty acids suitable for the manufacture of dark colored alkyd resins. (*Chem. Abs.* 45, 7801)

PATENTS

Oxidation of drying and semidrying oils. W. J. Keenan. *U. S.* 2,555,976. The drying rate of drying and semidrying oils can be accelerated by blowing with oxygen containing ketene or mixtures of ketene and diketene. For example: gaseous oxygen at 25° is passed through a reservoir of liquid ketene, maintained at -55°, at a rate of 240 ml./minute. The resultant gases are bubbled through 316 g. of vigorously stirred commercial raw linseed oil at 45°. After about two hours 0.55 mole of oxygen has been absorbed and the reaction is discontinued. The product has a viscosity of M on the Gardner scale and is somewhat lighter in color than the original oil. A film spread on glass is cured in 4 hours at 60-70° without drier.

Polymeric esters of natural drying oil fatty acids. W. J. Wayne. *U. S.* 2,556,268. Ethylene is copolymerized with vinyl acetate and the resulting copolymer hydrolyzed to give a polymeric substance having the empirical formula $(\text{CH}_2\text{CH}_2)_a(\text{CH}_2-\text{CHOH})_b$. Ethylene can also be copolymerized with carbon monoxide and the resulting copolymer reduced catalytically to give a polymeric substance having the empirical formula $(\text{CH}_2-\text{OH}_2)_c(\text{CHOH})_d$. The free hydroxyl groups of these polymers can be esterified with drying oil fatty acids. Films of these oils containing driers, dry faster than linseed oil films with drier. In addition the films are tougher and more durable than linseed oil films.

Unsaturated mono-hydric phenolic ether-modified drying oils and process of making same. J. B. Rust and W. B. Canfield. *U. S.* 2,563,870. Modified drying oils are obtained by heating drying oils with the allyl ethers of mono-, di-, and tri-allyl phenols, e.g., raw linseed oil (150 pts.) and the allyl ether of allyl phenol (45 pts.) are heated to 240-260° for five hours. A light colored oil with a Gardner viscosity of E-F is obtained which dries with driers to a hard non-tacky film in 24 hours. Allyl esters of allyl phenoxy acetic acid can be used in place of the allyl ethers. A varnish can be made by heating 80 parts of this oil with 50 parts of ester gum to 280-290°C. for 70 minutes. The advantages of these materials are that they give light coloring, non-yellowing films which are quite resistant to aqueous alkali.

Unsaturated polyhydric phenolic ether-modified rosin esters and process of making same. J. B. Rust and W. B. Canfield. *U. S.* 2,563,871. Modified rosin esters which are suitable for cooking with oils to make varnishes are prepared as follows: ester gum (100 parts) and the diallyl ether of diphenylol propane (25 parts) are heated to 250-260° for six hours. A light colored, brittle resin melting at 108° is obtained. Fifty parts of this resin and 80 parts of Z-2 bodied linseed oil are heated to 280-290° for two hours. With added drier the varnish air dries tack free in 4¼ hours.

Unsaturated monohydric phenolic ether-modified rosin esters and process of making same. J. B. Rust and W. B. Canfield. *U. S.* 2,563,872. Similar to *U. S.* 2,563,871, except that the allyl ether of mono-, di-, and triallyl phenols are used in place of the diallyl ether of diphenylolpropane.

Unsaturated polyhydric phenolic ether-modified drying oils and process of making same. J. B. Rust and W. B. Canfield. *U. S.* 2,563,873. Similar to *U. S.* 2,563,870, except that the diallyl ether of diphenylol propane is used in place of the allyl ether of allyl phenol.

Copolymers of diallyl phthalate and diallyl esters of dimerized unsaturated fatty acids. H. Dannenburg and T. F. Bradely. *U. S.* 2,564,395. A flexible coating material is prepared by copolymerizing diallyl phthalate with the diallyl ester of dimerized unsaturated fatty acids such as dimerized linseed fatty acids. The copolymerization is carried out at 200° using tertiary butyl hydroperoxide as catalyst. Other allyl esters of dimerized fatty acids may be used, such as dimerized soybean and dimerized cottonseed fatty acids.

Vegetable oil-hydrocarbon oil carbonyl compounds. *U. S.* 2,565,654. E. M. Geiser. Mixed butylenes and propylene are polymerized, using anhydrous hydrogen fluoride as catalyst. The acidic sludge from the polymerization is hydrolyzed in ice and water to give a sweet smelling oil. This oil is cobodied (1 part) with linseed oil (3 parts) by heating to 300°C. in the absence of air for three hours. The final mixture has a viscosity of 35 poises. The cobodied drying oil is mixed with a molar equivalent of trioxymethylene and 0.1% the combined weight of oxalic acid. This mixture on heating at 90°C. for two hours forms a pliable elastomeric mass soluble in toluene. A solution of the above polymer and the cobodied drying oil when spread in a thin film dries to a hard elastic film.

Drying oil - furfuraldehyde - mesityl oxide compositions. M. T. Harvey. *U. S.* 2,565,685. Mesityl oxide is reacted with furfuraldehyde using alkaline catalyst to give products ranging from viscous oils to brittle resins. When these are cooked with drying oils such as dehydrated castor or linseed oil they form varnishes resistant to alkali and having high dielectric strength. Other modifications are suitable for linoleum and brake lining compositions.

Treatment of conjugated oils. C. A. Coffey and E. B. Lukas. *U. S.* 2,566,169. Tung oil and other oils which tend to gas-check on drying in a gas contaminated atmosphere can be treated to avoid this by heating with certain disulfides or kerosene fractions which contain disulfides. For example, tung oil which has been heated to 440°F. for 1.5 hours with 0.1% diphenyl disulfide will dry to a clear smooth film. Other active disulfides are ditertiary hexyl disulfide, and dibenzyl disulfide.

Drying oil composition. J. D. Danford. *U. S.* 2,566,515. Drying oils are cobodied with unsaturated amines to give oils having superior adhesion and durability to weathering, e.g., raw linseed oil (2234) is mixed with octadecadienylbutenylisopropyl amine (41) and the mixture heated to 280-300° for 6 hours. After vacuum stripping to remove unreacted amine the product has a viscosity of 40 poises at 25° and a Gardner color of 12. It is soluble in all proportions in drying oils.

• Detergents

Lenore Petchaft, Abstractor

Synthetics in cotton detergency. H. L. Sanders and J. M. Lambert. (General Aniline & Film Corp., Easton, Penn.). *Textile Research J.* 21, 680-4(1951). It has been found that synthetic detergents can be built with phosphates and CMC so as to wash cottons as efficiently as soap does. Surface tension and interfacial tension tests on synthetics with alkaline builders show that the beneficial effect of builders is not due to any change in the surface activity of the detergent. The major role of the alkali might be to increase the negative charge on both the fiber and the soil through adsorption of the anions, thus helping to break the adhesive bond between soil and fabric through an electrostatic effect. An explanation of the action of CMC might be due to the fact that the CMC is adsorbed into the cotton, mechanically blocking the finer capillaries or interstices in the fiber, thus preventing penetration of the extremely fine soil particles.

Examination of detergent preparations. W. H. Simmons, *et al.* *Analyst* 76, 279-86(1951). Systematic testing for true soap, alkali carbonate, phosphate or silicates, abrasives or fillers, synthetic organic detergents of the sulfated or sulfonated types, sulfated glycerides, propylene glycol derivatives, quaternary derivatives, methyl- and carboxymethylcellulose, and naphthenic acid soaps is described as well as their determination. (*Chem. Abs.* 45, 7805)

The theory of washing. K. Swanston and R. C. Palmer. *J. Textile Inst.* 42, 675-90(1951). Review of various theories of detergency and factors involved in this process. The solubilization theory is explained and discarded as inadequate in its explanation in the light of later work. The emulsion theory based on work of N. K. Adam is now the more accepted explanation, and accounts for three main facts about detergency—that the final result of washing is an emulsion, that the detergent effect reaches its maximum at about the critical concentration for micelles, and explains the salt effect. However, other factors are still present and are discussed in this paper, namely, sorption of detergent by fibers, mechanical action, and the amount of detergent used.

Synthetic detergents. O. M. Morgan (National Aniline Division, Allied Chemical & Dye Corp., New York). *Rayon & Synthetic Textiles* 32, No. 9, 93-4, 96, 98, 106(1951). Review of uses of synthetic detergents in various aspects of textile processing including scouring rayon, nylon yarns and fabrics, blended fabrics and some of the new synthetics such as Dacron and Orlon, wool scouring and cotton scouring. Combinations of synthetics such as Naccenol with various additives for specialized operations are also described.

Combinations of soap and synthetic detergents. P. I. Smith. *Am. Perfumer Essent. Oil Rev.* 58, 201-2(1951). Review of use of non-ionic detergents with soap to disperse insoluble soaps, improve rate of solution and rate of rinsing of soap, and assist deodorant action. Additives such as CMC also improve these soap-synthetic compositions.

Bottle cleaning compounds. M. A. Lesser. *Soap Sanit. Chemicals* 27, No. 9, 39-42, 145(1951). A good bottle washing material must be free draining, not foam excessively, have good cleaning action, have sufficient germicidal properties, and exhibit free rinsibility. Formulations are given using alkaline salts and synthetic detergents.

High finish for soap cakes. Anon. *Am. Perfumer Essent. Oil Rev.* 58, 203(1951). The factors most important in achieving a smooth high gloss on soap cakes include the texture of the soap, amount of tallow present in the soap composition, the size and shape of the bar being finished, and the type of automatic soap press being used.

The effectiveness of some skin detergents. D. E. Shay (Univ. of Maryland, Baltimore, Md.). *Proc. Penna. Acad. Sci.* 24, 26-9(1950). A non-alkaline soapless skin detergent containing 3% bis(2-hydroxy-3,5,6-trichlorophenyl)methane (I) is superior to a liquid germicidal detergent containing alkylamine hydrochlorides with 2.5% phemerol, and both of these detergents are superior to a liquid soap containing I as 2% of the soap content. (*Chem. Abs.* 45, 7747)

Foaming and hydrolysis of soap solutions—reversibility and irreversibility of the adsorbed layer. M. Raison. *Compt. rend.* 232, 1660-1(1951). Foam formed from Na oleate (NaOl) contains an adsorbed layer of acid soaps, the composition of which is dependent upon the concentration of soap in the solution from which it is formed. The acid soap may be represented by the general formula $2\text{NaOL}\cdot n\text{HOL}$, where n is 3.4 at the lowest concentration of soap investigated ($0.4 \times 10^{-3}\text{M}$), decreases to 2 at $1.2 \times 10^{-3}\text{M}$, and becomes 1 at $2.5 \times 10^{-3}\text{M}$. Soap solutions formed by the collapse of foam have a larger surface tension than the original soap solution from which the foam was formed in the concentration range up to $10 \times 10^{-3}\text{M}$, the greatest difference in surface tension occurring at about $1 \times 10^{-3}\text{M}$, the values being 29 dynes/cm. for the initial solution and 36 dynes/cm. for the reformed solution. Above $10 \times 10^{-3}\text{M}$ both initial and reformed solution have the same surface tension (about 29 dynes/cm.). Previous workers have shown that the greatest hydrolysis of soap solution occurs at a concentration of $1 \times 10^{-3}\text{M}$. The effect of foam formation is to remove the acid formed by hydrolysis from the bulk of the solution thereby displacing the hydrolytic equilibrium more at low concentrations (where more acid soap is formed). From the results R. concludes that acid soap containing 2 or more molecules of acid per 2 molecules of NaOl has less effect in reducing the surface tension of water than does the acid soap containing only 1 mole. (*Chem. Abs.* 45, 7805)

PATENTS

Continuous method of washing soap. R. V. Owen (Lever Brothers Co.). *U. S.* 2,562,207. A continuous stream of soap is intimately mixed and agitated with a continuous stream of lye in a vessel so that the lye will extract glycerine from, and thereby wash, the soap. The mixture of lye and soap then passes from this zone to a quiescent zone, which may be in the same vessel. Here the soap and lye are allowed to separate by the settling action of gravity into an upper layer of washed soap and a lower layer of lye.

Apparatus for treating granular materials. J. J. Mahoney (Colgate-Palmolive-Peet Co.). *U. S.* 2,563,475. Description of apparatus for the treatment of hot spray-dried soap particles which comprises cooling the soap particles withdrawn from a spray tower on a stationary, perforated sloping bed or table down which the particles travel towards the packaging apparatus. The apparatus may also be used to condition powdered synthetic detergents.

Continuous saponification of fats. R. V. Owen (Lever Brothers Co.). *U. S.* 2,566,359. A continuous process of saponifying fat which comprises emulsifying fat and an aqueous saponifying agent and maintaining a substantially quiescent flow of the resulting emulsion so as to allow self-saponification of the fat to take place. This method results in reduction in the time and quantity of steam required for the saponification.

Wetting and detergent composition. E. A. Vitalis (American Cyanamid Co.). *U. S.* 2,567,159. A wetting and detergent composition consisting essentially of a higher alkyl sulfosuccinate and a water-soluble inorganic chromium salt which is capable of increasing the water solubility of the sulfosuccinates. **Process for manufacturing soap.** H. G. Kirschenbauer and J. H. Percy (Colgate-Palmolive-Peet Co.). *U. S.* 2,567,381. Soap of good color, odor, and stability can be manufactured by the conventional soap boiling process by adding in the mixture, prior to filling, a small amount of compound yielding phosphate ions, e.g. trisodium phosphate or phosphoric acid. These phosphate ions cause undesirable metals to form insoluble phosphate salts which settle in the nigre layer and may be separated from the less dense layer of finished soap.

Process of producing a detergent composition. J. Limburg (Shell Development Co.). *U. S.* 2,567,645. Method of producing a detergent of improved lime-resistance and detergent and wetting powers by mixing an aqueous solution of a higher alkyl sulfate salt with fatty acids and saponifying in situ to form soap. The resulting combination of alkyl sulfate and soap has properties superior to a physical mixture of the two components.

Process for washing in sea water. N. V. Dobbelman. *British* 656,248. A process for washing in hard or sea water using a soap base containing soluble fluoride or oxalate ions in such a quantity that they dissolve prior to the soap, thus binding the hardness causing cations.