

ucts, Sisley—*Corps gras savons* 1, 66; Götte—*Die Chemie* 57, 67; Kling—*Tek. Tik.* 74, 565; chemical analysis of quaternary ammoniums, DuBois—*Soap Sanit. Chemicals* 22, No. 11, 125.

The newly patented nonsoap organic detergents are derivatives of fats or by-products of the coal and petroleum industries. These and their methods of manufacture are not discussed in detail in this Review but are listed with only partial classification.

Those references to the patents on hydrocarbons containing sulfur, such as sulfonates and sulfates are: Allied Chemical & Dye Corp.—*U. S.* 2,364,767, 2,387,572, 2,393,526, 2,394,851, 2,397,133, 2,401,726.

American Cyanamid Co.—*U. S.* 2,385,314.

Atlantic Refining Co.—*U. S.* 2,406,763.

Chem. Fabrik Grünau A.-G.—*Ger.* 748,564 Cl. 30h.

Colgate-Palmolive-Peet Co.—*Can.* 434,340; *U. S.* 2,394,320-1.

E. I. duPont de Nemours & Co.—*U. S.* 2,398,426, 2,402,587.

Fife—*Brit.* 561,624.

Gordon & Likhman—*U.S.S.R.* 65,102.

Harvel Corp.—*U. S.* 2,412,264.

Industrial Patents Corp.—*U. S.* 2,394,834.

Jäger & Jäger—*Ger.* 745,637 Cl. 30h.

Kalle & Co. A.-G.—*Ger.* 742,194 Cl. 8i.

Monsanto Chemical Co.—*U. S.* 2,402,823 2,403,038.

National Oil Products Co.—*Brit.* 559,265; *Can.* 432,690; *U. S.* 2,392,945, 2,397,692.

Procter & Gamble Co.—*U. S.* 2,396,278.

Society of Chemical Industry in Basle—*U. S.* 2,399,434.

Solvay Process Co.—*U. S.* 2,381,658, 2,404,289.

L. Sonneborn Sons, Inc.—*U. S.* 2,396,673, 2,409,671.

Union Oil Co. of California—*U. S.* 2,411,819.

Victor Wolf Ltd.—*Brit.* 562,321, 563,482.

In some cases sulfur-containing detergents were prepared by sulfonating nitrogen derivatives, such as amines, amides, etc.:

Aktieselskabet Grindstedvaerket—*Dan.* 63,458.

Allied Chemical & Dye Corp.—*U. S.* 2,388,962.

American Cyanamid Co.—*U. S.* 2,390,476, 2,391,830.

Courtaulds Ltd.—*Brit.* 565,675.

E. I. duPont de Nemours & Co.—*U. S.* 2,390,253.

Everett *et al.*—*Brit.* 564,359.

J. R. Geigy Co.—*Brit.* 560,628.

Huppert—*U. S.* 2,384,837.

I. G. Farbenind. A.-G.—*Ger.* 745,555 Cl. 8i, 745,909 Cl. 8i.

Petrolite Corp.—*U. S.* 2,386,445.

Society of Chemical Industry in Basle—*U. S.* 2,398,990.

Soc. pour l'ind. chim. a Bale—*U. S.* 2,376,911.

Some special amines, amides, and quaternary ammonium compounds were patented as detergents:

Alien Property Custodian—*U. S.* 2,394,306-7.

Alrose Chemical Co.—*U. S.* 2,404,297-8.

Arnold, Hoffman & Co., Inc.—*U. S.* 2,410,788-9.

Commercial Solvents Corp.—*U. S.* 2,389,875, 2,402,791.

E. I. duPont de Nemours & Co.—*U. S.* 2,395,265, 2,395,971.

Emulsol Corp.—*U. S.* 2,388,154, 2,411,434.

General Aniline & Film Corp.—*U. S.* 2,382,185.

Harris—*U. S.* 2,409,275.

Heberlein Patent Corp.—*U. S.* 2,370,405.

Henkel & Cie. G.m.b.H.—*Ger.* 741,305 Cl. 12o.

Hunsdiecker & Vogt—*Ger.* 745,221 Cl. 8o.

Imperial Chemical Industries Ltd.—*U. S.* 2,386,142.

Industrial Patents Corp.—*U. S.* 2,412,113.

Montclair Research Corp.—*U. S.* 2,398,317.

Onyx Oil & Chemical Co.—*U. S.* 2,407,703.

Orelup—*U. S.* 2,388,281.

Parke, Davis & Co.—*U. S.* 2,406,902

Pennsylvania Salt Manufacturing Co.—*U. S.* 2,374,113.

Petrolite Corp.—*U. S.* 2,394,432.

Pure Oil Co.—*U. S.* 2,394,678.

Richards Chemical Works—*U. S.* 2,374,354.

Röhm & Haas Co.—*U. S.* 2,395,336, 2,395,989.

Shell Development Co.—*U. S.* 2,376,105, 2,402,495.

Victor Chemical Works—*U. S.* 2,406,423.

A number of new detergents or their intermediates could not be classified above. This miscellaneous group includes special esters, ethers, and organic phosphates:

E. I. duPont de Nemours & Co.—*U. S.* 2,382,874, 2,396,786, 2,397,602, 2,402,137.

Eastman Kodak Co.—*U. S.* 2,386,250.

Monsanto Chemical Co.—*U. S.* 2,380,699, 2,385,713.

Onyx Oil & Chemical Co.—*U. S.* 2,405,784.

Petrolite Corp.—*U. S.* 2,386,446.

Resinous Products & Chemical Co.—*U. S.* 2,385,790.

Virginia Smelting Co., Inc.—*U. S.* 2,404,913.

## Abstracts

### Oils and Fats

Edited by

M. M. PISKUR and SARAH HICKS

EDIBLE OIL INDUSTRY IN GERMANY. W. H. Goss (Northern Reg. Res. Lab., Peoria, Ill.). *Food Industries*, 19, 320-3 (1947). German oil refining is batchwise and not continuous like ours. Soybean oil reversion, a common problem, is combatted by the removal of lecithin or treatment with live steam. Fatty Et esters were added to margarine.

RENDERING TECHNOLOGY. M. Maillet (Etablissements Olida). *Inds. corps gras* 3, 38-46 (1947). This

review contains legal definitions of the products, and descriptions of raw material, 5 rendering processes, cooling, and packaging. The water bath, kettle, dry autoclave, vapor autoclave, and Danish Titan methods of rendering and equipment were illustrated and described.

CHARACTERISTICS OF CANADIAN LARD. H. J. Lips and G. A. Grant (Natl. Res. Labs. Ottawa) *Can. J. Research* 25F, 63-65 (1947). Mean values for

*Can. J. Research* 25F, 63-75 (1947). Mean values for measured properties of 33 samples of lard obtained from 26 packing plants across Canada were: I number, 58.7; saponification number, 193.9; melting point, 43.5°; smoke point, 382° F.; color, 8.8Y, 1.6R; unsaponifiable matter, 0.43%; fatty acid composition: saturated 45.6%, oleic 44.7%, linoleic 8.7%, linolenic 0.6%, arachidonic 0.4%; storage life at 26.7°, 9.2 weeks; Swift stability, 3.5 hr.; iodimetric peroxide, 1.6 ml. of 0.002 N thiosulphate per g.; ferrometric peroxide, 9.7 milliequiv. per kg.; Kreis test, 9.9; Stamm test, 2.3;  $\alpha$ -dicarbonyl test, 3.4; free fatty acid, 0.4%; fluorescence, 79.2. The distribution of values is shown by histograms.

THE PRESENCE OF  $\delta$ -TOCOPHEROL IN HOG FATS. J. R. Chipault and W. O. Lundberg (Univ. Minnesota, Austin). *Arch. Biochem.* 12, 317-18 (1947).  $\delta$ -Tocopherol may occur normally in the fats of hogs in small amounts, and, like the other tocopherols, is probably derived from the diet.

SOUTH AFRICAN FISH PRODUCTS. XXIV. THE OCCURRENCE OF  $\alpha$ -GLYCERYL ETHERS IN THE UNSAPONIFIABLE FRACTIONS OF NATURAL FATS. M. L. Karnovsky, W. S. Rapson, and M. Black (Univ. Capetown, So. Africa). *J. Soc. Chem. Ind.* 65, 425-8 (1946). The amounts of formaldehyde generated in the oxidation with periodic acid of the unsaponifiable fractions of a wide variety of fats from marine and other sources have been determined, and the results recorded in terms of percentage  $\alpha$ -glyceryl ethers, calculated as selachyl alcohol. It is demonstrated in this way that  $\alpha$ -glyceryl ethers are of wide occurrence in the unsaponifiable fractions from marine fats of many different types. They have been found less frequently, and in smaller amounts in the unsaponifiable fractions of land animal and vegetable fats.

TOCOPHEROLS AS ANTIOXIDANTS FOR VITAMIN A IN FISH LIVER OILS. L. O. Buxton (Natl. Oil Products Co., Inc., Harrison, N. J.). *Ind. Eng. Chem.* 39, 225-32 (1947).  $\gamma$ -Tocopherol was more effective for inhibiting peroxidation in the oils studied than was  $\beta$ -tocopherol, especially during the later stages of vitamin A destruction.  $\beta$ - and  $\gamma$ -tocopherol at a 0.10% concentration markedly increased the stability of vitamin A in the various oils examined. Lecithin at a 1.0% level enhanced the effectiveness of both tocopherols for inhibiting vitamin A destruction and peroxidation. No difference was observed between the antioxidant characteristics of pure natural  $\gamma$ -tocopherol and those of pure synthetic  $\gamma$ -tocopherol.

FLAVOR REVERSION IN HYDROGENATED LINSEED OIL. III. THE RELATION OF ISO-LINOLEIC ACID TO FLAVOR DETERIORATION. H. W. Lemon (Ontario Research Foundation, Toronto). *Can. J. Research* 25F, 34-43 (1947). Partially hydrogenated perilla oil, containing considerable iso-linoleic acid, developed the same odor when heated, as did partially hydrogenated linseed oil. A concentrate of iso-linoleic acid developed a similar odor when it was heated. Distillation of the acid, or removal of unsaponifiable substances, had no effect on the odor development. When fatty acid fractions obtained by crystallization of the acids from hydrogenated linseed oil were re-esterified with glycerol, and subjected to the heat test, most odor development occurred in the fraction containing most iso-linoleic acid. Increasing the selectivity of hydrogenation did not greatly affect the formation or hydrogenation of iso-linoleic acid. However, products of

high temperature (200-250°) hydrogenations were softer for equivalent I numbers, and had lower melting points than those from low temperature hydrogenations. Hydrogenation of partly polymerized linseed oil yielded a product that when heated did not develop the characteristic odor of hydrogenated linseed oil. IV. FURTHER PROCESSING STUDIES. H. J. Lips (Natl. Research Labs., Ottawa), H. W. Lemon, and G. A. Grant. *Ibid.*, 44-50. Flavor reversion could not be detected in samples of hydrogenated linseed oil stored under vacuum in the dark. In samples exposed to the air, reversion occurred without appreciable increase in peroxide oxygen or Kreis values, particularly in products of low I number, while accompanying changes in fluorescence were slight and erratic. An observed "bad area" for susceptibility in the lower I number range suggests that iso-linoleic acid is not the only cause of reversion. No improvement in flavor stability was obtained by: low to high temperature hydrogenation (110-240°), removal of impurities from the oil, or the use of linseed oil fraction from a commercial polymerization process.

RATION BISCUITS. IV. EFFECT OF TEMPERATURE AND SHORTENING TYPE ON KEEPING QUALITY. H. J. Lips, N. C. Crowson, and W. H. White (Natl. Research Labs., Ottawa). *Can. J. Research* 25F, 51-62 (1947). Biscuits prepared with hydrogenated vegetable shortenings were generally more stable (average storage life: 84, 22, and 13 weeks at 26.7°, 43.3°, and 60° respectively) than those prepared with animal-vegetable or blended vegetable shortenings. However, shortenings with Swift stabilities (110°) greater than 40 hr. did not yield products of increased keeping quality.

THE GLYCERIDE STRUCTURE OF NATURAL FATS. K. F. Mattil and F. A. Norris (Swift & Co., Chicago). *Science* 105, 257-9 (1947). An analysis of representative data showing the relationship of the molar concentrations of trisaturated glycerides to those of saturated acids in natural fats reveals that in the case of animal fats the glycerides are formed by a "random" or nearly "random" distribution of fatty acid radicals among the glycerol molecules. It has been shown that the "even distribution hypothesis" does not represent truly "even" distribution, but rather is an approach to the latter, being more or less arbitrarily fitted to experimental data. No general class of fats adheres to truly "even" distribution. Seed fats appear to approach the trisaturated glyceride contents anticipated by the "even distribution hypothesis," but even here data are inconclusive.

NORMAL AND DEFECTIVE FAT ABSORPTION IN MAN. A. C. Frazer (Birmingham, Eng.). *Schweiz. Med. Wochensch.* 76, 903-16 (1946). A review.

A COMPARISON OF THE COEFFICIENT OF DIGESTIBILITY AND THE RATE OF ABSORPTION OF SEVERAL NATURAL AND ARTIFICIAL FATS AS INFLUENCED BY MELTING POINT. M. E. Crockett and H. J. Deuel (Univ. So. California, School Med., Los Angeles). *J. Nutr.* 33, 187-94 (1947). The digestibility coefficients obtained were margarine (m.p. 34°), 97.0; Crisco (m.p. 43°) 97.3; prime steam lard (m.p. 37°), 96.6; bland lard (m.p. 48°), 94.3; hydrogenated lard (m.p. 55°), 63.2; and hydrogenated lard (m.p. 61°), 21.0. There was no evidence that any fat produced any abnormal physiological effect, such as diarrhea. The rates of absorption for 3 hours, expressed in mg. per 100 cm<sup>2</sup> per hour, were margarine, 37.7; Crisco, 37.1; prime steam

lard, 35.0; bland lard, 34.5; hydrogenated lard (m.p. 55°), 21.6. The values obtained for 6 hours were: margarine 34.7; Crisco, 34.3; prime steam lard, 38.3; bland lard, 31.4; hydrogenated lard (m.p. 55°), 21.6. A large proportion of the undigested fat in the tests with the hydrogenated lards were excreted in the form of soaps.

THE EFFECT OF CRUDE LECITHIN ON THE COEFFICIENT OF DIGESTIBILITY AND THE RATE OF ABSORPTION OF FAT. V. Augur, H. S. Rollman, and H. J. Deuel (Univ. So. California, School Med., Los Angeles). *J. Nutr.* 33, 177-86 (1947). The addition of lecithin to cottonseed oil or to a hydrogenated cottonseed oil markedly lowers the susceptibility to diarrhea caused by a large dose of these fats to rats. Fats containing 1/6 or 1/5 crude lecithin are absorbed more rapidly than a similar fat without any added phosphatide. It was found that hydrogenated cottonseed oil melting at 63° had a digestibility of 24 in the rat; that melting at 54° was digested to the extent of 69% while that melting at 46° had a digestibility coefficient of 84. These were increased by the addition of lecithin to 44, 83, and 88%, respectively. A considerably larger portion of the lipid in all cases was excreted as soaps than as neutral fat plus fatty acids.

SOME EFFECTS OF HIGH LIPID DIETS ON INTESTINAL ELIMINATION. IV. SATURATED FATTY ACIDS. Helen L. Wikoff, B. H. Marks (Ohio State Univ., College Med.), J. F. Caul, and W. F. Hoffman. *Am. J. Digestive Dis.* 14, 58-62 (1947). Measured amounts of fatty acids mixed with a standard dog food (Pard) were fed to dogs to determine whether intestinal elimination would be affected by the added acid in the same manner as by the addition of the corresponding triglyceride. Constipation was produced by 5% added stearic acid. The neutral ether extract of feces increased for every animal after the 5% stearic acid feedings but the so-called soap fat was less than the normal value in every case. The addition of 10% lauric acid to the normal diet did not affect the normal rate of elimination of the dogs. The feeding of diets containing caprylic, caproic, or butyric acid produced laxative effects in all cases. The intensity of the action varied inversely with the number of C atoms just as in the case of the triglycerides of the corresponding acids. The low acid numbers of all of the fractions indicate that neither the fatty acid as fed nor its soaps are present in the feces to any extent. These low acid numbers can only be explained by assuming that small amounts of free fatty acids are mixed with large amounts of non-titratable material or by a very large molecule having an acid radicle.

ISOLATION OF THE GROWTH FACTOR FROM THE FATTY ACID FRACTION OF SUMMER BUTTER. J. Boer, B. C. P. Jansen, and A. Kentie (Physiol. Chem. Lab., Univ. Amsterdam). *Voeding* 7, Suppl. No. 1, 45-8 (1946), also *J. Nutr.* 33, 339-58 (1947). An account was previously given of the growth-promoting effect for rats of summer butter compared with rape oil when either fat was present to the amount of 10% in a certain basal diet. It is now reported that the growth-promoting activity of the butter was present in the saponifiable fraction, and probably resided in an unsaturated isomer of oleic acid in which the double bond was present between C<sub>11</sub> and C<sub>12</sub>.

EFFECT OF DIETS ON THE DEPOSITION OF LIVER LIPIDES IN PARTIALLY NEPHRECTOMIZED RATS. S. Ludewig and A. Chanutin (Univ. Virginia, Charlottesville).

*J. Biol. Chem.* 167, 35-48 (1947). Evidence is presented to show that lipide metabolism is disturbed after experimental production of renal insufficiency by subtotal nephrectomy in rats. The total lipide concentrations of the livers of partially nephrectomized animals are lower than those of pair-fed intact rats. This was shown for a large variety of diets containing varying amounts of casein, hydrogenated fat, corn oil, cystine, cholesterol, vitamins, and methionine in the presence or absence of choline.

## PATENTS

SOLVENT EXTRACTION OF FATTY MATERIALS. E. N. Mortenson (Industrial Patents Corp.). *U. S.* 2,416,196. Solvent extraction apparatus is designed so that extraction is made at about the boiling temperature of water. The solvent selected must have a boiling point greater than that of water.

OIL EXTRACTOR. H. Truax (Indiana Farm Bureau Co-Operative Assoc. Inc.). *U. S.* 2,416,421. Special accessories for a continuous solvent soybean oil extractor were designed for the removal of fines from the miscella.

CONTINUOUS BUTTER MANUFACTURE. L. K. Riggs (Kraft Foods Co.). *U. S.* 2,414,837. The improved step in the process of making milk fat comprises adjusting the acidity of cream to about 4.2 pH and also raising the temperature to about 200°F., and then centrifuging the heated cream so as to break the original emulsion and produce a material containing from 80-95% of milk fat.

REFINING FATS AND OILS. H. C. Black and W. F. Bollens (Industrial Patents Corp.). *U. S.* 2,416,146. The oil is mixed with 1-10% water to precipitate gums, it is then treated with selective solvent-free fat acids and this followed by an alkali treatment.

REFINING CRUDE WOOL GREASE. E. Snyder (American Chemical Paint Co.). *U. S.* 2,417,329. Degras is emulsified by heating with soap and water; alkali treated and sulfonated oil is added to break the emulsion.

TRIGLYCERIDE REFINING. E. S. Liebscher. *U. S.* 2,415,140. Glycerol is added with the alkali refining agent to aid the separation of the foots.

REFINING OF GLYCERIDE OILS AND RECOVERY OF BY-PRODUCTS. M. Mattikow (Refining Uninc.). *U. S.* 2,415,301. The oil is refined with basic salts, such as Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, etc., water is added and the oil is centrifuged to separate sterols, glucosides, etc.

RECOVERY OF VALUABLE FRACTIONS FROM GLYCERIDE OILS. B. H. Thurman (Refining Uninc.). *U. S.* 2,415,313. The method of treating a crude glyceride oil to recover valuable minor constituents comprises subjecting the oil to a gum, precipitating with an aqueous agent, and separating the precipitated gums to produce a substantially gum-free oil; subjecting the resulting oil to an alkali refining to separate a soapstock free of gums and solvent extracting the soapstock to recover unsaponifiables.

HYDROXYLATION OF UNSATURATED ORGANIC COMPOUNDS CONTAINING AN ALCOHOL OR ETHER GROUP. N. A. Milas (Res. Corp.). *U. S.* 2,414,385. Process of making glycerol from allyl alcohol comprises reacting allyl alcohol with H<sub>2</sub>O<sub>2</sub> in an initially substantially anhydrous inert organic solvent medium and in the presence of OsO<sub>4</sub> as a catalyst for the reaction, and directly recovering glycerol from the resulting reaction mixture.

VITAMINIC PRODUCTS AND PROCESSES. N. D. Embree and E. M. Shantz. *U. S. 2,414,458*. The free vitamin A is first distilled from liver oil, the residue is then heated to convert vitamin A precursors to the vitamin.

FAT-SOLUBLE VITAMIN SOLUTIONS. L. Freedman and E. Green (U. S. Vitamin Corp.). *U. S. 2,417,299*. A fat derived dispersing agent is used as the emulsifier.

SIZING AND DRESSING MEANS. J. Bergier and A. Helbronner (Alien Property Custodian) *U. S. 2,415,408*. Sizing and dressing for artificial silk consists of 77 water, 9 ethanol, 9 neutral Na salt of abietic acid and approximately 2 each of triethanolamine, Na sulphoricinoleate and 1% of mineral oil.

TEXTILE TREATING COMPOUNDS CONTAINING SILICON AND THE PROCESS OF MAKING SAME. C. A. MacKenzie Montclair Res. Corp.). *U. S. 2,415,017*. A water-soluble, silicone-containing compound capable of rendering textile fibers water-repellent when deposited and decomposed by heat thereon is the product of reaction at about 90° of a tertiary amine with a reaction product of a mixture of formaldehyde, a silicone halide, and a fatty acid amine.

ANTICORROSIVE. F. B. Wells (Ellis-Foster Co.). *U. S. 2,417,028*. The metal is dipped into a 1-10% solution of hydrolyzed lanolin in xylene.

ANTI-SLUDGE COMPOUNDS FOR LUBRICANTS. J. M. Musselman (Standard Oil Co.). *U. S. 2,415,836-8*. The additive improver is a thiophosphoric compound made by the reaction of P<sub>2</sub>S<sub>5</sub> on ester wax, i.e., lanolin, sperm oil, or synthetic esters.

POUR DEPRESSOR. E. Lieber (Standard Oil Development Co.). *U. S. 2,415,699*. Acyl nitrites prepared from fat acids are condensed to yield the active product.

LOW POUR POINT LUBRICANT. A. J. Morway and J. C. Zimmer (Standard Oil Development Co.). *U. S. 2,417,264*. This grease contains mineral oil grease, Li soap, Zn soap, and Sn soap.

INSECT REPELLENT COMPOSITIONS. H. A. Jones and B. V. Travis. *U. S. 2,396,012*. A method of repelling insects comprises applying to the area from which the insects are to be repelled an insect repellent composition containing as its essential active ingredient 2-ethyl-*n*-caproic acid, pelargonic acid, or cyclohexanecarboxylic acid.

ALUMINUM SOAPS. A. I. Gebhart and J. Ross (Colgate-Palmolive-Peet Co.). *U. S. 2,417,071*. A process for preparing metal soaps comprises contacting an aqueous solution of a soap with an aqueous solution of a water-soluble salt of a metal giving a substantially water-insoluble salt of fat acid, and maintaining the ionic constituents of water-insoluble salt in the contacting solutions in stoichiometric proportions.

oils is preceded by conversion into conjugated forms which may be activated by the presence of an adjacent hydroperoxide group. It is suggested that the specific properties of the —CH=CH—CH<sub>2</sub>—CH=CH— group may favor, in the plant cell, the formation and stabilization of this particular form of polyethenoid unsaturation and thus lead to widespread predominance of linoleic (and to some extent linolenic) glycerides in the plant kingdom.

STUDIES ON TUNG OIL AND OITICICA OIL. A. Steger, J. van Loon, and P. J. van Vlimmeren (Tech. High School, Delft, Netherlands). *Fette u. Seifen 51*, 49-53 (1944). Hydrogenation experiments were run on samples of tung oil and the Me esters of tung and oiticica fat acids. Observed changes in I number, diene number, and other constants are discussed from the standpoint of reaction mechanism. Derivatives are reported for β-couepic (licanic) acid and γ-ketostearic acid from oiticica and Po-Yoak oils. The oximes melt at 60° and 85.1° respectively and the semicarbazones melt at 137-8° and 119°. (*Chem. Abs. 41*, 1472.)

ALUMINUM-ACTIVE LINOLEIC ACID-OXYGEN ADDUCTS. I. THE ALUMINUM NUMBER. E. Eigenberger (Deut. Tech. Hochschule, Prague, Czechoslovakia). *Fette u. Seifen 53*, 43-9 (1944). The aluminum number of an oil is determined by titration with an aluminum alcoholate. This constant is useful in following the formation of α-ketoles and β-diketones in the oxidation of drying oils. (*Chem. Abs. 41*, 1465.)

STANDOIL PREPARATIONS WITH THE USE OF SULFUR DIOXIDE. D. Cannegieter. *Verfchroniek 19*, 126-30 (1946). An address reviewing the work done on this subject based on the patents of H. J. Waterman, Industrial Chemical Industries, and Pieter Schoen—12 references, 6 graphs. (*Chem. Abs. 41*, 1465.)

REPLACEMENT OF LINSEED OIL. H. W. Chatfield. *Oil Colour Trades J. 110*, 1186, 1188, 1190 (1946). A discussion of the various materials which can serve as replacements for linseed oil (*Chem. Abs. 41*, 1464.)

UTILIZATION OF SAFFLOWER OIL. S. A. Saletore and R. K. Shrivastav. *J. and Proc. Inst. Chem. (India) 17*, 117-25 (1945). Safflower oil was found to be suitable for oil-cloth manufacture, giving a film of very good flexibility and abrasion resistance; it is not suited for the final coating owing to its low water resistance. When mixed with dehydrated castor oil it gives a film of improved flexibility, water resistance, hardness, and reduced tackiness. (*Chem. Abs. 41*, 1851.)

## PATENTS

PROCESS FOR ESTERIFYING A CATALYTICALLY DEHYDRATED AND HEAT-BODIED CASTOR OIL. A. E. Rheineck and S. B. Crecelius (Devoe & Reynolds Co.). *U. S. 2,415,969*. A varnish is made by heating castor oil progressively to reach a temperature of 220-350° with 0.005-0.2% of a heteropoly acidic compound of W until the castor oil is largely dehydrated and substantially heat-bodied, adding an additional amount of a polyhydric alcohol containing at least 3 C atoms in excess of that necessary to neutralize resulting free fatty acids, heating to cause such polyhydric alcohol to react and esterifying residual hydroxyl groups with a natural resin acid.

RESINOUS REACTION PRODUCT OF POLYMERIZED FATTY ACID ESTER, ROSIN, AND TRIALKANOLAMINE. C. F. Brown (U. S. Rubber Co.). *U. S. 2,416,433*. A resinous composition is obtained by heat reaction, at 180-300°, of

## Drying Oils Edited by HOWARD M. TEETER

MECHANISM OF OXIDATION AND REDUCTION OF THE UNSATURATED GROUPS IN DRYING OILS. T. P. Hilditch. *J. Oil Colour Chem. Assoc. 30*, No. 319, 1-16 (1947). Selective hydrogenation in the unsaturated fatty acid series is restricted to, and is a function of, compounds in which a single —CH<sub>2</sub>— group separates 2 ethenoid groups. In autoxidation, addition of O to the double bond occurs. The addition product rearranges to form a hydroperoxide with simultaneous shifting of a double bond. The polymerization of autoxidized

a mixture containing rosin, triethanolamine, ethylene glycol, a dimerized soybean oil fatty acid, and a polyvinyl acetal resin.

PRINTING INK. D. J. Bernardi and R. J. Florence (Interchemical Corp.). *U. S. 2,416,676*. A printing ink vehicle comprising limed tall oil has drying speed and printability similar to a linseed oil printing ink vehicle.

ROSIN-MALEIC ANHYDRIDE-NON-CONJUGATED FATTY OIL VARNISHES. L. K. Scott (Devoe & Reynolds Co.). *U. S. 2,417,327*. A step in this process of making varnishes comprises simultaneously reacting together rosin, maleic anhydride, and a fatty oil having non-conjugated ethylene linkages such as drying oils and semi-drying oils, at a temperature above 200° and not exceeding 320°, the maleic anhydride being present in less than equal molecular proportions relative to the rosin and in proportion of from about 1/5 mol to 1 mol of maleic anhydride for each mol of oil, the reaction being carried out in the absence of polyhydric alcohol.

REFINING OF FATTY OILS. Aerovox Corp. *Brit. 581,483*. Fatty oils, particularly castor oil, which tend to emulsify with water, can be refined, after the fat acids are neutralized, by the use of a series of treatments with absorbent earths. By such treatments the resistivity of castor oil has been increased from 1500-9000 megohms at 80° to over 100,000 megohms. (*Chem. Abs. 41, 1857.*)

SICCATIVE EMULSIONS. A. G. Rozental and E. O. Bukan. *U.S.S.R. 66,016*. Polymerized and oxidized vegetable oils are vigorously stirred in water in the presence of CaO. (*Chem. Abs. 41, 1854.*)

SICCATIVES. A. Ya. Drinberg and V. K. Tsyskovskii. *U.S.S.R. 66,249*. In the condensate obtained on cooling of the steam-vapor mixture formed in the oxidation of oil products, the insoluble fatty acids are saponified by usual means without removing the unsaponifiable constituents, and then are precipitated with a Mn salt or similar siccative metal salt. (*Chem. Abs. 41, 1854.*)

EMULSION OF A DRYING OIL. V. S. Varlamov. *U.S.S.R. 66,487*. The drying oil is mixed with water in the presence of siccatives prepared from noncorrosive and neutral metal oxides. (*Chem. Abs. 41, 1854.*)

## Soaps

Edited by  
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THE KRAFFT POINT. A FUNDAMENTAL NOTION IN THE PHYSICO-CHEMISTRY OF SOAPS. M. Demareq. *Ind. corps gras* 2, 341-52, 370-5 (1946); 3, 13-21 (1947). The Krafft point was described as the temperature at which a soap solution becomes opaque. It might be termed the point at which cogel or crystal formation takes place. This is a definite characteristic of soaps which varies only a little with the soap concentration, increases with increasing number of C atoms in the chain, and with Na soaps it is a little less than the solidification point of the corresponding fat acids. This physical concept of soap is discussed from the viewpoint of optical properties (microscopic examination, Tyndall effect), viscosity, elasticity, electric conductance, dilation, thermic effect, x-ray diffraction, and series of works and data of schools of Stauff, Thiessen, and McBain. The data of Krafft did not quite coincide with the point of cogel formation ac-

ording to McBain, possibly because of unobserved influences. The present author obtained Krafft point results concordant to point of cogel formation according to McBain by retarding hydrolysis of the soap by means of the presence of carbonates of the alkalies corresponding to the soaps being tested, i.e., for Na soaps, Na<sub>2</sub>CO<sub>3</sub> was used in amounts sufficient to raise the pH above 10. The Krafft points of the alkali stearates were: Li 145-150°, Na 79, K 48, Rb 52.5, and Cs 49°; results on other soaps were: Li oleate 72, Li caprate 123-125, Na laurate 38, and K palmitate 30.5°.

ACTION OF SULFURYL CHLORIDE ON OLEIC AND STEARIC ACIDS. Felix Bouquet and Charles Paquot. *Compt. rend.*, 223, 481-3 (1946). When 13.5 g. SO<sub>2</sub>Cl<sub>2</sub> was added little by little to 14.8 g. Me oleate, rapid reaction took place with the formation of *θ,ι*-dichlorostearoyl chloride (I) and evolution of HCl, SO<sub>2</sub>, and Me derivs. I was formed whether the reaction was carried out at -10°, at room temperature, or in the presence of a solvent such as ether or CCl<sub>4</sub>. AlCl<sub>3</sub> did not change the course of the reaction other than to give considerable tarry material. I reacted in the cold with alcoholic KOH to give K *θ,ι*-dichlorostearate. Both stearic acid and *θ,ι*-dichlorostearic acid reacted with SO<sub>2</sub>Cl<sub>2</sub> in the presence of pyridine to yield sulfonyl chlorides which, after saponification, yielded products very soluble in water and lathering freely. (*Chem. Abs. 41, 947.*)

THE EFFECT OF SALTS ON THE CRITICAL CONCENTRATION FOR THE FORMATION OF MICELLES IN COLLOIDAL ELECTROLYTES. M. L. Corrin and William D. Harkins (Univ. Chicago). *J. Am. Chem. Soc.* 69, 683-8 (1947). A systematic investigation of the effects of salts upon the critical concentrations of detergents, using the dye titration method, was made. It was found that the depression of the critical concentration of such electrolytes, as measured by the spectral change of a dye, is related only to the concentration of that ion of an added salt which bears a charge opposite to that on the colloidal aggregate. Within each class of detergents, it was found that the lower the critical concentration, i.e., the greater the tendency toward aggregation, the greater is the lowering of the critical concentration by equal amounts of salt.

A BACTERICIDAL DETERGENT FOR EATING UTENSILS. Albert F. Guiteras and Rebecca L. Shapiro (Foster D. Snell, Inc., Brooklyn, N. Y.). *J. Bact.* 52, 635-8 (1946). When cation-active agents are used as bactericides in detergent compositions, it is essential that the detergent be emulsifying and not saponifying. If the alkalinity of the detergent is sufficient to saponify fats, the resulting soap will inactivate the cation-active agent and render the solution completely inactive germicidally. (*Chem. Abs. 41, 1474.*)

THE EFFECT OF SOLVENTS ON THE CRITICAL CONCENTRATION FOR MICELLE FORMATION OF CATIONIC SOAPS. M. L. Corrin and William D. Harkins (Univ. Chicago). *J. Chem. Phys.* 14, 640-1 (1946). The effect of 0-20% of BuOH, PrOH, EtOH, MeOH, HOCH<sub>2</sub>CH<sub>2</sub>OH, and 1,4-dioxane on the critical concentration (0.02-0.07M) for micelle formation of dodecyl ammonium chloride in aqueous solution, and the effect of 0.15% of BuOH, PrOH, iso-PrOH, EtOH, glycerol, HOCH<sub>2</sub>CH<sub>2</sub>OH, and 1,4-dioxane on the critical concentration (0.004-0.015 M) for micelle formation of decyltrimethylammonium bromide in aqueous solution are shown graphically. The compounds

named first give the maximum depression of the critical concentration: the last 3 in each list cause a slight increase in the critical concentration. Ward's hypothesis, which attributes the initial drop in critical concentration to adsorption of solvent molecules on the surface of the micelle, is untenable. (*Chem. Abs.* 41, 1527.)

STRUCTURE OF SUBMICROSCOPIC SOAP RIBBONS. P. A. Thiessen and H. Erdmann. *Z. physik. Chem.* 193, 367-77 (1944). Crystalline Et stearate was saponified with alcoholic NaOH and from the gel was obtained completely parallel, macroscopic, and highly oriented bundles of soap filaments, 8 cm. long. These were studied with the electron microscope and x-rays. The fibers are not round but are ribbons with rectangular cross sections. Isothermal vapor pressure measurements showed no evidence for the existence of hydrates. (*Chem. Abs.* 41, 1856.)

SYNTHETIC DETERGENTS. G. L. Parkhurst (Oronite Chemical Co., San Francisco, Calif.). *Soap Sanit. Chemicals* 23, No. 3, 37-8 (1947). The competition between soap and synthetic detergents is discussed. The special fields in which synthetic detergents excel over soap include household applications in hard water areas, use in washing of wool and fine fabrics in both soft and hard water areas, and use as toilet and bar soaps in any water type. Synthetics also have the advantage of incorporation of greater quantity of builders than soap. The future of detergents is reviewed.

PROPERTIES AND USES OF SURFACE-ACTIVE CATIONS. R. R. Ackley (Onyx Oil and Chemical Co., Jersey City, N. J.). *Soap Sanit. Chemicals* 23, No. 3, 39-42, 93, 175 (1947). The properties of surface active cations are reviewed. They dissolve in water, concentrate and orient at interfaces. Reactions with soap, wetting agents, silicates, etc., are listed. Conductivity curves of decyl-, dodecyl-, and hexadecyltrimethyl-ammonium bromide solutions are included. Surface active cations denature proteins, and may precipitate them above their isoelectric points. Cation-active agents may also split symplexes and precipitate chromo-proteins; disintegrate blood cells. They impart positive charge to suspended particles and are strongly absorbed by cellulose, glass, and textiles—43 references.

DETERMINATION OF THE CRITICAL CONCENTRATION FOR MICELLE FORMATION IN SOLUTIONS OF COLLOIDAL ELECTROLYTES BY THE SPECTRAL CHANGE OF A DYE. M. L. Corrin and William D. Harkins (Univ. Chicago). *J. Am. Chem. Soc.* 69, 679-83 (1947). A spectral method for the determination of critical concentrations of detergent micelles is described. A detergent solution of known concentration (above the critical concentration) and containing the proper dye is merely titrated with an aqueous solution of the dye until there is a sharp change of color or a sharp reduction of fluorescence. The detergent concentration at this point is the critical concentration. Pinacyanol chloride and Rhodamine 6G were shown to be suitable for titration with anionic soaps, while Sky Blue FF, eosin, fluorescein, and acidified 2,6-dichlorophenolindophenol may be used with cationic detergents. Critical concentrations of K laurate, Na dodecyl sulfate, and Na decyl sulfonate were 0.0234, 0.00602, and 0.0400, respectively, when titrated with pinacyanol chloride, and 0.0234, 0.00612, and 0.0387,

respectively, when titrated with Rhodamine 6G. Results on decyltrimethylammonium bromide and dodecylammonium chloride were 0.0643 and 0.0127, respectively, with Sky Blue FF, 0.0635 and 0.0136 with Eosin, 0.0610 and 0.0130 with fluorescein, and 0.0602 and 0.0124 with 2,6-dichlorophenolindophenol.

PARAFFIN-CHAIN POLAR COMPOUNDS. Gerard Deseigne and Marcel Mathieu (Lab. Central Services Chim., Paris). *Mem. services chim. etat (Paris)* 31, 359-83 (1944). The following pure compounds were prepared and used in determinations of the surface tension (I) of aqueous solutions: Na oleate and laurate (II); Na sulfates (III) of C<sub>4</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, and C<sub>16</sub> aliphatic alcohols, by reaction with ClSO<sub>3</sub>H; Na sulfonates (IV) of C<sub>10</sub>, C<sub>12</sub>, and C<sub>14</sub> alcohols, by reaction of RBr and NaHSO<sub>3</sub>; C<sub>7</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, and C<sub>16</sub> acyl N-Me Na taurines (V) and C<sub>1</sub>, C<sub>2</sub>, and C<sub>4</sub> alkyl N-lauroyl Na taurines (VI), by reaction of the taurine derivative with RCOCl. As intermediates, N-methyltaurine, m. 245°, N-ethyltaurine, m. 183°, and N-butyltaurine, m. 181°, were prepared by reaction of 10 molecules amine with 1 molecule ClCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na in an autoclave at 100°. Solutions were prepared at varying concentrations in highly purified H<sub>2</sub>O and I was determined at 40° with a duNouy balance. In a given group and for I concentration I was lowered as the chain length was increased. For III and IV, I was lowered with increasing concentration to a constant value in the range of 39-43 dynes/sq.cm. The concentration range in which the rapid drop in I occurred was lowered as the chain length was increased. For II and V, I passed through a minimum value with increasing concentration. The concentration at this minimum was lowered with increasing chain length. II produced greater lowering of I than III or IV of equal chain length. Increasing the length of alkyl substituent in VI produced a lowering of I at concentrations below 0.002 mols./l. Na lauroxyethane-phosphonate produced a very sharp and marked drop in I at about 0.00012 mol./l. The rapid drops and minimum obtained in I curves are believed to be due to the formation of soap micelles. (*Chem. Abs.* 41, 706.)

#### PATENTS

IMPROVEMENTS IN SOAP PRODUCTS. (Lever Brothers & Unilever, Ltd.). *British* 581,799. The solubility and calcium soap dispersing properties of a soap product are improved by the addition of from 1-15% by weight of guanidine stearate at any stage of the soap-making operation.

SOAP DRYING. Edwin T. Webb (Baker Perkins Ltd.). *Brit.* 581,203. Liquid soap (I) is sprayed into a vacuum chamber, the resulting dried soap being agitated to produce flakes or powder. The water content of I is about 30%, which by suitable regulation of temperature or vacuum is reduced to about 5% for soap powder or 14% if bar or flakes are to be formed. In the latter case the soap withdrawn from the chamber will be in a plastic form. The required temperature can be obtained by preheating I if desired. If it is desired to control the alkalinity of the finished soap, CO<sub>2</sub> or fatty acids can be introduced into the spray nozzle in proportionate amounts. A sketch and description of the proposed apparatus are included. (*Chem. Abs.* 41, 1858.)