

# Report of the Literature Review Committee

## Annual Review of the Literature on Fats, Oils, and Detergents. Part I.

I. I. RUSOFF, General Foods Corporation, Tarrytown, New York

### Introduction

The Annual Review of Literature Committee has attempted to bridge the gap between the last review, which was published in the Journal in 1958, and this current review. However it is not certain that the 1958 Literature was complete. This review does not provide for an economic appraisal of fats, oils, soaps, and detergents inasmuch as this field is being adequately covered in monthly issues of the Journal.

### Production Processes

**ANIMAL FAT AND FISH OIL.** Three improvements in animal tissue-rendering processes are reported. The Centriflow Process employs low temperature and short contact to accomplish good efficiency and ease of operation (Sullivan, *J. Am. Oil Chemists' Soc.*, 36, 70-73). The centrifugal rendering process maintains the fragile qualities of fatty tissues and produces not only high quality fat but protein tissue in an undamaged state (Downing, *J. Am. Oil Chemists' Soc.*, 36, 319-321). In a dry rendering process, packing-house materials are cooked and centrifuged while hot to separate most of the fat (Dormitzer, *U. S.* 2,875,222). The detections of the refining of lard by the aniline point (Kaufmann and Thieme, *Fette, Seifen, und Anstrichmittel*, 58, 585-592); and by the ultraviolet absorption spectrum (Kaufmann *et al.*, *ibid.*, 995-996) are reviewed.

The bitter taste and odor of whale oil is removed by homogenizing the oil with casein, water, and sodium hydroxide and then separating the oil by centrifugation (Tada and Nakayama, *Japan* 2841, [1958]).

**VEGETABLE OILS.** Processing of several vegetable oils are reported. The continuous process known as the Westphalia-Enfida process produces an oil of "estra" quality (Renaultt *et al.*, *Oléagineux*, 14, 95-104). Pectinase treatment of olive pulp before hydraulic pressing improves oil yields 2.7-10% (Anon., *Grasas y Aceites*, 9, 243-248). Coagulants are used for cleaning of oil or fats from seeds or nuts containing small solids or colloids (Andrews, *Ger.* 950,150). Sesame oil is reviewed by K. R. Varma (*Oléagineux*, 13, 793-801). The processing, storage, and nutritive value of cottonseed oil from nine Indian varieties are compared with American varieties (Subrahmanayan *et al.*, *J. Proc. Oil Technologists' Assoc.*, India, Kanpur, 10, 64-69). A deep red oil containing 80% of palm oil carotenoids is obtained by mixing various antioxidant-containing natural oils with carotenoid-containing extract of palm oil. The solid components are separated by fractional crystallization, and the liquid fraction is deacidified, dried, and deodorized in vacuum (Brinckman *et al.*, *Brit.* 804,685).

Several studies are reported concerning the raw materials of fat processing. The equipment used for the disintegration of raw materials is reviewed (Kaufmann and Thieme, *Fette, Seifen, und Anstrichmittel*, 59, 983-990 and 1096-1104). The moisture limits for stable storage of a number of vegetable oil seeds and nuts in bags or loosely in heaps are determined (Bartoszak, *Tłuszcz i Srodki Piorace*, 2, 218-221). The problems of water in the manufacturing process of fats are discussed, such as water in the maturation, drying, and germination of vegetable seeds, water in alkali refining, treatment of crude oil by steaming, separation of wax from rice-bran oil by steaming, etc. (Hidaka, *Abura Kagaku*, 5, 362-366).

The storage and transportation of crude and refined oils are reviewed (Olin, *Nord. Symposium om Harskning af Fedtstoffer*, 2, 203-211). A study of refined cottonseed oil held in storage for longer periods than are generally used in industry showed that there has been insignificant decreases in market value of seven out of eight drums (Baumann, *J. Am. Oil Chemists' Soc.*, 36, 28-34). The apparatus for the liquefaction of fat in railroad tank car is discussed in detail. (Shorin, *Masloboino-Zhirovaya Prom.*, 24[3], 32-37).

**BY-PRODUCT FATS.** A plant specifically designed to use waste acid from a chlorine dioxide bleaching process produces tall oil by a new continuous process at lowest cost (Sullivan, *J. Am. Oil Chemists' Soc.*, 36, 124-127). Tall oil is fractionated by

partial vaporization under reduced pressure (Sisson *et al.*, *U. S.* 2,894,880) and by fractional distillation (Hanson *et al.*, *U. S.* 2,886,492).

Fat in pig skins is extracted, refined, and used in the manufacture of toilet soaps (Akator *et al.*, *Masloboino-Zhirovaya Prom.*, 25[1], 36-38). A new method for processing peanuts increases the yield of oil and improves the quality of protein (Subrahmanyan *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 66-70). The purification of lanolin is described (Fayaud, *Ger.* 1,018,175). The recovery of wool grease is improved if the wash water is agitated with at least one surface-active ionic or anionic agent before the final scavenging operation (Raoul *et al.*, *Belg.* 526,672).

**EXTRACTION.** A number of new or improved extraction processes are patented. In a multiphase extraction process the material to be extracted is moistened first with miscella, then sprayed with pure solvent after leaving the bath (Gehle *et al.* *Ger.* 951,031). In a continuous-extraction process the seeds are extracted in bucket chain-extractors, and, before steaming, the residue is squeezed out (Depmer, *Ger.* 966,724). Another apparatus for continuous extraction of oil-containing seeds is patented in Germany (Süss, *Ger.* 962,011). In a solvent-extraction process, finely ground vegetable material is suspended and extracted in a solvent (Andrews, *U. S.* 2,850,511). A double

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soak process is used for the filtration-extraction of vegetable oil-bearing materials (D'Aquin *et al.*, *U. S.* 2,357,411). The process of solvent extraction of soybean oil is briefly described (McDonald, *Soybean Digest*, 19[1], 16). Peanuts are prepared to improve press capacity and extraction yield (Greek, *Tuszcze i Srodki Pioracc*, 2, 221-227). A study of the steam expenditures and ways of increasing the heat-utilization coefficient in oil-extraction plant indicated that, when the rate of feed to the distillation column is increased up to 8.7-9.3 cu. m./hr., steam consumption is reduced by 8% (Zarnitskii *et al.*, *Trudy Krasnodar. Inst. Pishchevoi Prom.*, 1956[14], 75-80). The optimum conditions for the removal of solvent from miscella are reported (Beleborodov and Chudnovskaya, *Masloboino-Zhirovaya Prom.*, 24[8], 13-17).

Alcohol, benzene, trichloro-ethylene, and hexane are the solvents studied for extraction. Benzene is found as the best solvent from a study of the solvent extraction of cottonseed (Chaudhuri and Nandi, *J. Indian Chem. Soc.*, Ind. & News Ed., 19, 87-94). The use of trichloro-ethylene in processing olive pulp (Catalano, *Olearia*, 11, 257-261); the use of ethanol for the extraction of oil from vegetable oil-cakes (Kaparathi and Chari, *J. Am. Oil Chemists' Soc.*, 36, 81-83); and the use of industrial alcohol for the extraction of wheat bran (Rao and Krishnamurthy, *Food Sci. [Mysore]*, 7, 147-148) are reported.

The influence of certain variables upon the direct, continuous, solvent extraction of sunflower seed meats is discussed (Furman *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 454-457). By using the experimental results, an oil content reduction from 53 to 1.68% in one operation is achieved in a full industrial-scale run. Soybean flasks of different thicknesses are extracted in nine solvents, and the theory and design methods of vegetable oil extraction are generalized (Othmer and Jaatinen, *Ind. Eng. Chem.*, 51, 543-546).

Oxidation during extraction and refining of oils and fats is determined by the color developed between carbonyl compounds and benzidine (Wode, *Nord. Symposium om Harskning af Fedstoffer*, 2, 181-193). In the same symposium the above method is reported by Møller as applicable to the determination of quality of crude oils but not to the determination of the stability of the finished product (*ibid.*, 195-202a). In the extraction of soybeans, plant balances show 0.44-0.72% more oil than do analytical results on the original soybeans (Semenov, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov.*, 1954 [15], 94-104). This is attributed to the decomposition of lipoproteins and sugar lipids during plant processing.

REFINING. Several new or improved processes are reported. Treatment with a sulfonated phenol-aldehyde ion exchange resin under anhydrous conditions is used to remove free fatty acids and other organic impurities (Gutkin, *U. S.* 2,863,890). A miscella refining method is reported in which a solution of the crude oil in a volatile solvent is mixed with foots, then treated with alkali (Schmitt, *U. S.* 2,878,275). The soda ash process is improved by mixing the crude oil with only a slight excess of soda ash so that evolution of carbon dioxide is prevented (Thurman, *U. S.* 2,876,242). A two-step process is used to remove free fatty acids in an oil. After neutralization with an alkali or an alkali metal carbonate solution, the soaps are separated, and in a second step the residual soaps in the oil are removed by centrifugation (Steinacker and Möller, *Ger. 965,733*). The washing of degummed oil with an aqueous solution of phosphate prevents foam formation (Hayes and Wolff, *U. S.* 2,881,195). Treating an oil with sodium hydroxide after it had been purified by phosphoric and oxalic acids and decolorized with hydrogen peroxide is described (Giuffria and D'Arrigo, *Boll. informaz. ind. olearia i saponiera*, 4, 3-7).

The following phases of refining are reviewed: the recent progress in the continuous refining of fatty oils (Braae, *Chem. & Ind.*, 1958, 1152-1160), the refining and hydrogenation of edible fats, oils, and waxes, with emphasis on olive and soybean oil production (Schwareman, *Chim. & Ind.*, 80, 587-592), the refining of vegetable oils for human consumption and for motor lubrication (Bourjol and Ortigues, *Chim. & Ind.*, 80, 712-715).

The centrifugal contactor for water-washing vegetable oil shows a number of advantages (Podbielniak *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 238-241). One- to ten-car capacity with one centrifugal contactor produces a higher quality of refined oil with 50% lower neutral oil loss in wash water. Complete neutralization and utilization of coconut, palm kernel, and other vegetable oils are obtained by treating the oil with alkali hydroxide and ethanol-amines (Weiss, *Israeli* 10,995). Up to 200 p.p.m. of diazinon residue in olive oil is removed by decolorizing with a mixture of "Rumsil" activated clay and activated carbon (Alessandrini *et al.*, *Rend. ist. super. sanit.*,

21, 1116-1125). The amounts of copper and iron are decreased to a half by alkali treatment but are not decreased by bleaching and washing. 1.5 p.p.m. of copper and 20.5 p.p.m. of iron are present in solvent-extracted crude oil; and 1.0-1.2 p.p.m. of copper and 12.5-13.1 p.p.m. of iron in pressed crude oil (Yonezawa, *Nosan Kakô Gijutsu Kenkyû Kaishi*, 3, 82-83).

The application of modern apparatus and rationalized oil-refining processes can lead to economic improvement of various units (Demper, *Fette, Seifen, und Anstrichmittel*, 61, 354-356). Automatic control system eliminates the necessity for operators skilled in the art of vegetable oil refining. They need only to be given the analysis of the feed stock; then they can set the controls and press the buttons. (Doyle *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 271-280).

BLEACHING AND DEODORIZATION. Waxes, oils, and fats are continuously bleached with chromic sulfuric acid (Schimer and Voit, *Ger. 957,508*). Animal or vegetable fats or oils can be used directly for soapmaking after being bleached with sodium chlorate solution and stirred with hydrochloric acid, phosphoric acid, oxalic acid, or metaphosphate (*Fr. 1,033,284*). Palm oil is bleached *in vacuo* with 0.1-0.5% fuller's earth at 175° or higher (Brinckman *et al.*, *Brit. 807,600*). Olive-husk oil is decolorized with hydrogen peroxide after its alcohol solution had been mixed with glycerol and refluxed (Cubeddu, *Ital. 536,559*). Tung oil is decolorized and deodorized without a substantial increase in viscosity by heating at 170-190°F. in the presence of about 5% of a solid absorbent (Watts, *U. S.* 2,867,639). After the absorbent is removed, at least 20% of the treated oil is further heated at 475-500°F. for no longer than 15 min. and is then added to the bulk of the adsorbent-treated oil. The use of bleaching earths in place of acid refining for decolorization of rapeseed oil and a pressing technique for lowering the color of cottonseed oil are recommended (Sterlin, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov.*, 1954[15], 105-113). The evaluation of activated clays for bleaching vegetable oils is described (Krejčinović *et al.*, *Kem. i ind. [Zagreb]*, 6, 77-82).

The effect of refining on the decrease in peroxide value depends on the type of earth used and temperature of bleaching (Grau and Mirna, *Fleischwirtschaft*, 10, 694-697). Increasing the amount of bleaching earth is more efficient than increasing the temperature for the bleaching of tallows and lards (Trizis and Uzzan, *Rev. franç. corps gras*, 5, 499-514).

Acid-activated Bagheshapura clay and activated carbon made from rice hulls are very effective for bleaching cottonseed oil (Murthy and Rao, *J. Proc. Oil Technologists' Assoc., India, Kanpur*, 10, 121-126). The fractions of clays from Lebrija rich in attapulgit are most active decolorants for vegetable oils (Callizo and García, *Anales edafol. y fisiol. vegetal*, 17, 935-972).

Two processes are reported for reclamation of oil and bleaching clay. The filter-press mud is extracted with an azeotropic mixture of benzene and alcohol or of alcohol with benzene, toluene, or trichloro-ethylene. The bleaching clay thus freed from fatty materials is activated by heating at 400-600° for 1-60 min. (Sethuraman *et al.*, *Indian* 61,157). Oils and fats are extracted from exhausted bleaching earths by treating several times with a solvent in a rotary drum (*Ital. 532,224*).

Deodorization of fish oil is effected by blowing hydrogen chloride gas into the oil heated at 150-300° (Kashima, *Japan* 784 [1958]). Whale oil deodorized in hydrogen atmosphere at 275° for three hr. or at 300° for 45 min. inhibits development of fishy flavors during storage (Khorin, *Masloboino-Zhirovaya Prom.*, 25[3], 34-35). Odorless fish-liver oil is collected in the anode chamber when the oil is placed in a vessel with semi-permeable membrane and carbon electrode with direct current at 200 volts (Kanai, *Japan* 3632 [1958]). A design of a plant for continuous deodorization of oils and fats is described (*Ital. 550,404*). During the deodorization of peanut oil, the rate of hydrolysis is a function of the free fatty acid content and moreover increases in direct proportion with the absolute pressure (Sarkadi, *J. Am. Oil Chemists' Soc.*, 36, 143-145).

DEACIDIFICATION. Ion exchange resins are used for deacidification of olive oil (Foresti and D'Arrigo, *Olearia*, 12, 16-18). The total acidity as oleic acid drops from 4.3 to 0.006% after the olive oil was mixed with Zerolit FF for 4 hr. Olive oil can be deacidified by passing its solution in an organic solvent through an aluminum oxide adsorption column (Minutilli and Ruggieri, *Pubbl. univ. cattolica S. Cuore, Ann. fac. agrar.*, Ser. 5, Atti convegno appl. tec. cromatogr. prod. agr., 53, 150-157). The deacidification of peanut oil with urea is economical but not complete (Louty, *Olearia*, 11, 213-217). Vegetable oils containing up to 4% acids are deacidified without injury to

their organoleptic characteristics by freezing and separating the liquid portions by centrifugation (Romeo, *Ital. 531,502*). Stirring column in a reaction vessel is described for the continuous deacidification of fats and oils (Schwartzkopff and Eger, *Ger. 955,411*).

**FRACTIONIZATION AND WINTERIZATION.** Various means are reported for the fractionation of fatty acids as well as triglycerides. Cottonseed oil is winterized in miscella by slow stepwise cooling (Cavanagh, *U. S. 2,883,405*). The crystallization of stearin is promoted by the presence of small amounts of moisture in the oil due to their formation of tiny nuclei (*Brit. 801,102*). Model mixtures of glycerides are efficiently separated in an apparatus designed to separate materials by automatic recrystallization in a thermal gradient (Magnusson and Hammond, *J. Am. Oil Chemists' Soc.*, **36**, 339-343). Molecular distillation at  $10^{-3}$  mm. Hg pressure and temperature of  $120-200^{\circ}$  is used to fractionate a number of vegetable oils (Kozin and Zlatopol'skaya, *Sbornik Nauch. Rabot Moskov. Inst. Narod. Khoz.*, 1956[8], 32-46).

Solid portions of crude fatty acids are separated from liquid portions by hexane dissolution and precipitation (Martinenghi and Viarengo, *Ital. 582,596*). Mixture of fatty acids are separated by fractionation at  $0-5^{\circ}$  in inert solvents (Martinenghi and Viarengo, *Ital. 550,734*). Tallow fatty acids are separated into saturated acid and a fraction containing oleic acid by fractional crystallization of an aqueous ethanol solution of the acids (Zahcer *et al.*, *Indian 62,263*). Saturated and unsaturated fatty acids are separated by aging an aqueous solution of the acid soaps at a temperature below  $30^{\circ}$  (Kairys *et al.*, *U. S. 2,895,976*), and by extracting their soap solution with methanol or ethanol (Notewarp *et al.*, *Norway 91,409*). Oleic acid essentially free from linoleic acid is obtained by cooling a partially neutralized methanol or ethanol solution of the fatty acids to  $0-8^{\circ}$  (Smull, *U. S. 2,858,324*). On the other hand, linoleic acid of about 95% is separated from safflower oil fatty acids by liquid-liquid extraction, using furfural and hexane as solvents in a Podbielniak "double-pup," centrifugal extractor (Beal and Brekke, *J. Am. Oil Chemists' Soc.*, **36**, 397-400).

Methyl esters are more than a hundred times more soluble in sulfur dioxide than the acids (Schlenk and Ener, *J. Am. Oil Chemists' Soc.*, **36**, 145-149). Acids, methyl esters, and glycerides can be fractionated efficiently in this solvent.

**HARDENING.** A number of new processes of hydrogenation are reported. High selectivity is obtained when cottonseed oil is hydrogenated in the presence of a nickel catalyst in a foam condition produced by passing hydrogen through a fritted glass bottom in the reactor (Elvovich *et al.*, *Zhur. Priklad. Khim.*, **32**, 187-193). A hardened vegetable oil containing less than 2% iso-acid and all of the carotenes present in the natural oil is produced by hydrogenation at a temperature below  $100^{\circ}$  (Kaufmann, *U. S. 2,852,541*). The addition of at least 0.05% of phospholipid prior to hydrogenation improves the plasticity and flavor stability of a hydrogenated fat (Merker, *U. S. 2,903,468*). The difference between melting point and solidification point of a hardened fat made by the continuous process of Bolton-Lush is improved by a new process which has a plurality of individual chambers superimposed one upon the other (*Brit. 804,604*). A continuous hydrogenation process is controlled remotely by proper arrangement of a panel (Okugov and Kopylenko, *U. S. S. R. 115,610*).

The hydrogenation of sunflower oil (Freier and Constantinescu, *Lucrařile inst. cercetări aliment.*, **2**, 91-97), Nageswar oil (Mukerjee, *J. Proc. Oil Technologists' Assoc., India, Kanpur*, **10**, 117-120), castor oil (van Loon, *Fette, Seifen, und Anstrichmittel*, **60**, 899-903), and a number of vegetable and fish oils (Bradbury *et al.*, *Ind. Eng. Chem.*, **51**, 1111-1120) are reported.

The selectivity and activity of catalysts for hydrogenation are reported. A Mn-Cr-Cu catalyst reduces only polyunsaturated fatty acids and does not attack oleic acid (Kuwata and Takume, *Japan 3223* [1958]). The depleted formate nickel catalyst is more selective than fresh catalyst for hydrogenation of sunflower oil (Kolesnikov, *Trudy Kras. nodarsk. Inst. Pishchevoi Prom.*, 1955[11], 81-82). Palladium catalyst selectively produced *trans*-isomers (Zajcev, *Fette, Seifen, und Anstrichmittel*, **60**, 1051-1052). Margarine oil is produced in one step by nonselective hydrogenation in the presence of moisture and a small amount of mineral acid or an aliphatic hydroxy acid (Merker, *U. S. 2,862,941*).

The rate of hydrogenation is increased when nickel formate catalyst is supported on neutral carriers such as Supercel (Nanavati and Aggarwal, *J. Proc. Oil Technologists' Assoc., India, Kanpur*, **12**, 83-91). The neutral supports are superior

to acid carrier of the type of fuller's earth or Kieselguhr both with regard to consistency of hydrogenated product and selectivity of hydrogenation. The productivity of nickel catalyst is slightly improved by blending with 50% and above of cobalt. (Tyutyunikov and Koshel, *Masloboino-Zhirovaya Prom.*, **25**, [2], 14-15). The greater the activity of the catalyst, the greater is the development of iso-oleates (Kolesnidov, *Izvest. Vysshikh Ucheb. Zavedenii, Pishchevaya Tekhnol.*, 1958[5], 48-52). Methods for preparing catalysts and the effect of various factors of the hydrogenation process to selectivity are described (Arnold *et al.*, *Ind. Eng. Chem.*, **50**, 1370-1379). The hydrogenation odors are due to volatile aldehydes and acids formed from moisture in the oil or hydrogen, which is also blamed for depressing selectivity.

Magnetized grids are used to remove catalyst from the hydrogenation product (Bremer, *U. S. 2,875,220*). The spent nickel-copper catalyst containing 8% soap increases the acidity of the hydrogenation product (Golendeev *et al.*, *Zhur. Priklad. Khim.*, **31**, 1722-1731). Determination of nickel in oils by a rapid x-ray spectrographic method using a cobalt internal standard (Dwiggins and Dunning, *Anal. Chem.*, **31**, 1040), and by a colorimetric method (Kameneva and Koblyanskiĭ, *Trudy Krasnodar. Inst. Pishchevoi Prom.*, 1955[11], 39-42), are reported.

To avoid the formation of odoriferous substances during the hydrogenation process, it is necessary either to remove the low-molecular-weight triglycerides or employ a catalyst which does not promote the formation of half acetals (Tyutyunikov and Grechishnikova, *Masloboino-Zhirovaya Prom.*, **24**[6], 8-12). To decrease loss of oil during hydrogenation, the hydrogenation temperature and water content of the hydrogen used should be decreased. (Vengerova, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov*, 1954[15], 128-137). The formation of positional isomers during the hydrogenation of methyl linoleate under various conditions is reported (Cousins *et al.*, *J. Am. Oil Chemists' Soc.*, **36**, 24-28).

A product similar to butterfat with a melting point of  $26-27^{\circ}$  is obtained by elaidinizing peanut oil at  $215^{\circ}$  with 1% of granular selenium (Prakash *et al.*, *J. Proc. Oil Technologists' Assoc., India, Kanpur*, **10**, 89-96).

**INTERESTERIFICATION.** A number of patents are devoted to the interesterification of lower-molecular-weight fatty acids into natural fats and oils. A fat with Wiley melting-point of  $95$  to  $100^{\circ}$ F. and a setting point of  $20$  to  $23^{\circ}$  is obtained by the rearrangement of a coconut type of oil with lower fatty acid glycerides from coconut oil, followed by mixing with palmitic acid triglycerides (Drew, *U. S. 2,874,056*). The stability and polarity of natural fats are improved by transesterification with low-molecular-weight fatty acids in xylol with sodium methylate catalyst (Taufel *et al.*, *Nahrung*, **2**, 178-192). The interesterification of coconut oil with hardened whale oil and cottonseed oil is described by Becker and Clemens (*Ger. 1,009,611*); that of coconut oil and lard by Nelson (*U. S. 2,892,721*); and that between a lauric oil and a hardened nonlauric oil by Cochran *et al.*, (*U. S. 2,859,119*).

The flavor stability of a normally reverting fat is improved by interesterifying it after hydrogenation with a normally non-reverting type (Cochran *et al.*, *U. S. 2,859,120*). Mixed varnishes are prepared by transesterification of a drying oil and a semidrying oil (Jekliński, *Zeszyty Nauk. Politech. Gdańsk. Chem.*, **2**, 9-27).

A shortening which produces pound cakes with increased volume is obtained by adding saturated triglyceride flakes to the modified product of tallow with at least one other fat (Steffen, *U. S. 2,855,310*). Nelson described the process of random distribution of the acyl radicals in at least two triglyceride compositions having a stable *beta* crystal structure (*U. S. 2,855,311*).

The limitations and uses of transesterification of fats for practical purposes are discussed (Yakubov, *Masloboino-Zhirovaya Prom.*, **25**[3], 19-22). No *cis-trans* isomerization or conjugation is detected during interesterification (Kaufmann and Grothues, *Fette, Seifen, und Anstrichmittel*, **61**, 425-459). Mono- and diglycerides arise in small quantities. Polymerization begins only at higher temperatures.

The directed or controlled interesterification of triglycerides has been studied. Directed rearrangement is effected by continuous agitation of a mixture of triglycerides which has been rapidly chilled to cause the sudden formation of a cloud of extremely minute crystals with a uniform dispersion of catalyst (Holman and Going, *U. S. 2,875,066*). A continuous controlled interesterification process is accomplished by initiating the crystallization of glycerides as soon as they are formed to displace the chemical equilibrium (Placek and Holman, *Chim. et ind.*, **81**, 526-534). Another continuous process for the di-

rected interesterification was carried out at a low temperature to yield a material containing a high concentration of trisaturated glycerides with an enhanced cloud-point (*Brit. 799,263*).

Various catalysts for interesterification of triglycerides are studied (Tüffel *et al.*, *Fette, Seifen, und Anstrichmittel*, 60, 456-461). A catalyst for interesterification is made of an alkali metal dispersed on an inorganic alkali metal salt of a strong acid (Weiss, *et al.*, *U. S. 2,865,759*). A powdered, solid catalyst, 10-50 millimicrons in size, is produced by spray drying 20% sodium methylate in ethyl alcohol (*Brit. 796,808*). Nickel catalyst is used to obtain interesterification up to 70% by heating soybean oil and butyric acid (Kaufmann *et al.*, *Fette, Seifen, und Anstrichmittel*, 60, 919-930). An alkali metal glycerate catalyst is used to rearrange lard and a low-molecular-weight glyceride by heating under reduced pressure (Van Akkeren, *U. S. 2,872,463*). Plural metal soap is used as catalyst for a continuous rearrangement between a mixture of higher fatty acid triglycerides and low fatty acid triglycerides (Brokaw, *U. S. 2,879,281*). The preparation of sodium methoxide as a catalyst for the transesterification of cottonseed oil is reported (Artamonov *et al.*, *Masloboino-Zhirovaya Prom.*, 25[3], 22-25).

When sufficient alkali metal alcoholate is used to react with the free fatty acids to form soaps and to furnish an excess of catalyst, acid is added in an amount sufficient to neutralize excess alkali but not to decompose the soaps which occlude color bodies after the interesterification is completed (Van Akkeren and Ast, *U. S. 2,878,374*). Water and an acidic agent are used for the inactivation of the alkali metal catalyst for interesterification (*Brit. 802,129*). A differential colorimeter which is suitable for the differential thermal analysis of fats offers a qualitative test for the interesterification of triglycerides (Kaufmann and Schnurbusch, *Fette, Seifen, und Anstrichmittel*, 61, 177-181).

**SPLITTING.** The acid hydrolysis of hydrogenated fat is accelerated by the presence of surface-active anionic and nonionic emulsifying agents and cationic adsorbers (Rozhdestvenskiĭ, *Masloboino-Zhirovaya Prom.*, 25[3], 31-34). Cation exchange resin is used for Twitchell splitting of Chrysalis oil (Koga, *Kagoshima Daigaku Nogakubu Gakujutsu Hokoku*, 7, 149-155). The effect of the resin seems to be not due to its catalytic action but to liberation of free dibutyl-naphthalene sulfonic acid. The saponification velocity of Chrysalis oil in the organic solvent system is decreased with decreasing of carbon number of the solvent (*ibid.*, 156-162). The mechanism of acid hydrolysis of fat is discussed (Bespyatov, *Masloboino-Zhirovaya Prom.*, 25[4], 9-12). An approximate formula for the determination of the maximum attainable completeness of fat hydrolysis is given (Molchanov, *Trudy Krasnodarsk. Inst. Pishchevoi Prom.*, 1955[12], 101-107).

Used copper-nickel catalyst contains up to 8% nonextractable Mg, Ca, Ni, and Na soaps (Goldenev *et al.*, *Masloboino-Zhirovaya Prom.*, 24[9], 17-22). The Mg and Ca soaps promote the splitting of fat during its hydrogenation at relatively high temperature, causing the increase in the free fatty acid content of the finished product. Odor and color bodies in fat splitting are removed by a continuous process (Ives and Thompson, *U. S. 2,895,975*). The fat is hydrolyzed with water under pressure, and the reaction products are immediately passed through a high-vacuum distillation zone where water and color- and odor-causing bodies are flashed off.

**PARTIAL ESTERS.** Monoglycerides from olive oil are prepared in the presence of urea with acetone and isopropyl alcohol as solvents (Rigamonti and Vaciera, *Olearia*, 12, 49-52). Yield of monoglycerides is not above 62% because the di- and triglycerides are occluded in the precipitate formed. Mono-esters are produced by the reaction of a triglyceride of an hydroxy fatty acid with a polyhydric alcohol containing no more than one primary hydroxyl group and at least one secondary hydroxyl group (Smith, *U. S. 2,902,500*). Partial esters of linseed oil are prepared by transesterification with a mixture of ethylene glycol and diethylene glycol (Mlejnek *et al.*, *Chem. průmysl*, 7, 41-44). The reaction of a higher acylated triglyceride with an hydroxy-containing reactant which consists of glycerol with a lower acylated triglyceride or a lower acylated glycerol partial ester comprising glycerol and a mixture of lower acylated glycerols is described (Embree and Brokaw, *Brit. 808,634*).

Partial glycerides are prepared by a reaction of a phosphatide with water in the presence of an anion exchange material (Beal, *U. S. 2,885,414*). Vegetable oils are deacidified by esterification with glycerol (Cruz and Romero, *Grasas y aceites*, 9, 64-73).

The esterification and transesterification techniques for the preparation of specific glycerides and of fatty glycerides of

desired properties are reviewed (Peterson and Way, *Ind. Eng. Chem.*, 51, 1081-1085). Partial esters of fatty acids and polyhydroxy alcohols are used as emulsifying agents (Golant and Petrov, *Masloboino-Zhirovaya Prom.*, 25[2], 16-19).

**BY-PRODUCTS.** A process has been developed for producing pharmaceutically pure sterols from tall oil pitch. A plant using this process to produce 1,000 lbs. of sterol per day is brought into operation (Steiner and Fritz, *J. Am. Oil Chemists' Soc.*, 36, 354-357). Stigmasterol and sitosterols are separated and purified from a solid phytosterol mixture (Fevig *et al.* *U. S. 2,905,677*). Sterols are separated from rapeseed oil soap stock (Niewiadomske, *Zeszyty Nauk. Politech., Gdańsk Chem.*, 1957 [2], 47-58). Hydroxy acids are formed in small amounts during the double pressing of sunflower seeds with expeller presses (Rzhekin and Pogokina, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov.*, 1954[15], 4-11).

The by-products of cottonseed crushing industry are reviewed (Prakash *et al.*, Symposium on Cottonseed and By-Products, Hyderabad, India, 1958, Sect. VI, 8-19). Pure gossypol is isolated from the gums obtained by water washings of crude hexane-extracted cottonseed oil (Pons *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 328-332). Over-all yields of purified gossypol from gums range from 41-36% for products of 98-99% purity respectively. Preliminary cost study indicates that crude gossypol-acetic acid can be produced at a cost of \$2.64 per lb. at an annual production of 113,500 lbs. and pure gossypol at \$5.55 per lb. at an annual production of 81,000 lbs. (Koltun *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 349-352). Under anaerobic conditions the fixation of gossypol in cottonseed oil is a reaction of the second order with respect to gossypol (Pons *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 337-339).

Oils and fats are recovered from decolorizing substances in an apparatus consisting of a rotating drum and auxiliary attachments (*Ital. 532,234*). The organic distillates from the deodorization process are recovered by a continuous process (Fiala, *J. Am. Oil Chemists' Soc.*, 36, 375-379). The operation of this system essentially eliminates barometric condenser-water disposal problems, and the deodorizers could be put on a closed-circuit water system.

Low-cost acidulated refinery soapstock is utilized directly as raw material for producing the mixed methyl esters of cottonseed oil fatty acids (Eaves *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 230-234). Processing acidulated foots containing 12.4% of neutral oil at the foregoing conditions resulted in esterifying 83-86% of the fatty acids. Reprocessing the same material after dehydrating it and restoring the initial methanol to fatty acids ratio increased the percentage of fatty acids esterified by about 5%. Fatty materials are recovered from vegetable oil soap stock by mixing and agitating with a water-insoluble solvent, such as aromatic hydrocarbon, halogenated hydrocarbon, or petroleum naphtha (Kelly, *U. S. 2,877,249*). Oil and proteins are recovered from press water obtained from animal material by successive centrifugation and partial evaporation (Borek, *U. S. 2,888,449*).

## Products (excepting detergents)

**EDIBLE, PHARMACEUTICAL, AND COSMETIC FAT PRODUCTS.** The problem of rancidity in milk is reviewed in some detail (Herrington, *Ann. Rept. N. Y. State Assoc. Milk Sanitarians*, 30, 87). Phospholipid interactions with casein in milk is the subject of a thesis. (Husaini, *Univ. Microfilms*, Ann Arbor, Mich., L. C. Card No. *Mc. 58-5350*; *Dissertation Abstr.*, 19, 919-920). Precursors to the radiation-induced oxidation flavor of milk fat are investigated (Hoff *et al.*, *J. Dairy Sci.*, 42, 468). A study of effect of synthetic antioxidants on stability of milk fat and sweet-cream butter has been made, and the well-known fat antioxidants are re-evaluated. The esters of gallic acid, especially propyl and dodecyl gallates, were highly effective in prolonging the induction period of milk fat and sweet-cream butter during their exposures to ultraviolet light and heat at 102° (Zalashko, *Molochnaya Prom.*, 20 [2]). An estimation and analysis of the monoglyceride content of milk is made (Jensen and Morgan, *J. Dairy Sci.*, 42, 232-239). Of several methyl ketones in evaporated milk, only heptanone-2 is considered to be of possible flavor significance (Wong *et al.*, *J. Dairy Sci.*, 41, 1699). A modified cream has been prepared to contain 22 to 28% butterfat, 15 to 16% non-fat milk solids, and no more than 60% water (Roberts, *U. S. 2,878,126*).

The influence of setting on the hardness of butter was investigated. The extent of setting, which is defined as the hardness increase during storage of the butter, is shown to be largely dependent on initial hardness; the harder butter displays the greater degree of setting. Setting was always less

however in continuously made butter when compared with conventional butter made in the same season. Rapid cooling of the cream resulted in a harder conventional butter, with an increase in extent of setting. The extent of setting may be permanently lessened by printing (De Man and Wood, *J. Dairy Sci.*, 42, 56). The effect of storage on the phospholipids and on the partition of phosphorus in butter has been studied (McDowell, *J. Dairy Research*, 25, 475). In a study of the composition of the phosphatides of butter made from ripened cream, the phosphatides isolated from butter serum have the ratio, lecithin:cephalin:sphingomyelin 30:45:25 (Koops, *Neth. Milk Dairy J.*, 12, 226). A critical review with 63 references was prepared on the addition of extraneous fats and their detection in butter (Vitagliano and D'Ambrosio, *Ann. fac. agrar. Univ. Napoli Portici [Naples]*, 22, 35). In a study of the effect of chlorinated water on the keeping quality of butter, it was concluded that butter washed with contaminated water developed rancidity within 21 days at 37–41° F. whereas water from the same source containing 5 parts per million residual chlorine gave butter which retained good flavor for six weeks. No chlorine "taint" was detected in the butter washed with water containing as much as 200 parts per million (Lewis, *et al.*, *J. Soc. Dairy Technol.*, 11, 186). A simplified method for the determination of the softening point of butterfat is given (Dixon, *Australian J. Dairy Technol.*, 14, 22). A simplified Ramsey-Patterson partition chromatographic method is described for use on short-chain fatty acids (butyric through capric) normally found in dairy products. (Kemp and Hetrick, *J. Dairy Sci.*, 41, 1494).

The patents that issued on the composition or processing of butter include: a substitute butterfat prepared by the interesterification of lard and coconut oil (Nelson, *U. S.* 2,892,721); a process for making hard butter from an unsaturated glyceride which involves hydrogenation, solvent crystallization, and interesterification (Barsky *et al.*, *U. S.* 2,898,211); and an apparatus for the continuous production of butter (Masek and Malik, *U. S.* 2,861,784). The introduction of vitamin C and tocopherol into butter indicates prolonged preservation as these vitamins repress fermentation (Novotel'nov and Stavrovaizvest, *Vysikh Ucheb Zavedni Pishchevaya Technol.*, 1958, No. 4, 64–68).

In a study of antioxidants for lard preservation, it was found that additions of tannin, isobutyl gallate, vitamin C and tocopherol, or mixtures of vitamin C and tocopherol are effective for lard stability when stored at room temperature for 347 days or oxidized intensely by bubbling water-free 97–99° air at a rate of 140 ml./min. for 5–15 hr. (Pysznik, *Prace Inst. Przemyslu Miesnego*, 1, 163).

In a study of the spreading properties of table margarines, the general aspects and the rheological problems were given consideration (Naudet *et al.*, *Rev. franç. corps gras*, 6, 4). The method of Smith and Bryant is adapted to the determination of extremely small quantities of water and is considered in connection with the determination of the water content of fats used for manufacture of margarine (Lowry and Lechartier, *Rev. franç. corps gras*, 5, 550). Three emulsifiers prepared by esterification of C<sub>16</sub> and C<sub>18</sub> fatty acids with glycerol, lecithin, and oxypolymerized oil emulsifier are compared in hydrogenated fat and margarine (hydrogenated fat plus 16% water) with regard to improving plasticity or thixotropy. Oxypolymerized oil was the poorest emulsifier.

The presence of water (16%) improves plasticity 1.5 times (Petrov *et al.*, *Izvest. Vysikh Ucheb. Zavedni Pishchevaya Tekhnol.*, 1958, 5–39). A fat is produced by the interesterification of a coconut type of oil with 1 to 20% of lower fatty acid glycerides from coconut oil, followed by physical mixing of the product with 1 to 15% of triglycerides of the palmitic acid fraction from coconut oil (Drew, *U. S.* 2,874,056). Lactones for flavoring fat-containing foods are described (Wode and Holm, *U. S.* 2,903,364). The rheological aspects of margarine and shortenings are reviewed (Enomoto *et al.*, *J. Japan Oil Chemists' Soc.*, 7, 511) and the measurement of the hardness of margarine and fats with cone penetrometers was investigated (Haighton, *J. Am. Oil Chemists' Soc.*, 36, 345). Needle and cone penetrometers are employed to test hardness of margarine (Sambuc and Naudet, *Rev. franç. corps gras*, 6, 10). Consistency of margarines is defined as the force necessary to extrude it through an orifice and by the sectilometer of Mohr, whereby the force used when cutting the sample with a steel wire is measured (Sambuc and Naudet, *Rev. franç. corps gras*, 6, 18).

Spectrophotometric determination of sorbic acid in margarine is done by employing slight modification of the method of Luckman and Melnick (Onrust, *Chem. Weekblad*, 54, 498). Laboratory tests for the production of a uniform shortening

are described (Woerfel and Bates, *Food Technol.*, 12, 674). A continuous process for the manufacture of an all-fat plastic shortening is patented (McGowan and Teasdale, *U. S.* 2,853,390) and a process for the production of shortening containing at least 25% tallow is disclosed (Steffen, *U. S.* 2,855,310).

A liquid shortening having a creamy consistency at room temperature is prepared from an edible triglyceride oil containing substantially no normally solid triglycerides, a minor amount of mono- and diglycerides of fatty acids containing at least 16 carbon atoms and not more than one double bond, and a small amount of a free fatty acid containing at least 16 carbon atoms and not more than one double bond (Broek, *U. S.* 2,868,652). A stable fluid shortening is prepared from an edible oil and 3 to 8% by wt. of a saturated long-chain fatty acid triglyceride containing at least one behenyl radical per molecule (Thompson, *U. S.* 2,875,065). A plastic shortening is prepared from at least 90% of a low-temperature rearranged and partially hydrogenated mixture consisting of at least 80% lard and no more than 20% tallow (Holmon and Going, *U. S.* 2,875,067). A wide-plastic range spread for the Canadian Armed Forces consists of hydrogenated edible tallow and acetoglycerides made from hydrogenated soybean oil (Lemon, Avis, and Haynes, *J. Am. Oil Chemists' Soc.*, 36, 45). An emulsified oleaginous spread containing a high amount of component essential fatty acids contains 75 to 92% of vegetable oils (Phillips, *U. S.* 2,890,959).

A review has been prepared on the topic "Fatty Acids in Foods" (Coons, *J. Am. Dietetic Assoc.*, 34, 242). The design, construction, and operation of a pilot-plant-size plasticizer for shortening and margarine is described (Harrington, Bates, and Stingley, *J. Am. Oil Chemists' Soc.*, 36, 539). The text of two communications relates to the incorporation of crystalline  $\beta$ -carotene in fat-based foods (Bauernfeind *et al.*, *Food Technol.*, 12, 527–535), and its success and acceptability in water-based foods (Bunnell *et al.*, *Food Technol.*, 12, 536–541). A solid carotenoid concentrate is prepared by dissolving at least 15% by wt. of carotenoid in cetyl alcohol (Klaui and Moor, *U. S.* 2,874,058). The industrial synthesis of carotenoids for use as food colors is described (Isler, *Food Technol.*, 12, 520–526). A process is designed for the preparation of an hydrogenated vegetable oil containing less than 2% iso-acids and all of the carotenes present in the natural oil (Kaufmann, *U. S.* 2,852,541). A difference in results of the catalytic hydrogenation of 9,10-epoxyoctadecyl acetate is attributed to the relative position of the oxirane center with respect to the acyl or alkoxy oxygen atoms of the ester (Fore and Bickford, *J. Org. Chem.*, 24, 620–622). At least two triglyceride compositions, having a stable  $\beta$  crystal structure, are found. The mixture has an acyl content of at least 95% C<sub>16</sub> and C<sub>18</sub> fatty acids, of which 73 to 80% are C<sub>18</sub> and 20 to 27% are C<sub>16</sub> acids. The mixture is heated to at least 50° C. in the presence of an alkaline catalyst so that random redistribution of the acyl radicals will occur (Nelson, *U. S.* 2,855,311).

An unsaturated fat which normally turns rancid and reverts is partially hydrogenated to a stability against reversion at least equal to that of 94° hydrogenated cottonseed oil (Cochran *et al.*, *U. S.* 2,859,120). Fat for use in chocolate mixes, ice cream mixes, shortening, and cake mixes is improved by the addition of 0.5 to 5% of a C<sub>22</sub> and C<sub>24</sub> fatty acid ester of a mono-alkyl-glucoside (Barsky and Babayan, *U. S.* 2,886,438). Properties of coconut and palm kernel oils are improved by the addition of a small amount of a C<sub>12</sub> to C<sub>15</sub> primary amine (Hampson and Freeman, *U. S.* 2,903,369). Interchange of ester radicals in specified triglycerides at about 120° C. in the presence of NaOCH<sub>3</sub> is disclosed (Becker and Clemens, *Ger.* 1,009,611). Oxidation of shortening and margarine is reviewed in a Japanese symposium on oxidation of foods and its prevention (Murata, *Abura Kagaku*, 7, 302). Selected topics of the symposium are: rusting of fish products and its prevention (Nonaka, *ibid.*, 317), and the oxidation of foods and its prevention (Kihara, *ibid.*, 322). Threads on a container for edible oils are coated with a film of an alkali metal dihydrogen orthophosphate salt (Holman, *U. S.* 2,871,130).

Influence of the extraction of lipids from flour on gluten development and breakdown is investigated (Blokma, *Chemistry and Industry*, 1959, 253). Flour bleaching or treatment with ammonium persulphate, benzoyl peroxide, and ascorbic acid produce little essential fatty acid destruction (Fisher *et al.*, *Chem. and Ind.*, 1958, 1361). The storage qualities of a baked product consisting of flour:fat:sugar in a ratio of 3:2:1 are followed with and without the addition of 10 micrograms of copper per gram of fat (margarine). The baked product at 18–20° in the absence of copper gives an increase in peroxide number from 1.5–42.7 during 21 weeks of storage. In the presence of copper the peroxide number is 322 at the end of

the same period (Täufel and Serzisko, *Ernährungs forschung*, 3, 100-107). Rancidity is inhibited in mantecas (a Spanish bakery product containing sugar, flour, and lard) by using antioxidants in the product or in the paper wrapper (de la Borbolla y Alcalá and Vargas Romero, *Grasas y aceites* [Seville, Spain] 9, 55-59).

Deterioration of flour is accompanied by oxidative and hydrolytic processes, involving the oxidation of double bonds of fatty acids, hydrolysis of glycerides, and the formation of lactides and estolides (Sosedov *et al.*, *Biokhim Zerna, Sbornik*, 1958[4], 206). The effect of unsaturation in wheat oil on baking strength is given consideration (Hart and Hutchinson, *Chem. and Ind.*, 90, 3). A cloud-point test is described as a means of characterizing the polyglycols of polyoxyethylene (8) stearate, employed extensively in yeast-raised baked goods (Brewster and Brandner, *J. Agr. and Food Chem.*, 7, 348-349). Staling of yeast-raised bakery products is inhibited by the addition of 0.1 to 1% by wt. of flour of 3-stearoyl-D-glucose to the dough (Naylor, *U. S.* 2,856,870). In the preparation of bakery products there is incorporated into the mix prior to baking 0.1 to 3.0% by wt. of a monoglyceride composition containing 50 to 95% of higher triglycerides and 5 to 50% of purified, saturated fatty acid monoglycerides (Kuhrt and Van Graafeiland, *U. S.* 2,871,124-5; 2,871,128). Staling of yeast-raised bakery products is inhibited by the addition of ascorbyl palmitate or hydrogenated ascorbyl palmitate to the dough (Ofelt and Hodge, *U. S.* 2,889,227). A monograph is given for use with a refractometric method for determining percentage of concentration of fat in bakery products (Kocharyan, *Khlebopekar. i Konditor. Prom.*, 3[10], 12). Breads containing 0.5-2% polyglycol-400-monostearate were analyzed. The polyglycol-400-monostearate extracted from bread samples had a hemolytic action against fresh blood corpuscles (Kliffmüller, *Deut. Lebensm.-Rundschau*, 54, 59).

Results are described on the acceptability of baked goods prepared with fats high in polyunsaturated fatty acids (Vail, *J. Am. Dietet. Assoc.*, 35, 119-121). The detection of lower fatty acids in dough and bread by paper chromatography is discussed (Croes, *Chem. Weekblad*, 54, 396). The use of lecithin in the production of bread containing defatted soya-flour as a protein supplement was found to improve volume and baking quality (Adler and Ponerauz, *J. Sci. Food Agr.*, 10, 449-456). The changes of various properties of edible oils on open-air heating are studied (Toi and Ota, *Kasei-gaku Zasshi*, 8, 205). A continuous conveyor for carrying foods through heated fat has been designed (Pack, *U. S.* 2,853,937). In another patent sliced potatoes are immersed in fat at 350 to 380° F. for 15 to 30 seconds, immediately withdrawn, and fried in fat at 250 to 300° F. for 2 to 5 min. (Buechele and Adacusky, *U. S.* 2,855,308). Other patents are: a jacketed kettle for potato chip frying (Seeh Jr., *U. S.* 2,861,514), a deep fat frier (Lutze, *U. S.* 2,867,164); a novel frying oil consisting of a deodorized, hydrogenated vegetable seed oil with an iodine value of 75 to 94, a melting point of 80° to 95° F., and a setting point of 55° to 65° F. (Melnick and Gooding, *U. S.* 2,874,055) and a deep fat fryer (Smoot and Smoot, *U. S.* 2,875,632).

A study of the continuous production of mayonnaise has been made (Smith and Rees, *J. Am. Oil Chemists' Soc.*, 36, 217). A salad and dessert topping involves incorporation of a cellulose derivative (Diamond and Powell, *U. S.* 2,868,653) while the addition of at least 0.001% of a metal chelating agent is disclosed in emulsified salad dressing (Stapf, *U. S.* 2,885,292). The effect of various foods on the lecithin content of egg yolk mixed with them has been studied (Vercillo, *Rend. ist. super. sn. sanita*, 22, 23). Addition of small amounts of very hard fats is useful in improving the performance of molded chocolate bars (Guice, Lovgren, Feuge, and Coster, *J. Am. Oil Chemists' Soc.*, 36, 4). In connection with viscosity increase, due to solid-fat formation in tempering chocolate coatings, a laboratory tempering kettle-viscometer has been developed (Duck, *Mfg. Confectioner*, 38[7], 9). Manufacture of cocoa-butter substitute from hydrogenated peanut, sunflower, and rape oils by the use of a crystallization method is described (Pokornyl, *Mastoboino-Zhirovaya Prom.*, 24[11], 17). Measurement of oxidation of cacao butter, edible fats, and products containing fats is reviewed (Kleinert, *Rev. intern. chocolat.*, 14, 9, 69, 114, 164). Determination of foreign fats in cacao butter is performed by use of low temperature crystallization and chromatographic techniques (Purr, *Fette, Seifen, und Anstrichmittel*, 61, 119). The use of glyceryl monostearate and related emulsifiers in candy is described (Knightly, *Mfg. Confectioner*, 38[6], 33). Food compositions having hypercholesterolemic activity consist of an edible fat in which is incorporated a sterol, preferably  $\beta$ -sitosterol in excess of that present in the edible fat (Beveridge, *Can.* 567,202). Carboxymethylated soybean

protein containing 7-9% carboxymethyl groups yield dispersions that exhibit resistance to putrefaction and do not gel on the addition of formaldehyde (McKinney and Uhing, *J. Am. Oil Chemists' Soc.*, 36, 49). Changes of fat in frozen mackerel during storage are studied (Khalina, *Izvest. Tikhookean. Nauch.-Issledovatel. Inst. Ryb. Khoz. i Okeanograf.*, 42, 299). A review was published on fat content of animal rations with 24 references (Maymone, *Ann. Sper. Agrar* [Rome], 12 Suppl. 1-11). A method is described for growing yeast for animal feeds, with a yeast yield equivalent to 45% of the sugar content of the olive oil waste (Ursinos, *Grasas y Aceites*, 9, 248-258). New patents on animal feeds are: detoxifying cottonseed meal (King, *U. S.* 2,873,190); cottonseed meal in laying hen diets (King *et al.*, *U. S.* 2,873,191); leguminous feeds (Horvath, *U. S.* 2,849,317); vitamin E fortified feeds (Baxter, *U. S.* 2,891,864); a dry stable feed supplement (Wilson, *U. S.* 2,899,307); and a poultry feed (Ely and Foy, *U. S.* 2,899,308). The possible toxic factor of trichloro-ethylene-extracted soybean oil meal is discussed (Picken *et al.*, *J. Am. Chem. Soc.*, 81, 909-915). A flash desolventizing process removes hexane to produce high-quality, essentially undenatured, soybean protein flakes for industrial uses (Brekke, Mustakas, Raether, and Griffin, *J. Am. Oil Chemists' Soc.*, 36, 256). Information is recorded on making feed yeasts from waste liquor of soap manufacture (Otsuka and Tada, *J. Agr. Chem. Soc. Japan*, 32, 805-810). A coating for the interior of cans to prevent adhesion of meat prepared from 25 to 75% by wt. of an alkylene bis-stearamide synthetic wax and 75 to 25% of a synthetic rubber is disclosed (Clark and Raisch Jr., *U. S.* 2,884,392). A coated sausage casing is disclosed (Dowd and Glaser, *U. S.* 2,866,710). Plasticizers for films used in packaging meat to preserve the red color of meat are disclosed (Snyder and Ferner, *U. S.* 2,900,260-261). Formation of bitter taste in a baked oat cereal product is prevented by incorporation of 0.1 to 12.0% of coconut oil (Blongvist and Malu, *U. S.* 2,868,648). A process for making cereal flakes with an oil content not more than 4% is disclosed (Grandel, *U. S.* 2,879,167). Information is given on primary antioxidants, synergists, and metal de-activators for use in the stabilizing of food products and includes animal and vegetable fats and oils (Hea, *J. Sci. Food Agr.*, 9, 621-632). An investigation of the effect of wrapping paper on fat stability was made (Kwapniewski *et al.*, *Przemysl Spozyczy*, 12, 412). A metallic foil sheet, coated on one side with a shortening which is pliable at room temperature, has a melting point above 140° F., and is used for wrapping foods before cooking is described in a patent (Shorr, *U. S.* 2,902,371). Essential fatty acids as food supplements are reviewed (Aaes-Jorgensen, *J. Agr. Food Chem.*, 7, 246).

A process has been developed for producing pharmaceutically pure sterols from tall oil pitch (Steiner and Fritz, *J. Am. Oil Chemists' Soc.*, 36, 354). A bifidogenic composition is prepared from a glycerophosphatide and cystine or cysteine (Keck, *U. S.* 2,872,382). Prior to incorporation into food compositions, essential fatty acid compounds are reacted with urea to form urea-inclusion products (Holman, *U. S.* 2,875,060). A gelled glycerol fatty acid partial ester as a pharmaceutical carrier is disclosed (Brokaw and Lyman Jr., *U. S.* 2,895,879). A sulfonamide composition comprising a lipid aqueous emulsion carrier is patented (Feinstone, *U. S.* 2,867,565). A fat emulsion for oral and intravenous use contains metabolizable oil, sugar, water, and ethylene oxide-polypropylene glycol condensate (Meyer, *U. S.* 2,870,019). A method of preparing sustained release particles is patented (Grass and Robinson, *U. S.* 2,875,130). In a discussion of flavomatics from fats, those fats containing low-molecular-weight fatty acids in their triglycerides (e.g., milk fat, coconut oil) are important flavorwise. Some flavomatics derived from fats are used in strawberry and other flavors although those from proteins and carbohydrates are more important (Broderick, *Am. Perfumer Aromat.*, 72[5], 49).

Several vitamin products are described in the patent literature: a vitamin oil in particulate form (Espoy, *U. S.* 2,858,215); a stabilized powdered oil-soluble composition (Dunn, *U. S.* 2,897,119); two products containing stabilized vitamin A materials (Lehman, *U. S.* 2,895,878), and (Allegretti, *U. S.* 2,897,118); and a process for making shark liver oil and vitamin A concentrates (Mahdihassan *et al.*, *Brit.* 810,643). The determination of vitamin D in multivitamin mixtures is discussed by Theiqvat and Campbell (*Anal. Chem.*, 31, 1375-1377), and a new patent was given on stabilized vitamin D (Cannalunga, *U. S.* 2,862,852). A water-dispersible carotenoid composition and a method for the production of carotenes are patented (Bauerfeind and Bunnell, *U. S.* 2,861,891) and (Anderson, *U. S.* 2,890,989), respectively. Rosenberg has been granted *U. S.* 2,855,306 on a fat-soluble vitamin composition.

A clear nonaqueous solution is prepared from a low-molecular-weight aliphatic alcohol and an oil by the addition of a low-molecular-weight aliphatic ester of a higher fatty acid (Lubowe, *U. S. 2,865,859*). An aerosol composition is prepared from a sun-screening agent, a propellant, and a water-repellent, film-forming liquid ester vehicle of high flash point (LaVia, *U. S. 2,853,423*).

**EMULSIFIERS.** Partial esters of fatty acids and polyhydroxy alcohols are reviewed (Golant and Petrov, *Masloboino-Zhirovaya Prom.*, 25[2], 16-19[1959] and 25[3], 15-18). A fatty acid diester of an alkyl glucoside is used as an auxiliary suspending agent for suspension polymerization of a vinyl halide in the presence of a maleic-vinylidene interpolymer (Lynn and Mohrman, *U. S. 2,862,913*). The stabilizing effect of free palmitic and stearic acids on fat emulsions is investigated (Kozin and Klyueva, *Sbornik Nauch. Rabot Moskov. Inst. Narod. Khoz.*, 1953[3], 65). Waxes suitable for self-polishing aqueous emulsions are disclosed (Kolling and Rappen, *Ger. 1,009,612*). Products obtained from synthetic paraffins by treatment with sulfur dioxide and oxygen are patented as easily emulsifiable materials for furniture, floor, and leather waxes (Schöller, *Ger. 967,233*). The quality of frozen confections is improved by the addition of 0.01 to 0.1% of an emulsifying agent, such as fatty acid esters of glycerol and sorbitol and 0.025 to 0.35% of a polyphosphate (Harrison, *U. S. 2,853,391*). Stable dispersions of vegetable phosphatide are prepared by successively extracting the phosphatides with a lower alcohol, dispersing the resulting fractions in glyceride oils or other suitable carriers, and finally heating the dispersions to remove the alcohol (Julian and Iveson, *U. S. 2,849,318*).

Aqueous fat emulsions, stable to autoclaving, are prepared by emulsification of a vegetable oil and lecithin in the presence of readily volatile aqueous-organic solvents and subsequent removal of the organic solvent (Degwitz, *U. S. 2,853,419*). A mixture of polyethylenoxide waxes having a molecular weight of 1,000-10,000 treated with phosphorus pentoxide or phosphorus oxychloride, with stearyl alcohol and octadecyl alcohol condensed with 12 moles of ethylene oxide in white oil, is stated to yield electrolyte-stable emulsions (Heyden, *Ger. 956,048*). If ozone is absorbed in an emulsion of water-insoluble, unsaturated organic compounds and water, the stability of the emulsion is greatly increased (Mihara *et al.*, *Japan 9,220* [1957]). An investigation of the effect of various emulsifiers on the stability of fats indicates that the addition of 10% of "Tweens," "Myrj," and "Brij" shortened the induction period of lard and olive oil. "Spans" prolonged the induction period (Finholt and Hopp, *Medd. Norsk Farm. Selskap*, 20, 33 [1958]). Studies on dispersion of ultrasonic velocities in palmitic acid indicated no detectable ultrasonic dispersion in palmitic acid, contrary to previously reported results (Rao, *Ricerca sc.*, 28, 2106 [1958]). A demulsifier is obtained by air oxidation of the gas oil-solar oil fraction at 140-150° in the presence of calcium naphthanate as catalyst (Masumyan and Danielyan, *U.S.S.R. 113,860*).

**ESTERS, ACIDS, ALCOHOLS, AND OTHER FAT DERIVATIVES.** A review is given of progress in the chemistry of synthetic glycerides of fatty acids since 1940: 153 references (Hartman, *Chem. Rev.* 53, 845). The differences between synthetic glycerol esters and natural oils and the food law aspects of the former are discussed, (Custot, *Ann. fals. et fraudes*, 51, 401). Esterification and transesterification for the preparation of specific glycerides are reviewed (Peterson and Way, *Ind. Eng. Chem.*, 51, 1081). Six new glyceride esters of adipic acid are prepared and their properties determined (Ward, Gros, and Feuge, *J. Am. Oil Chemists' Soc.*, 36, 667). Synthetic olive oil is prepared, and its properties are compared with the natural product (Staub and Widmer, *Mitt. Gebiete Lebensm. und Hyg.* 49, 61). Synthesis of pure glycerides of elaeostearic acid and their behavior during autoxidation is discussed (Kaufmann and Thomas, *Fette, Seifen, und Anstrichmittel*, 61, 211). A dissertation on triacid triglycerides was published (Watson, *Univ. Microfilms*, Ann Arbor, Mich., L. C. Card No. Mic. 58-5186, 72 pp.: Dissertation Abstr. 19, 2484). Mixed glycerol compositions are prepared by reaction of a higher acylated triglyceride with an OH-containing reactant in two patents (Embree and Brokaw, *Brit. 808,634*; *Brit. 745,566*).

Other patents on products or processes involving glycerides or waxes disclose: rearranged triglycerides from a mixture of non-lauric oil and a lauric oil (Cochran *et al.*, *U. S. 2,859,119*); an excipient prepared by the transesterification reaction between polyoxyethylene glycol, natural hydrogenated glycerides, and partially hydrogenated triglycerides (Monot, *U. S. 2,890,983*); an adduct prepared from alkyl or alkoxy-alkyl fumarate and a triglyceride in which two of the alkyl groups are short-chain (Dazzi, *U. S. 2,891,083*); nitrocellulose plasticized with the

aceto-acetic acid ester of castor oil (Bader and Vogel, *U. S. 2,895,844*); epoxidized diacetoglycerides (Swern and Knight, *U. S. 2,898,348*); neutralization of vegetable oils involving the use of mono-, di-, triethanolamine (Weiss, *Israeli 10,995*); the preparation of fatty alcohols in the form of discrete solid particles by forcing the molten material through nozzles as a jet with exposure to vibration into a cooling tower (Cox, *Brit. 810,006*); esters of organic acids prepared by treating the acids in the liquid phase with CO at an elevated temperature in the presence of a hydrogenation catalyst (Dehydag Deutsche Hydriewerke G.m.b.H., *Brit. 806,814*). A process is described for the production of a complex compound of magnesium sulphate and phosphatidyl choline (Debay and Sackur, *U. S. 2,899,449*). From the stand-point of speed of reaction, color of the final products, ease of removal of catalyst, and catalyst cost, litharge is the preferred catalyst for the preparation of methyl glucoside diesters (Gibbons and Swanson, *J. Am. Oil Chemists' Soc.*, 36, 553). A review is made of diethylene glycol fatty acid esters, 60 references (Schneider, *Fette, Seifen, und Anstrichmittel*, 59, 876).

O-Palmitoyl-lactic acid and various other new fatty compounds containing lactic acids are prepared and their phase behavior is described (Wootton and Lutton, *J. Am. Chem. Soc.*, 81, 1762). Vinyl  $\alpha$ -bromo esters have been prepared in 30-60% yield from vinyl acetate and the appropriate C<sub>2</sub> to C<sub>18</sub> straight chain  $\alpha$ -bromocarboxylic acid. By heating the vinyl  $\alpha$ -bromo esters with triethyl phosphite, the corresponding vinyl  $\alpha$ -diethylphosphonates were prepared in 35-75% yield (Sasin *et al.*, *J. Am. Chem. Soc.*, 80, 6336). Reactions of long-chain acids with thiolacetates are reported (Sasin *et al.*, *J. Org. Chem.*, 24, 1143). The reaction of lauric acid esters with sulfuric acid is reviewed and a cyclic carbonium ion mechanism is believed to be involved (Bauman and Krems, *J. Am. Chem. Soc.*, 81, 1620). The alkali-catalyzed reaction of ethylene oxide or propylene oxide with fatty acids is shown to be complex, and mono- and diesters were formed in comparable amounts (Wrigley, Smith, and Stirton, *J. Am. Oil Chemists' Soc.*, 36, 34). Saturated fatty esters may be easily labelled with tritium in high specific activity by the Wilzbach procedure of gas exposure (Nystrom, Mason, Jones, and Dutton, *J. Am. Oil Chemists' Soc.*, 36, 212). Several patents involve nonglyceride esters of fatty acids: laurylestere of acrylic acid for copolymers suitable as oil additives (Southwood and Bricknell, *Brit. 806,197*); process for preparing esters from phenylstearic acid and glucose (Linn, *U. S. 2,890,229*); preparation of fatty acid esters of oligosaccharides (Thomas Hedley and Company Ltd., *Brit. 804,197*); esterification of dibasic and other acids with diols carried out in the presence of boric acid (Kutepow and Himmele, *Ger. 1,014,979*); a yarn dressing prepared from a mineral oil and the acetylated derivative of 2-methoxy-ethyl-ricinoleate (Chandler, *U. S. 2,865,855*).

The preparation of monoglycerides from olive oil by glycerolysis in the presence of urea is discussed (Rigamonti and Vaciera, *Olearia*, 12, 49). Partial glycerides are obtained in a patent by the reaction of a phosphatide with water in the presence of an anion exchange material at 100° to 150° (Beal, *U. S. 2,885,414*). Other patents on partial glycerides include: mixed diglycerides (Embree and Brokaw, *Ger. 1,008,099*; see *U. S. 2,764,605*); continuous process for preparing monoglycerides (Birnbau, *U. S. 2,875,221*); monoglyceride diacetates (Ault and Feuge, *U. S. 2,895,966*); production of monoesters (Smith, *U. S. 2,902,500*). An improved method for preparing glycerol ethers is discussed in which the procedures of Davis *et al.* and that of Baer and Fischer are combined (Gupta and Kummerow, *J. Org. Chem.*, 24, 409).

A method for the preparation of highly purified erucic acid is described (Pasero *et al.*, *Rev. Franç. Corps Gras*, 6, 301). Improved methods for the preparation of ricinelaic acid by claudinization with nitrite-nitric acid solution and fractional crystallization are described, and infrared spectra absorptivity values are reported (McCutcheon *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 115). Phenols and phenyl ethers are added to the active center of oleic acid. Infrared spectra are used to identify the various products and to show that ring isomers form (Roe *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 656). Various patents deal with the preparation of anhydrides of long chain fatty acid (Nichols and Schipper, *U. S. 2,877,247*); long-chain unsaturated ketones and the corresponding oxodicarboxylic acid (Menon *et al.*, *Indian 55,757*); and hydroxy acids (Case, *U. S. 2,895,974*). The synthesis of unsaturated fatty aldehydes (Mangold, *J. Org. Chem.*, 24, 405), and the preparation of higher fatty aldehydes (Kaufmann and Spanuth, *Chem. Ber.*, 91, 2127) is described.

Organomercury carboxylates of higher fatty acids are disclosed (Kaufmann, *Ger. 960,280*). Methyl esters of lauric,

stearic, and oleic acids are thermally oxidized at 200°C. From the analytical values and the decomposition products a possible mechanism through a free radical system has been proposed (Ramanathan *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 244). Information is given on catalytic autooxidation of methyl  $\eta$ -propyl and  $\eta$ -butyl petroselinate. The greatest hydroperoxide concentration is obtained with the methyl esters (Gold and Skellon, *J. Applied Chem.*, 9, 389). The rate of oxidation of the esters of oleic acid (potassium permanganate in acetone) in relation to the structure of the ester alkyl radicals (methyl, ethyl, propyl, butyl) is studied. The increase in size of the alkyl radical decreases the rate of oxidation of esters of oleic acid (Bulatskii, *Trudy Odessk. Univ.*, 4, 103). The preparation and properties of oxides of higher aliphatic 2,3-unsaturated acids are described (Artamonov, *Zhur Obshchei Khim.*, 28, 1355). Work has been carried out on the oxidation of unsaturated fatty acids and their urea adducts. The hollow channel structure of urea completely protected the double bonds against the addition of ozone (Makita, *Rev. Phys. Chem. Japan*, 23, 31). Carbonyl compounds principally formed by autooxidation of ammonium linoleate are found to be  $\eta$ -hexanal 2-octanal, and 2,4-decadienal (Badings, *J. Am. Oil Chemists' Soc.*, 36, 648).

Paper chromatography is used for the detection and separation of organic peroxides (Milas and Belic, *J. Am. Chem. Soc.*, 81, 3358). Fat hydroperoxides are converted to cyclic peroxides in the presence of alcoholic OH (Kartha, *J. Sci. Ind. Research (India)*, 17B, 284). The 9,12-diketo-10-hydroxystearic acid is prepared by the oxidation of 12-ketolaic acid (Nichols and Schipper, *U. S.* 2,894,964). Unsaturated fatty acids are reacted in the vapor phase with ozone at subatmospheric pressures and temperatures between 176.5 and 360° to produce ozonides (Thorp and Gaynor *U. S.* 2,857,410). The preparation of aliphatic diacids from saturated acids by nitric oxidation is discussed in two papers: (Perron, *Rev. franç. corps gras*, 5, 371); (Hill and Kucieski, *U. S.* 2,858,336). Ozonization of unsaturated acids in the presence of solvents and water yields ozonides that on decomposition give dibasic and monobasic acids (Maggiolo, *U. S.* 2,865,937). Azelaic acid is recovered from a mixture of ozonized acids (Niegowski and Maggiolo, *U. S.* 2,897,231). The preparation of adipic acid from cyclohexane in a continuous manner is patented (Karl, *Ger.* 1,012,296). The preparation of C<sub>10</sub> aliphatic dicarboxylic acids is disclosed in a patent which involves the reaction of oleic and linoleic acid esters with carbon monoxide and hydrogen at high pressures and subsequent oxidation (Alm and Shepard, *U. S.* 2,891,084).

Aliphatic dicarboxylic acids are prepared by oxidation of aliphatic compounds and a heat-treatment with reducing agents (Marzin, *Ger.* (East) 11,412).

Oleic acid is reacted with carbon monoxide at 270° in the presence of a nickel catalyst to obtain isomeric heptadecane dicarboxylic acids in 80% yield, based on oleic acid (Reppe *et al.*, *Ger.* 1,006,849). A method for the preparation of urea salts of dicarboxylic acids is disclosed (Alsberg and Jeffers, *Brit.* 805,507). The chromic acid and Oppenauer oxidation of ricinoleic and ricinelaic acid to unsaturated keto acids has been investigated (Nichols and Schipper, *J. Am. Chem. Soc.*, 80, 5705). A number of epoxy and hydroxy keto acids were prepared by oxidation of 12-oxo-*cis*-9-octadecenoic acid, 12-oxo-*trans*-9-octadecenoic acid, 12-oxo-*trans*-10-octadecenoic acid, and 9,12-dioxo-10-octadecenoic acid (*ibid.*, 5711). Amides and esters of C<sub>18</sub>-keto fatty acids and several unsaturated C<sub>18</sub>-acids were prepared by the mixed carbonic-carboxylic anhydride method. An extension of this procedure provided a novel route to the synthesis of long-chain acid anhydrides (*ibid.*, 5714). Methyl ricinoleate is oxidized by tert-butyl chromate to give an oxidation product in 71% yield (Maruta and Suzuki, *Kogyo Kagaku Zasshi*, 60, 31). Dehydration of castor oil with substituted mono- and disulfonic acids is studied (Rajadhyaksha and Dole, *Indian J. Appl. Chem.*, 31, 95). Castor oil is dehydroxylated by heating with 150% by weight water at 10–60 atmospheres pressure for about 9 hr. to give 9,11-octadecadienoic acid (Pintsch-Bamag A.G., *Brit.* 805,918). The 1,3-diolein and 1,3-distearin esters of fumaric, succinic, and adipic acids are prepared by reaction between the 1,3-diglycerides and the acid chlorides of the dibasic acids in the presence of pyridine or quinoline (Feuge and Ward, *J. Am. Chem. Soc.*, 80, 6338). A process for making fatty acid diglyceride diesters of dibasic acids is patented (Feuge and Ward, *U. S.* 2,874,175).

Mixtures of fatty acids, short-chain dibasic acids, and glycerol, when combined in such proportions that the mole ratio of fatty acid to dibasic acid is one or more, yield on esterification polyesters which are much more viscous than are edible oils and fats (Feuge and Gros, *Ind. Eng. Chem.*, 51, 1019).

Alkali fusion of some branched-chain fatty acids is discussed (*Collection Czechoslov. Chem. Commun.*, 24, 744). When *cis*, *trans*-conjugated methyl linoleate is heated at 250° with selenium, the product consisted of a mixture of isomer *cis*- and *trans*-octadecenoates and cyclized material that appears to be a mixture of dialkylbenzene and dialkylcyclohexene and can be converted to *o*-phthalic acid in 54% yield (Teeter *et al.*, *J. Org. Chem.*, 23, 1156). A process of aromatizing linoleic acid compounds consists in heating linoleic acid or its esters to about 270° in the presence of a noble metal active hydrogen transfer catalyst (Baldwin *et al.*, *U. S.* 2,868,815).

The rate of chlorine addition and substitution of oleic acid in CCl<sub>4</sub> is recorded. The addition reaction is rapid and takes precedence. The ratio of substitution to addition increases with increase of temperature but decreases with decreased oleic acid or chlorine concentration to a level of about 25% of the total reaction (Veijola, *Suomen Kemistilehti*, 31B, 307). With aqueous chlorine almost complete saturation of triolein occurs; the main reactions are the addition of chlorine and HOCl to the double bond. With ClO<sub>2</sub>, 25–50% of the double bonds in triolein are modified at room temperature. The reaction is accelerated by light and is probably a free radical in nature (Leopold and Mutton, *Tappi*, 42, 218). Halogenated fatty acids which are formed during the I. V. determination of oleic, linoleic, and ricinoleic acid, were examined (Awe and Grote, *Fette, Seifen, und Anstrichmittel*, 61, 1). In the reaction of methyl oleate and methyl erucate with equivalent amounts of *N*-bromosuccinimide, bromination occurs in the allylic position farthest from the carboxyl group. Products of dehydrobromination contain 30–40% conjugated dienoic acids (Nanavati *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 226). Patented halogenated compounds and processes are: chlorinated fatty acids (Blaser and Wedell, *Ger.* 961,531), chlorofluorocarbon oils and waxes (Frey and Kahrs, *Ger.* 1,008,280; see *Brit.* 761,963) and  $\alpha$ -chlorinated fatty acids (Steinbrunn, *Ger.* 1,014,092).

Various ricinoleic acid derivatives have been cyano-ethylated with acrylonitrile. The infrared spectra of these compounds have been determined, and some of their properties are described (Dupuy *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 659). New reactions of fatty isocyanides with halogens, alkylating agents, and acid chlorides are reported (Jungermann and Smith, *J. Am. Oil Chemists' Soc.*, 36, 388). Some communications contain information on preparation, properties, or uses of derivatives of fats containing nitrogen. The reaction of CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH:CHCOOH where n = 5, 6, 7, and 9, with NH<sub>2</sub>OH in aqueous alcohol solution, has been studied. Formation of respectively CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH(NHOH)–CH<sub>2</sub>CO<sub>2</sub>H in 50–60% yield has been noted (Kologrivova and Belov, *Trudy Vsesoyuzn. Nauch.-Issledovatel. Inst. Sintet. i Natural. Dushistyykh Veshchestv*, 1958, No. 4, 70). Ammonia reacts with the oxide of petroselinic acid (Pigulevskii *et al.*, *Zhur Priklad. Khim.*, 32, 937). Adduct formation of long-chain fatty acids with urea is described (Taufel *et al.*, *Nahrung*, 2, 255).

A review is made of synthesis of fatty acid nitriles, 8 references (Naumenko and Khaskin, *Masloboino-Zhirovaya Prom.*, 24, [10] 13). Fatty acid amide derivatives are made (Zussman, *Soap Chem. Specialties*, 35 [4] 51). The use and analysis of fatty acid amides are discussed, and the chemistry of the mercury compound (R·CONH)<sub>2</sub>Hg is summarized (Kaufmann and Skiba, *Fette, Seifen, und Anstrichmittel*, 59, 498). The separation of fatty acid amides, C<sub>10</sub>–C<sub>18</sub>, is carried out by paper chromatography (Kaufmann and Skiba, *Fette, Seifen, und Anstrichmittel*, 60, 261). The synthesis of elaidic, oleic, linoleic, and linolenic acid amides is carried out as follows: treat the free acid with formamide in nitrogen at 150–160° for 4 hr., dissolve in acetone, and crystallize at –20° (*ibid.*, 362). The mass spectra of 35 aliphatic amides, comprising primary, secondary, and tertiary forms, are tabulated and correlated (Gilpin, *Anal. Chem.*, 31, 935). A vehicle for enriching foods without causing undesirable browning is prepared by dissolving in a fat between 10 to 20% by wt. of an *N*-acylated aliphatic  $\alpha$ -amino acid (Tawn, *U. S.* 2,850,387). Unsaturated fatty acids are reacted with ozone. The ozonide is decomposed by steam distillation. The resultant acid aldehyde is reacted with ammonia. The product is reduced with hydrogen in the presence of Raney nickel so as to form the *omega*-amino acid (Otsuki and Funahashi, *U. S.* 2,862,940).

A continuous process for the production of fatty acid hydroxy amides is disclosed (Schurman, *U. S.* 2,863,888). Other patents refer to special amide compositions, their preparation or purification: preparation of *N,N,N',N'*-tetraalkyl diamide of dimeric linoleic acid (Dazzi, *U. S.* 2,875,218); purification of *N*-high or fatty acid amides of lower mono-amino-carboxylic acids (Epstein, *U. S.* 2,881,193); preparation of anhydrosorbityl



amides (Boettner and Rainey, *U. S. 2,891,052*); as part-amides of C<sub>8</sub>-C<sub>22</sub> fatty acids (Steinhauer and Merica, *U. S. 2,891,082*). A process is described for the preparation of fatty acid monoesters of diglucose ureide (Osipow and York, *U. S. 2,903,445*). A process is disclosed for the preparation of fatty acid monoester of N-urea glucoside (Osipow and York, *U. S. 2,903,446*). Fatty acid amide preparation (Seletzky, *Fr. 1,132,247*). Local anesthetic agents are prepared; the simpler type has the general formula (R<sub>2</sub>NCOCH<sub>2</sub>)NC<sub>6</sub>H<sub>4</sub>OH (Bruce *et al.*, *Brit. 802,995*). Preparation of diamide of adipic acid and  $\delta$ -cyanovaleramide (Zilberman and Kulikova, *U.S.S.R. 115,895*). A process is described for the preparation of isothiocyanates by the reaction of halides of ethylenically unsaturated fatty acids with inorganic thiocyanates (Nischk and Holtshmidt, *U. S. 2,877,244*). A long-chain conjugated polyolefinic monocarboxylic fatty acid is reacted with a compound having the radical -CH=CH-NO<sub>2</sub> (Teeter *et al.*, *U. S. 2,901,495*). Ester nitriles are obtained in improved yield, with the formation of small amounts of dinitrile, by treating the half-ester of the dibasic acid with ammonia in the vapor phase in the presence of a dehydrating catalyst (Duxbury and Edgar, *Brit. 805,651*).

Many compounds are produced by oxidation. Condensation products of epoxidized fatty esters with amines are disclosed (Tawn, *Brit. 811,797*). Many of 31 acyloxy or aryloxy esters prepared from hydroxystearic acids are found to be primary plasticizers for a vinyl chloride-vinyl acetate copolymer (95:5). They are found to have outstanding low-temperature performance when employed at the 35% level (Knight, Witnauer, Palm, Koos, and Swern, *J. Am. Oil Chemists' Soc.*, 36, 382). Prolonged treatment of linolenic acid with alkaline ethylene glycol produces a large amount of cyclic monomeric material together with small amounts of dimeric and other products (Scholfield and Cowan, *J. Am. Oil Chemists' Soc.*, 36, 631). Also 10,11-dihydroxy and 10,11-epoxy-9,12-diketostearic acid and derivatives are disclosed (Nichols, *U. S. 2,852,521*; *U. S. 2,852,522*). Epoxidized esters are obtained by the epoxidation of a mixture of pentaerythritol benzoate tri- and di-oleates (Dazzi, *U. S. 2,889,338*). Hydrazides are prepared by the reaction of hydrazine with epoxidized ethenoid C<sub>10</sub>-C<sub>22</sub> fatty acid esters containing 1 to 3 oxirane groups (Findley, *U. S. 2,892,848*). Epoxylation products of unsaturated fatty acid amides are disclosed (Orthner and Fuchs, *U. S. 2,905,702*). Alkenyl esters of monoethylene fatty acids are epoxidized with peracetic acid (Union Carbide Corp., *Brit. 788,530*).

Cis-2-, -3-, -4-, and -6-octenoic acids are prepared by the catalytic semihydrogenation of the octenoic acids. *Trans*-3-, -4-, and -6-octenoic acids are obtained either directly or indirectly, starting with a *trans*-alkenoic acid obtained by a Knoevenagel condensation. Physical properties are determined for all of the acids and most of the intermediates (Knight and Diamond, *J. Org. Chem.*, 24, 400). Chain-lengthening of fatty acids is achieved by adding the acid chlorides to C<sub>2</sub>H<sub>4</sub>, dehydrochlorinating the resulting 2-chloroethyl alkyl ketones, oxidizing the vinyl ketones with potassium permanganate to  $\alpha$ -oxo acids, and reducing, or by treating the 2-chloroethyl alkyl ketones with potassium cyanide or with NaCH(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and hydrolyzing the condensation products to  $\beta$ - and  $\gamma$ -oxo acids, respectively, which are finally reduced to the fatty acids (Kaufmann and Stamm, *Chem. Ber.*, 91, 2121). The rate of paraffin oxidation and the quality of the acids produced as affected by the catalyst content is discussed (Perchenko, *Masloboino-Zhirovaya Prom.* 25 [2] 22).

A simplified procedure for synthesis of oleic-1-C<sup>14</sup> acid is discussed. Bergstrom's method for the introduction of a C<sup>14</sup> atom in the carboxyl position by means of the nitrile synthesis is modified for small-scale experiments (von Schuching and Stutzman, *J. Org. Chem.*, 24, 345). Preparation of fatty acids and alcohols from olefins through ozonolysis is reported (Bertsch *et al.*, *Chem. Techn. (Berlin)*, 10, 690). Synthesis of *trans*-4-decenoic acid is discussed (Iuvakiri, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 78, 1460). The (+)- and (-)-12-methyloctadecanoic acids have been prepared from (+)- and (-)-2-octanols (Prout *et al.*, *J. Org. Chem.*, 24, 826). The extraction of low-molecular acids C<sub>7</sub>-C<sub>8</sub>, from acid wastes in the manufacture of synthetic fatty acids is carried out (Alferova *et al.*, *Masloboino-Zhirovaya Prom.*, 25 [1] 28). Continuous rectification of synthetic fatty acids is critically discussed (Koldovkin, *Khim. i Tekhnol. Topliv i Masel*, 4, [6] 67). A synthesis of DL-*cis*-9,10-methylene-octadecanoic acid is described, and the synthetic acid is found to be identical with dihydrostereulic acid (Hofmann and Yoho, *J. Am. Chem. Soc.*, 81, 3356). An investigation of the composition of fatty acids obtained by oxidation of paraffin is carried out (Man'kovskaya and Asnina, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov*, 1954 [15], 212).

Factors controlling the settling of unsaponifiables in the course of manufacture of synthetic fatty acids are investigated (Man'kovskaya and Oleinikova, *Masloboino-Zhirovaya Prom.*, 24 [12], 17). An investigation is made on composition of unsaponifiable matter obtained by thermal treatment of soap in manufacturing of synthetic fatty acid (Man'kovskaya and Tyutyunnikova, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov*, 1954 [15], 217). Three methyltetracosanoic acids have been synthesized with branches near the 10-position: 8-, 9-, and 11-methyltetracosanoic acids. The syntheses are accomplished via the hydroxy ester resulting from reaction of an  $\eta$ -alkylmagnesium bromide with an appropriate sec-butyl keto ester (Cason and McLeod, *J. Org. Chem.*, 23, 1497). Substances controlling the odor of synthetic fatty acids are investigated (Man'kovskaya *et al.*, *Masloboino-Zhirovaya Prom.*, 25 [4], 13). Application of the chromatographic method for analysis of synthetic fatty acids is discussed (Ladyzhnikova, *Masloboino-Zhirovaya Prom.*, 24[9], 28). New utilizations of synthetic fatty acids prepared by oxidation of paraffin are investigated (Nicolescu *et al.*, *Rev. franc. corps gras*, 5, 384). Preparation of synthetic fatty acids is disclosed in various patents: higher-molecular fatty acids (Luther, *Ger. 958,557*). Long-chain aliphatic carboxylic acids (Baronetzy and Fuchs, *Ger. 960,188*). Catalytic oxidation of paraffin hydrocarbons to fatty acids (Engelmann, *Ger. [East] 14,370*). Fatty acid mixtures (Imhausen and Keunecke, *Ger. 950,367*). Fatty-acid preparation from stearin pitch (Schramm, *Ger. 961,650*). Fatty-acid preparation from paraffins by oxidation (Brucke *et al.*, *Ger. 966,064*). Treating oxidation products of paraffinic hydrocarbons in the production of fatty acids (Moshkin, *U. S. S. R. 116,947*). Unsaturated fatty acids (Marzin, *Ger. [East] 9,560*). Preparation of unsaturated fatty acids (Marzin, *Ger. [East] 9,566*). Oleyl-, linoleyl-, and linolenyl-aldehydes are prepared by a modified Grundmann synthesis. The procedure can be used for the preparation of radio-active aldehydes on a milligram scale (Mangold, *J. Org. Chem.*, 24, 405). Linoleic, linolenic, and eleostearic aldehydes and their derivatives are prepared (Kaufmann and Kirschnek, *Fette, Seifen, und Anstrichmittel*, 60, 1125). A study of positional isomers formed during the partial hydrogenation of methyl linoleate showed the greatest concentration of double bonds in the 10 position, and the concentration in the other positions decreased as the distance from a 10 position increased (Cousins *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 24). Hydrogenation with nickel catalysts has been reported for castor, corn, cottonseed, herring, sunflower, tall, tallow, train, and whale oils or fatty acids. Hydrogenolysis with copper catalysts has been described for cottonseed oil, mixed fatty acids, ethyl stearate, and synthetic spice oils (Bradbury *et al.*, *Ind. Eng. Chem.*, 51, 1111). A process is described for the non-selective hydrogenation of an unsaturated oil in the presence of moisture and a small amount of mineral acid or an aliphatic hydroxy acid (Merker, *U. S. 2,862,941*). It has been found that addition of diborane to the ethylenic bond of methyl oleate proceeds smoothly without significant reduction of the carbomethoxy group (Fore and Bickford, *J. Org. Chem.*, 24, 920). The effects of catalyst concentration, temperature, pressure, agitation, diffusion, and hydrogen solubility on the rate and selectivity during hydrogenation and hydrogenolysis are studied (Arnold *et al.*, *Ind. Eng. Chem.* 50, 1370). Unsaturated alcohols are prepared in 92% yield from oleic acid, sulfur olive oil, or the fatty acids from olive oil by treating with hydrogen at 265° under 200 atmospheres for 2-3 hrs., using 10% copper chromite as catalyst and 3.75% cadmium carbonate to protect the double bonds (Martinez Moreno *et al.*, *Grases y Aceites*, 9, 60). Unsaponifiables obtained as by-products in the manufacture of synthetic fatty acids are reduced to a mixture of fatty alcohols by the Meerwein-Ponndorf method by using aluminum propoxide, aluminum isopropoxide, or aluminum butoxide (Postol'nyl, *Masloboino-Zhirovaya Prom.*, 24[10], 15). Condensation of fatty alcohols and boric acid at 110-115° *in vacuo* and cleavage of the resulting esters at 98° are successfully used for separation of fatty alcohol from unsaponifiable-II in the course of manufacturing synthetic fatty acids from paraffin (Kudryashov *et al.*, *Masloboino-Zhirovaya Prom.*, 24[11], 26). Sodium reduction of the wax fatty acid esters in jojoba oil (liquid wax) yielded quantitatively a mixture of unsaturated long-chain alcohols from the acid moiety of the jojoba oil (Molaison, O'Connor, and Spadaro, *J. Am. Oil Chemists' Soc.*, 36, 379). Catalytic hydrogenation is applied to the manufacture of wax alcohols from esters of montanic acid (Runge, *Fette, Seifen, und Anstrichmittel*, 61, 31). A new method is described for determining aldehydes in fatty alcohols prepared by catalytic hydrogenation under high pressure (Etienne, *Olii minerali, grassi e saponi, colori e vernici*, 35, 185).

A mixture of the esters of  $C_6$  to  $C_{22}$  fatty acids and the corresponding free fatty acids is converted to the esters of a reducing alcohol by a process of transesterification with an excess of the alcohol. The product is treated directly with finely dispersed sodium in the presence of a minor amount of a dispersing agent. The product is hydrolyzed, and the desired fatty alcohols are isolated (Hansley *et al.*, *U. S.* 2,865,968). Other patents for the production of fatty alcohols are: preparation of pure myristic alcohol from castor oil (Russos and Bourgeois, *U. S.* 2,897,243); fatty alcohols (Branconier and LeBihan, *Brit.* 795,383; see *U. S.* 2,844,633); higher aliphatic alcohols (*Société Belge de l'azote et des produits chimiques du Marly S. A.*, *Brit.* 795,573); unsaturated aliphatic alcohols (Dehydtag Deutsche Hydrierwerke G.m.b.H., *Brit.* 806,619); alcohols (Marten and Roelen, *Ger.* 947,706); unsaturated higher-molecular-weight alcohols (Rittmeister, *Ger.* 965,236). Eighty-eight amine salts of long-chain fatty acids are prepared, purified, and characterized (Mod *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 616). Details are given for the preparation of 72 complex salts of palmitic and stearic acids with  $M^{II}$  ( $M^{II} = Mn, Ni, Co, Cu, Zn, \text{ and } Cd$ ) (Fisel, *Acad., rep. populare Romine, Filiala Iasi, Studii cercetari stiint.*, *Scr. I.*, 6, 295). Salts of higher fatty acids are prepared that are complexes of copper distearate or dipalmitate with 1 mole/amine (Fisel, *Acad., rep. populare Romine, Filiala Iasi, Studii cercetari stiint.*, 7[12], 13). Dry acetates of sodium, copper, or cobalt are treated with an ether solution of the unsaturated acids. The precipitated salt is filtered off and washed free of acetic acid with ether (Kuznetsov and Muzeeva, *U. S. S. R.* 114,712).

**FATTY MATERIALS IN LUBRICATION, METAL WORKING, AND TEXTILE OILING.** In a study of the corrosion behavior of nondrying fats in connection with lubrication it is concluded that attack on iron is not related to the total acidity of the oil, which increases with age, but rather to the volatility and reactivity of the acids formed (Bukowiecki, *Schweiz Arch. Angew. Wiss. Tech.*, 24, 295-303). Some problems in oxidation stability tests are discussed (Wakana, *Abura Kagaku*, 7, 263-275). The acid monoester 2-ethylhexyl hydrogen sebacate has been identified in bis(2-ethylhexyl) sebacate lubricating oils that are used in gas turbines (Dismukes, *J. Am. Oil Chemists' Soc.*, 36, 154). Lubricant additives are prepared from vegetable materials, by hydrogenation, treatment with sulfur or thionyl chloride in the presence of aluminum chloride, and subsequent sulfonation or reaction with hydroxylamines (Compagnie française de raffinage, *Fr.* 55,811; addition to *Fr.* 972,891. The preparation of alkyl esters of alkoxy-acyloxy stearic acid that are suitable for use in lubricants is disclosed (Gast, Cowan, and Teeter, *U. S.* 2,873,255). A novel cutting oil is prepared from 80 to 90% of a sulfurized mineral oil, 1 to 20% of a partial fatty acid ester, and an oil-soluble chlorinated E. P. compound (Hughes and Stine, *U. S.* 2,852,468). The modern application of metal soaps is reviewed in a lecture (Rosenthal, *Fette, Seifen, und Anstrichmittel*, 60, 267).

**FATTY MATERIALS USED IN TEXTILE TREATMENT, WATER PROOFERS, ANTICORROSIIVE COMPOUNDS, DEFOAMERS, WELL DRILLING FLUIDS, INCENDIARY PREPARATIONS, AGRICULTURE, WAX COMPOSITIONS, AND MISCELLANEOUS PRODUCTS.** A self-emulsifying size for paper is a blend of higher aliphatic ketene dimer with less than 5% of a higher fatty acid as emulsifying agent and emulsion stabilizer (Arlt Jr., *U. S.* 2,901,371). The wear resistance of sisal buff is improved by impregnating it with an aqueous 27.0% emulsion of heavy-bodied soya bean oil containing an emulsifying agent and heating the impregnated buff to about 300°F. (Vaughan, Hislop, and Hanna, *U. S.* 2,890,137). Compositions of commercial synthetic waxes are discussed (Charrin, *Peintures, Pigments, Vernis*, 34, 513-514). A study of wax crystal structure versus water-vapor transmission indicates that large wax plate crystals, oriented parallel to the base sheet give a low water-vapor transmission rate. Some factors favoring formation of large oriented plate crystals are related (Fox, *Modern Packaging*, 32[2], 141-149, 196). Polysiloxanes in the silicone oils are added to leather and floor wax compositions to improve water resistance and enhance luster (Schneider, *Swiss* 323,323). An emulsion containing wax, solvent naphtha, polyoxyethylene sorbitan monostearate and water is sprayed and dried to give a powdered wax (Sato, *Japan* 9,469[1956]). A powdered non-agglomerating wax is disclosed (Brennecke, *Ger.* 944,212). Light-colored, hard waxes of good oil-binding capacity are made from montan waxes in admixture with Fischer-Tropsch macroparaffins (Klein *et al.*, *Ger. [East]* 12,543). Waxes with properties different from those of the natural waxes are obtained by condensing high-molecular organic acids with amino alcohols. The acids are derived from natural waxes (Établissements Procoffeff, *Fr.* 1,020,823).

Electrolytically produced tin plate is oiled with a mixture of an antioxidant, salad oil, and partial glycerides derived from cottonseed oil (Farbak and Kasmen, *U. S.* 2,899,328). A bath for use in hot-dip tinning operations is a blend of palm oil and pentatriacontenyl succinic acid anhydride (Nelson, *U. S.* 2,886,465). An analysis is presented of the changes in palm oil employed in hot-dip tinning during continuous use up to four weeks (Jorand, *Oléagineux*, 14[2], 73-81). Freshness of peaches is preserved by coating them with a highly atomized spray of wax dissolved in a refined vegetable oil (Gerwe and Slade, *U. S.* 2,866,709).

Systematic investigation of some 21 castor polyols as base materials for preparing urethane foams is carried out, and it is concluded castor polyols can serve as effective urethane components (Ehrlich *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 149). A study of urethane foams from castor oil and elaidinized castor oil indicates that increasing crosslinks in the foam did not improve water resistance but did improve shrinkage characteristics (Yeadon *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 541). 4-ricinoleyl-morpholine and various other nitrogen derivatives are screened for their plasticizing characteristics (Magne *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 635). Methyl vinyl ketone-methyl- $\alpha$ -eleostearate adduct and derivatives are found to be highly compatible and efficient as primary plasticizers for vinyl chloride copolymers (Placek *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 651). A highly porous, neutral, and stable polymer, useful for preparing cation exchange resins is prepared from cashew nutshell oil (Govindan, *Indian* 59,497). A process is described for the preparation of foamable styrene particles containing 0.5 to 20 parts of  $C_{12}$  to  $C_{20}$  fatty acids, their salts or monoesters (Colwell and Platzer, *U. S.* 2,857,341).

Synthetic waxes are prepared by reacting a dicarboxylic acid or derivative with a condensation product of a fatty acid or derivative and an alkylolamine. The free carboxyl group facilitates emulsification (Ivanovsky and Groszek, *Brit.* 802,727). High-molecular esters with properties similar to those of natural waxes are prepared by catalytic addition of carbon monoxide and hydrogen to higher-molecular olefins (Rottig, *U. S.* 2,844,612). Light-colored waxes with a high content of montanic acid are prepared from mixtures of montan wax and solid paraffins. The esters present in the refined mixtures are hydrolyzed, and the resulting alcohols are oxidized to montanic acid (Presting and Walther, *Ger. [East]* 11,873). Heat-stable waxes for paste waxes are disclosed (Kolling and Rappen, *Ger.* 1,005,504). Stable wax pastes which do not dry and have good plasticity are obtained (Hessler, *Ger.* 938,146). Water-free polishes containing partially neutralized wax-acid paraffin are disclosed (Kolling and Rappen, *Ger.* 1,007,911; see *U. S.* 2,871,210). A method is disclosed for preparing adhesive coating compositions from a saturated higher fatty acid, an aluminum trioleolate, and microcrystalline wax (Duro, *U. S.* 2,875,081).

Fluid lanolin is prepared by reacting crude lanolin with urea in methanol. After complex formation is completed, the mixture is slurried in ether and filtered. The ether solution is washed with mineral acid and water. Fluid lanolin is recovered by evaporation of the ether (Noble and Scanlan, *U. S.* 2,857,412). A novel process for the purification of lanolin is disclosed (Payaud, *Ger.* 1,018,175). During the process of the recovery wool grease, the wash water, containing at least one ionic or anionic surfactant, is agitated slightly before the final scavenger operation. After it is submitted at 70-80° to centrifugation (Raoul *et al.*, *Belg.* 526,672).

A plasticizer for polyvinyl resins is prepared by the reaction of a peracid with the lower alkyl of polyhydric alcohol esters prepared from unsaturated oils (Greenspan and Gall, *U. S.* 2,857,349). A polyester composition prepared from a dihydric alcohol and two dicarboxylic acids is stabilized against degradation by heat, by the addition of 0.1 to 10 parts by wt. of a 2,4,5-trihydroxy phenone of a  $C_4$  to  $C_{18}$  fatty acid (Knowles and Moore, *U. S.* 2,856,383). The nomenclature of tall oil fatty acids and their derivatives is given in a lecture of the Tall Oil Symposium (Sheers and Berkman, *J. Am. Oil Chemists' Soc.*, 36, 163). A soft waxy material separated from saponified tall oil according to *U. S.* 2,591,885 is described and compared with lanolin in regard to chemical and physical properties (Bestul *et al.*, *Soap Chem. Specialties*, 34[10], 49). The filler binding composition in linoleum is prepared by reacting dilinoleic acid with pentaerythritol by heating (Dunlap and Parker, *U. S.* 2,873,201). A homogeneous vehicle for suspending a vitrifiable ceramic composition is prepared from 0.5 to about 55% by wt. of azelaic acid and at least 35% of  $C_{12}$  to  $C_{22}$  fatty acids (Morris, *U. S.* 2,872,326). Sugars are crystallized in the presence of a  $C_8$  to  $C_{22}$  fatty acid ester of a glucoside (Kent, *U. S.* 2,871,148). Novel mineral additives are disclosed (Gottshall and

Kern, U. S. 2,902,499). n-Deca-2,4-dienal was identified as a major component of the carboxyl compounds in deodorization distillates from cottonseed oil, soybean oil, beef tallow, and lard. The compound also was demonstrated as a principal carbonyl component in the heat decomposition of methyl linoleate in the presence of moisture. Flavor and odor qualities of the dienal are described by the term "deep fried" (Patton *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 280). A review is made of by-products of the cottonseed crushing industry (Prakash *et al.*, *Symposium Cottonseed and By-Products, Hyderabad, India, 1958*, Sect. VI, 8). Derivatives and isolation of pure gossypol is discussed (Chander and Seshadri, *J. Sci. Ind. Research*, 17B, 279). The influence of heat and air oxygen on gossypol is reported in a communication (Rzhekhin, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Zhirov*, 1954 [15], 55). By-products from the cracking of castor oil and their uses (Dupont, *Olearia*, 12, 53). A method is disclosed for the recovery of oryzanol from the distillation residue of rice-oil fatty acids (Tsuchiya and Okubo, *Japan 1149* [1958]).

### Products (excepting detergents)

**DRYING OILS, PAINTS, RESINS, AND PLASTICIZERS.** Review papers covered the following aspects of drying oils: economies (McHale, *J. Am. Oil Chemists' Soc.*, 36, 604), extraction methods for isolation from oil-bearing materials (Wingard, *ibid.*, 483), refining methods (Mattikow, *ibid.*, 491), 50 years of progress in the utilization of inedible fats and oils (Seofield, *ibid.*, 436), use in "classical" varnishes, which were defined as solutions or mixtures of drying oils, and varnish resins (Rheineck, *ibid.*, 574), use in floor coverings (Dunlap, *ibid.*, 590), and use in printing inks (Dunning, *ibid.*, 586). A review covered the reactions at or near the double bond of unsaturated oils and acids and discussed the following commercially useful products: soaps as polymerization catalysts, vinyl plasticizers and stabilizers, epoxy resin modifiers, and polymeric fatty acids (Goebel, *ibid.*, 600). A lecture on uses of metal soaps included their use in paints and plastics (Rosenthal, *Fette, Seifen, und Anstrichmittel*, 60, 267).

Reviews on the use of specific oils in protective coatings, which in some cases also included production of the oils, covered soybean (Taggart, *Soybean Digest*, 19 [7], 16), safflower (Purdy *et al.*, *J. Am. Oil Chemists' Soc.*, 36, [9], 26), tung (Greenfield, *J. Am. Oil Chemists' Soc.*, 36, 565), and castor oils (Bolley, *ibid.*, 441), and tall oil and naval stores (Barnes and Taylor, *Tappi*, 41 [8], 16A). A study of the changes occurring in stored linseed oil over a period of four to five years showed that the warmer storage locations were detrimental to oil quality (Baumann, *J. Am. Oil Chemists' Soc.*, 36, [10], 24). Drying properties of four varieties of safflower oil varied with the iodine number. Safflower varnishes were slightly superior to linseed varnishes in water and scratch resistance (Aslam, *Pakistan J. Sci. Ind. Research*, 1, 312). A mono- and diglyceride fraction of cuttle fish oil had poor drying characteristics. Destearinated fractions of interesterified cuttle fish oil containing less than 10% of saturated acids dried but remained tacky (Marumo and Tomiyama, *Yushi Kagaku Kyo Kaishi*, 3, 9, 67). Of two varieties of perilla oil, the one having the lower iodine number (173 versus 178-181) had better drying properties (Mazhdrakov and Popov, *Compt. rend acad. Bulgare sci.*, 11, 197). Drying properties of mixtures of linseed oil with *Argemone mexicana* seed oil were reported (Chinwala and Desai, *J. Indian Chem. Soc., Ind. and News Ed.*, 20, 70). Kamala seed oil consisted of polymeric triglycerides which were too reactive for use in paints and varnishes. Alcoholysis of the oil with monohydric alcohols gave a product similar to tung oil which could be used in protective coatings (Aggarwal, *Paint Manuf.*, 29, 50; Menon *et al.*, *J. Sci. Ind. Research [India]*, 17A, 279). Oil from the seeds of *Oenothera lamareckiana* was intermediate between drying and semidrying oils and could be used as a substitute for linseed oil (Mazhdrakov and Popov, *Bulgar. Akad. Nauk. Izvest. Khim. Inst.*, 5, 209). Rubberseed oil, whose drying properties were between those of linseed and soybean oils, was used to produce varnishes similar to those from linseed oil (Aslam and Imam, *Pakistan J. Sci. Ind. Research*, 1, 224). Analytical values were reported, and refining conditions were studied for walnut oil. This was a typical drying oil and was converted into an immersion oil by blowing with air (Aizenberg, *Trudy Kishinev. Sel'skokhoz. Inst.*, 11, 63; Referat. Zhur. Khim. 1958, Abstr. No. 2690). Three varieties of Xanthium oil, a semidrying oil, were investigated (Popov and Ivanov, *Bulgar. Akad. Nauk., Izvest. Khim. Inst.*, 5, 377).

Studies of the oxidation of fatty acids and their simple derivatives have a bearing on drying oil chemistry because

they help to explain the mechanisms by which oils dry. The oxidation of methyl laurate, methyl stearate, and methyl oleate at 200° for varying lengths of time was followed by measuring the weight loss and by analyzing the volatile products (Ramanathan *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 244). The oxidation of esters of *cis*-octadeca-6-enoic acid (petroselinates) was studied by determining the position of the hydroperoxide groups in the initial products and the compositions of the final products (Gold and Skellon, *J. Applied Chem.*, 9, 389). Following the initial oxidation of methyl linoleate, the amount of hydroperoxide in the product decreased rapidly as the extent of oxidation increased. The products were isolated by countercurrent distribution (Kern and Schneko, *Die Makromolekulare Chemie*, 32, 184). Paper chromatography was used to study the products of oxidation of methyl linoleate at room temperature and at 150-200°. Seven aldehydes were identified (Lathlean, *Paint J. Australia-New Zealand*, 3 [1], 12). Oxidation of ammonium linoleate in dilute aqueous solution at 37° produced carbonyl compounds (Badings, *J. Am. Oil Chemists' Soc.*, 36, 648). The products of oxidation of ricinoleic acid at 120° in the absence of catalysts or in the presence of cobalt ricinoleate or uranium ricinoleate were identified (Gulbekian and Skellon, *J. Applied Chem.*, 9, 224). The amounts of polymeric materials in the products of oxidation of methyl oleate, methyl linoleate, methyl linolenate at various temperatures were determined. The amount of polymeric material increased with the increasing temperature of oxidation and with increasing unsaturation of the methyl esters (Khan, *Pakistan J. Sci. Ind. Research*, 1, 12; *Pakistan J. Sci. Research*, 10 [4], 149). The volatile products formed by the oxidation at room temperature of the acids and esters of sardine oil were identified (Toyama *et al.*, *Mem. Fac. Eng. Nagoya Univ.*, 9, 125). Methyl linoleate hydroperoxide had the same effect upon the rate of oxidation of pure methyl linoleate as did the autocatalyst formed during the autoxidation of methyl linoleate (Kern *et al.*, *Die Makromolekulare Chemie*, 32, 191). The relative autoxidation rates of methyl oleate, linoleate, and linolenate as determined by a method involving decrease in iodine number were 1:2:4 (Kartha, *J. Sci. Ind. Research [India]*, 17B, 135). The rate of decomposition of linoleate hydroperoxide, catalyzed by hematin and by other metallic derivatives, was studied by a spectrophotometric method. The structures of the products of the hematin-catalyzed decomposition were determined (Maier and Tappel, *J. Am. Oil Chemists' Soc.*, 36, 8, 12).

Oxidation of oils was the subject of the following reviews: recent studies on the oxidation of oils (de Radzitzky, *Ind. chim. Belg.*, 23, 233); oxidation of fats and oils (Ishii, *Kagaku [Kyoto]*, 11, 662), peroxides in the field of fatty substances (Paquot, *Actions chim. et biol. radiations*, 4, 3), autoxidation and autooxidative polymerization (Privett, *J. Am. Oil Chemists' Soc.*, 36, 507), the significance of organic peroxides in the chemistry of fats (Rieche, *Fette, Seifen, und Anstrichmittel*, 60, 637), reaction mechanism of autoxidation and bond energies (Takashi, *Abura Kagaku*, 7, 248). The oxidation of drying oils and its catalysis by metallic dryers was explained on the basis of resonance theory (Myers, *Ann. N.Y. Acad. Sci.*, 79, 1). In the presence of alcoholic hydroxyl, fat hydroperoxides were converted to cyclic peroxides. Acetic acid had the same effect (Kartha, *J. Sci. Ind. Research [India]*, 17B, 284). Oxidation of vegetable oils was studied by a method involving saponification of the oxidized oils, isolation and weighing of the oxidized acids (Rzhekhin and Pogokina, *Masloboino-Zhirovaya Prom.*, 24, [10], 6). The autoxidation pattern of ghee followed that of its constituent unsaturated fatty acids. It was not affected by the presence of the saturated fatty acids or of the glyceryl radical in spite of the fact that these constituted 75% of the total fat (Kartha, *J. Sci. Ind. Research [India]*, 17B, 237). Six different triglycerides containing one or more *α*-oleostearate radicals were synthesized. Their film-forming properties were studied, and the amounts of oxygen required for their oxidation were determined (Kaufmann and Thomas, *Fette, Seifen, und Anstrichmittel*, 61, 211). Paper chromatography was used to identify the carbonyl compounds formed during autoxidation of sardine oil, linoleic acid and oleic acid. The dark color of oxidized fish oils was attributed to these carbonyl compounds (Nonaka, *J. Tokyo Univ. Fisheries*, 43, 127). The products of the autoxidation of linseed oil at various time-intervals were studied by paper chromatography and infrared spectroscopy. Hexanal and heptanal were identified (Kaufmann and Vogelmann, *Fette, Seifen, und Anstrichmittel*; 61, 561). Lead, cobalt, and bismuth soaps increased the rate of polymerization when linseed oil was oxidized at 90°. Organic sols of metals also acted as polymerization catalysts but were less effective

than the soaps (Lunina, *Nauch, Doklady Vysshei Shkoly, Khim. i Khim. Tekhnol.*, 1958 [2], 275). Chloroprene catalyzed the autoxidation of fish oil. The presence of copper accelerated this effect, but that of carotenoids or vitamin A decreased it (Mkhitarian, *Izvest Akad. Nauk. Armyan. S.S.R., Khim. Nauk.*, 11, 109).

Chemistry of a thermally oxidized oil was the subject of a thesis (Perkins, *Univ. Microfilms*, L.C. Card Mic. 58-5475; Dissertation Abstr. 19, 959). Thermal oxidation of corn oil at 200° produced polymers which had a high oxygen content, were present as hydroxyl and carboxyl compounds, and which contained unsaturation which was difficult to hydrogenate (Perkins and Kummerow, *J. Am. Oil Chemists' Soc.*, 36, 371). The unsaponifiable portion of natural fats contained autoxidation inhibitors which acted as retardants in drying oils (Stein *et al.*, *Ger.* 936,646).

Heating of *cis*, *trans*-conjugated methyl linoleate at 250° with selenium produced *cis*- and *trans*-octadecenoates and cyclic compounds which appeared to be dialkylbenzene and dialkylcyclohexene (Teeter *et al.*, *J. Org. Chem.*, 23, 1156). Linseed oil was polymerized by heat alone and by heat and air at several elevated temperatures. The degree of polymerization was calculated from a formula which included iodine number and bromine number (Taniewski and Bulezynska, *Przemyst Chem.*, 35, 324). Polymerization of linseed oil at 250° under nitrogen was followed for 16 hrs. by a variety of analytical methods (Taufel *et al.*, *Deut. Lebens. Rund.*, 54, 245). Stand oils prepared by heating in an inert atmosphere were of better quality than those prepared in air. The amount of conjugation increased with time of heating (Minutilli, *Olii minerali, grassi e saponi colorati e vernici*, 35, 2). The wear resistance of sisal buff was improved by impregnating it with an aqueous emulsion of bodied soybean oil and heating at 300° F. (Vaughan *et al.*, *U.S.* 2,890,137).

Drying oils may be improved by processes which increase the number of or change the location or geometric configuration of the double bonds in the fatty acid moiety. Linseed, hempseed, corn, cotton, soybean, peach kernel, peanut, and mustard seed oils were molecularly distilled, and the fractions were analyzed (Kozin and Zlatopol'skaya, *Sbornik Nauch. Rabot Moskov. Inst. Narod. Khoz.*, 1956 [8], 32; Referat. Zhur., *Khim.* 1957, Abstr. No. 2758). The drying properties of *Aleurites moluccana* and rubberseed oils were not improved by molecular distillation (Cruz *et al.*, *Philippine J. Sci.*, 86, 241). *Cis-trans* interconversions of methyl oleate, linoleate, and linolenate, on treatment with nitrogen oxides, were studied. The extent of polymerization of the esters increased with time (Khan, *Pakistan J. Biol. Agr. Sci.*, 1, 107). Aluminum chloride was the best of several catalysts evaluated for the catalytic isomerization and polymerization of linoleic and linolenic acids at 250° (Sorokin and Shuvalova, *Trudy Moskov. Khim. Tekhnol. Inst. im. D. I. Mendeleeva*, 1956 [23], 79). Anthraquinone and iodine were the best of several catalysts evaluated for the improvement of the drying properties of sunflower oil by isomerization (Yukhnovskii and Popenker, *Trudy Khar'kov. Politekh. Inst.*, 4, 159; Referat. Zhur., *Khim* 1956), Abstr. No. 52651). A review covered the preparation, composition, and use of dehydrated castor oil (Bolley, *J. Am. Oil Chemists' Soc.*, 36, 518). The efficiencies of several substituted sulfonic acids were determined as catalysts in the dehydration of castor oil (Rajadhyakasha and Dole, *Indian J. Appl. Chem.*, 21, 95). Castor oil was dehydroxylated by heating with water under pressure (Pintsch-Bamag Akt.-Ges., *Brit.* 805,918). "S-oil," one of the distillate fractions from the cracking of castor oil, contained undecyclic, ricinoleic, linoleic, and palmitic acids. It could be used in the manufacture of varnishes and plastics (Dupont, *Olearia*, 12, 53). Unsaturated fatty acids suitable for the preparation of drying oils were prepared by heating halogenated acids in high-boiling alcohols or ketones. The presence of solid or dissolved alkali hydroxide facilitated the dehydrohalogenation reaction (Marzin, *Ger. [East]* 9560; *Ger. [East]* 9566). Methyl esters of fatty acids and various drying oils were brominated by treatment with N-bromosuccinimide, then dehydrobrominated by heating in pyridine or quinoline (Nanavati *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 226).

Synthesis of glycerides of fatty acids was the subject of a review (Hartman, *Chem. Rev.*, 58, 845) and of a thesis (Watson, *Univ. Microfilms*, L.C. Card Mic. 58-5186; Dissertation Abstr. 19, 2484). The interesterification of vegetable oils and animal oils in xylene, using various catalysts, principally sodium methoxide, was studied (Taufel *et al.*, *Fette, Seifen, und Anstrichmittel*, 60, 456). Interesterification of methyl oleate, triolein, and soybean oil under various conditions was studied. No *cis-trans* isomerization or conjugation occurred.

Polymerization occurred only above 150° (Kaufmann and Grothues, *ibid.*, 61, 425). Cod liver and linseed oils were interesterified with various catalysts at 200°. Drying properties of the products were investigated (Jedlinski, *Zeszyty Nauk. Politech. Gdansk Chem.*, 2, 9). Interesterification of highly unsaturated oils with glycerides of low-molecular-weight acids with a tin catalyst produced drying oils (Kaufman, *Ger.* 938,738).

Esters of unsaturated fatty acids with polyhydric alcohols other than glycerol, sometimes in combination with glycerol, have drying properties. A product for use in linoleum was prepared by esterifying dilinoleic acid with pentaerythritol (Dunlap and Parker, *U.S.* 2,873,291). Esters were prepared from  $\alpha$ -D-glucopyranoside, cameline oil, and tall oil, using lead monoxide and zinc oxide catalysts (Jedlinski, *Przemyst Chem.*, 35, 229). Fatty acid esters of several nonreducing saccharides, including sucrose, were prepared by interesterification with the fatty acid esters of ethylene glycol, glycerol, erythritol, pentaerythritol, mannitol, and sorbitol in the presence of a substituted morpholine or piperidine (Hedley and Company, *Brit.* 804,197). Two moles of unsaturated fatty acids were reacted with one mole of the aluminum enolate of acetoacetic ester, malonic diethyl ester, or acetylacetone. A mixture of this product with glycerides was a drying oil (Weiss, *U.S.* 2,871,135), as was the reaction product of a  $C_{18}$ - $C_{20}$  saturated or unsaturated fatty acid with an aluminum enolate (Reisinger, *U.S.* 2,885,297).

Reviews covered the use of drying oils and drying acids in oil-modified alkyd resins (Kraft, *J. Am. Oil Chemists' Soc.*, 36, 583) and the use of various polyols in alkyds (Barr *et al.*, *Paint and Varnish Production*, 48 [11], 43). The use of maleic-modified soybean oils in paint vehicles, the use of soybean oils in alkyds, and the properties of various soybean oil derivatives were reviewed (Helme and Molines, *Peintures, pigments, vernis*, 34, 385). While structural modifications of alkyds and polyesters through the  $\beta$ -hydroxyl group of glycerol had been studied, present manufacturing methods were probably not satisfactory for producing such modifications (Mills, *Paint Technology*, 23, 129). An alkyd gel for use in thixotropic paints was prepared by treating an alkyd at 100–250° with an aluminum soap (Rinse, *U. S.* 2,892,780). Tall oil acids were used with soy or linseed acids or oils for the modification of phthalic-pentaerythritol alkyds by the "high polymer technique." This technique permitted the use of higher percentages of tall oil acids without lowering quality (Roberts *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 166). Alkyds were prepared from drying oils or acids, dicarboxylic acids such as phthalic, isophthalic, terephthalic, succinic, adipic, azelaic, or sebaic, and a partial allyl ether of pentaerythritol (Campbell, *U. S.* 2,885,375). Esterification of the free hydroxyls of cuttle fish oil with maleic or phthalic acid improved its drying properties (Marumo and Tomiyama, *Yushi Kagaku Kyokaiishi*, 3, 70). Drying properties of isano oil were improved by heating it with fatty, rosin, maleic, or phthalic acids (Kaufmann, *Ger.* 955,414). Alkyds were prepared from cameline oil, tall oil,  $\alpha$ -D-glucopyranoside, and phthalic anhydride (Jedlinski, *Przemyst Chem.*, 35, 229). Oil-modified alkyds containing isophthalic acid (Heckles, *U. S.* 2,861,047; Carmody, *U. S.* 2,884,390), 5-tert-butylisophthalic acid, 4-tert-butylorthophthalic acid (Schlatter and Lum, *U. S.* 2,895,932), and hexachloroendomethtetrahydrophthalic acid were described. The latter was used as a baked prime coat on metal articles (Barret and Flitter, *U. S.* 2,873,210). Products were prepared from a vegetable or fish oil or long-chain fatty acid, a glycol or polyol, and a benzene tricarboxylic acid or anhydride (Bolton, *U. S.* 2,856,374; Van Strien, *U. S.* 2,870,102). Similar products were prepared with diaminodurene or ethylene diamine as an additional ingredient (Bolton and Van Strien, *U. S.* 2,860,113; *U. S.* 2,860,114). Other products were prepared from acidulated soap stock, polyhydric alcohol, and an  $\alpha,\beta$ -unsaturated polycarboxylic acid (Christenson and Borman, *U. S.* 2,891,919), fatty oil or acids, polyhydric alcohol, an  $\alpha,\beta$ -unsaturated dicarboxylic acid, and 2,5-endomethylene- $\delta$ -3-tetrahydrobenzyl alcohol (Dean and Sehefbauer, *U. S.* 2,867,593), and a fatty acid, an aliphatic polycarboxylic acid, and an alkylene oxide-polyhydric alcohol adduct (Hensley *et al.*, *U. S.* 2,889,293).

Fatty acids can be converted into polymers or polymerizable materials by other means than esterification with polyols. One such method is esterification with vinyl compounds. Kinetics of the polymerization of several vinyl esters of short-chain saturated aliphatic acids were reported (Kurian and Muthana, *Die Makromolekulare Chemie*, 29, 1, 19, 26). Treatment of vinyl esters of  $\alpha$ -bromo fatty acids with triethyl phosphite replaced the bromo group with the diethyl phosphonate group.

These vinyl esters formed low polymers when heated with benzoyl peroxide (Sasin *et al.*, *J. Am. Chem. Soc.*, **80**, 6336). Saturated acids from the oxidation of paraffin were chlorinated, dehydrochlorinated to introduce unsaturation, esterified with allyl alcohol, and then epoxidized to yield polymerizable products. A similar product from cotton oil acids was condensed with maleic acid (Nicolescu *et al.*, *Rev. franc. corps gras*, **5**, 384).

Another nonpolyol path to fatty polymers is through the reaction of fatty acid derivatives with polyamines to yield polyamide resins. The following combinations of reactants were reported: oleic, linoleic, or soybean acids with unsaturated diamines (these products were then epoxidized) (Orthner and Fuchs, *U. S.* **2,905,702**), epoxidized fatty oils or esters with aliphatic polyamines (Förster, *U. S.* **2,890,228**), epoxidized fatty acids with polyamines or with aminoalcohols (Tawn, *Brit.* **811,797**), polymeric fatty acids with polyamines (Peerman and Floyd, *U. S.* **2,881,194**), polymeric fatty acids and saturated dicarboxylic acids with alkylene diamines and polyalkylene polyamines (Peerman and Witteoff, *U. S.* **2,886,543**). Polyamides prepared from polymeric fatty acids and polyamines were combined with alkyd resins of maleic, fumaric, citraconic, mesaconic, itaconic, or aconitic acids (Peerman, *U. S.* **2,889,292**). A polyamide resin prepared from a fatty acid, a polymeric fatty acid, and a polyamine was dispersed in a paint vehicle to render the vehicle thixotropic (Wright *et al.*, *U. S.* **2,861,048**).

Epoxidation of unsaturated centers in fatty materials is another method of increasing their reactivity. New methods for improving yields in epoxidation reactions involved the use of partially preformed peracetic acid and agitation control (Wohlers *et al.*, *Ind. Eng. Chem.*, **50**, 1685). The effects of variations in the amount and concentration of hydrogen peroxide were studied in the epoxidation of soybean oil by the partially preformed peracetic acid method on the epoxide contents of the products (Sack and Wohlers, *J. Am. Oil Chemists' Soc.* **36**, 623). Resins were prepared from phthalic anhydride and epoxy derivatives of the following oils: neatsfoot oil, lard oil, triolein, soybean oil, perilla oil, trilinolein. Properties of the resin improved with increasing unsaturation of the initial oil (Gelb *et al.*, *ibid.*, **283**). A mixture of pentaerythritol benzoate tri- and dioleate was epoxidized (Dazzi, *U. S.* **2,889,338**).

A crude polymerized fatty acid mixture was improved by treating it with zinc to remove halogen-containing substances (Hampton, *U. S.* **2,894,939**). Condensation of unsaturated fatty chains with reactive olefins is a means of improving drying oils. Safflower oil was treated with dibutyl or dimethyl maleate at 290° in a sulphur dioxide atmosphere. The products were different from the Diels-Alder adducts of *trans,trans*-9,11-linoleic acid (Miller *et al.*, *J. Am. Oil Chemists' Soc.*, **36**, 394). An olefinic nonconjugated glyceride oil was condensed with an alkyl fumarate (Dazzi, *U. S.* **2,862,012**). A triglyceride with two short-chain alkyl groups was condensed with an alkyl or alkoxyalkyl fumarate (Dazzi, *U. S.* **2,891,083**). Condensation products prepared from cyclopentadiene and sunflower, castor, or tung oils in the presence of stannic chloride gave wrinkled, brittle films. Films from the liseud oil product were satisfactory (Yukhnovskii *et al.*, *Zhur. Priklad. Khim.*, **31**, 1091).

In copolymerizing vinyl compounds with fatty oils or acids the usual procedure was to heat the components in the presence of a peroxide catalyst. A review covered the modification of drying oils with vinyl compounds, particularly with vinyltoluene (Helmreich, *J. Am. Oil Chemists' Soc.*, **36**, 523). Products prepared from the following groups of ingredients were described: an alkyd resin, vinyl acetate, and vinyl chloride (Christenson, *U. S.* **2,865,874**), eleostearic acids from tung oil and methyl vinyl ketone (Placek and Bickford, *J. Am. Oil Chemists' Soc.*, **36**, 463), an alkyd containing an  $\alpha,\beta$ -unsaturated dicarboxylic acid, and a vinylbenzene (Konen and Boller, *U. S.* **2,877,194**), an oil-modified alkyd, vinyl cyanide, an acrylic acid ester, and a vinyl aromatic compound (Sample and Williams, *U. S.* **2,890,185**; Sample, *U. S.* **2,890,186**), a drying oil and a styrene compound (Boelhauer *et al.*, *U. S.* **2,852,478**), destearinated fractions of cuttle fish oil, maleic acid, and styrene (Marumo *et al.*, *Yushi Kagaku Kyokaiishi*, **3**, 109), an oil-modified alkyd, a styrene derivative, and an unsaturated nitrile (Chapin, *U. S.* **2,862,898**), an aliphatic ester of a drying oil acid and vinyltrihalosilane or vinyltrialkoxysilane (Olson, Christenson, *U. S.* **2,894,922**), a drying oil or drying oil acids and an acetylenic compound, such as methyldivinylacetylene or 2-methyl-5-hexene-3-yne-2-ol (Marsel and Happel, *U. S.* **2,902,457**). A copolymer of a drying oil and vinyltoluene was mixed with a nondrying alkyd

resin to give a paint vehicle (deGroot and Hofferth, *U. S.* **2,857,347**). A coconut-maleic-phthalic alkyd was copolymerized with butyl methacrylate and then mixed with a pigment, a volatile organic solvent, and a nitrocellulose lacquer to give a liquid coating composition (Walus, *U. S.* **2,857,344**).

Many materials of complex composition have been prepared by combining a drying oil product with one or more resins of other types. These combinations may be made by simply mixing the various polymeric materials, by causing them to react with one another, or by mixing and then reacting the various monomeric materials which would ordinarily go into the preparation of the separate resins. The following groups of ingredients involving resins of the olefin type were reported: a drying or semi-drying oil, a copolymer of a C<sub>4</sub> to C<sub>6</sub> conjugated diolefin and styrene, and an oil-soluble resin (Koencke, *U. S.* **2,853,396**), a drying oil, natural or butadiene-styrene or butadiene-acrylonitrile rubber, and a reactive pigment (Lox, *U. S.* **2,901,447**), drying oils and an olefin-diolefin resin resulting from heat polymerization of a piperylene-containing petroleum fraction, and a manganese carboxylate soap (McKay, *U. S.* **2,880,188**). Mixtures involving aldehydes included: a thermosetting resin prepared from tall oil, furfural or furfuryl alcohol, and an aromatic aldehyde (Frey, *U. S.* **2,863,747**), a product useful in preparing cation-exchange resins prepared from cashew nutshell oil and formaldehyde (Govindan *et al.*, *Indian* **59**, 497). Mixtures involving phenol-formaldehyde resins were a conjugated drying oil, a titanium ester, and a phenol-formaldehyde resin or a dehydrated castor oil-modified alkyd resin (used as a paint) (Beacham, *U. S.* **2,901,450**), tung oil, oiticica oil, air-blown and heat-bodied fish oil, and a resin-modified phenol-formaldehyde resin (a wrinkle-drying coating) (Lederman, *U. S.* **2,853,458**), a higher fatty acid, and a phenylphenol or alkyl-phenol-formaldehyde resin (Mohr and Capener, *U. S.* **2,878,199**), a drying oil fatty acid, styrene or methyl methacrylate, phenoxyethanol, and formaldehyde (Hanle *et al.*, *U. S.* **2,880,187**). Combinations including amino-aldehyde resins were a long-oil alkyd, maleic acid-triethylamine salt, and a butylated dimethylolurea (Shelley, *U. S.* **2,871,209**), a tall oil-phthalic anhydride-trimethylololthane alkyd, and styrene or methyl methacrylate or urea-formaldehyde resin or melamine-formaldehyde resin (Kraft and Forschirm, *J. Am. Oil Chemists' Soc.*, **36**, 164), an oil-modified alkyd, a polyalkylene glycol, and a water-soluble lower alkanol-modified melamine-aldehyde resin (Christenson and Hart, *U. S.* **2,853,459**), a drying oil alkyd, a polyalkylene glycol, a polystyrene or divinyl latex, and a water-soluble aminotriazine-aldehyde resin (Christenson *et al.*, *U. S.* **2,852,475**), an amine salt of a modified alkyd, a latex of polystyrene, polyvinyl chloride, butadiene-styrene, or an acrylic resin, and a water-soluble amine-aldehyde resin (Cummings, *U. S.* **2,852,476**). The latter three products were water-dispersible materials.

A review covered the preparation of drying oils from unsaturated acids and synthetic polyols with emphasis on epoxy resins as the polyols (Tess, *J. Am. Oil Chemists' Soc.*, **36**, 496). Combinations involving epoxy resins were a short oil alkyd, epichlorohydrin, and a terminally unsaturated compound, such as styrene, diallyl phthalate, diallyl cyanamide (Yusem, *U. S.* **2,895,929**), the preceding product plus a melamine-formaldehyde or urea-formaldehyde resin (Yusem, *U. S.* **2,895,930**), dehydrated castor acids and epoxy resin (Chatfield, *Paint, Oil and Colour J.*, **134**, 573), a drying oil or drying oil acids and an epoxy resin (mixed with butadiene-styrene copolymer and used as a coating for sausage casings) (Dowd and Glaser, *U. S.* **2,866,710**), drying oil acids and the resin from bisphenol and epichlorohydrin (mixed with a pigment, drier, and polyalkylene polyamine to give a wrinkle finish) (Lederman, *U. S.* **2,867,591**), an oil-modified phthalic alkyd and an epoxy resin partially esterified with a vegetable fatty acid or rosin acid (Carmody, *U. S.* **2,887,459**), a drying oil or semidrying oil and the epoxy resin from epichlorohydrin and 4,4'-dihydroxydiphenyldimethylmethane (Stoesser *et al.*, *U. S.* **2,875,165**), drying oil acids and the epoxy resin obtained by copolymerizing glycidyl methacrylate with other methacrylates (Ringwald and Hanson, *Brit.* **793,776**), polymeric fatty acids, an alkylene polyamine, and an epoxy resin (Morris and Chaplick, *U. S.* **2,867,592**), an epoxidized fat or fatty acid ester, a polyamine, and an epoxy resin from polyhydric phenols and epichlorohydrin (Förster, *U. S.* **2,890,184**), an unsaturated fatty acid, an alkyl acrylate or methacrylate, and an epoxy resin (McNabb, *U. S.* **2,877,195**). In the case of the third product in the above list the use of dehydrated castor acids with a higher degree of conjugation gave products with lighter color, better drying rate, and less tendency to blister than did acids with lower conjugation.

A review paper discussed isocyanate-modified drying oils (Stanton, *J. Am. Oil Chemists' Soc.*, 36, 503). Another review on polyurethanes and unsaturated polyesters discussed the use of diglycerides in polyurethanes (Erlandsen, *Fette, Seifen, und Anstrichmittel*, 61, 227). A study was made of the effect of varying ingredient percentages in urethane foams made from castor oil and tolylene diisocyanate. Modification of the castor oil by hydrogenation, elaidinization, partial epoxidation, or aging at elevated temperature and humidity improved the water resistance and decreased the shrinkage of the foams (Yeadon *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 16,541). A study was made of the foam properties of polyurethanes made from tolylene di-isocyanate and 21 different polyols derived from castor oil (Ehrlich *et al.*, *ibid.*, 149). A product was prepared from castor oil, acetylated castor oil, pentanediol-1,5, and m-tolylene di-isocyanate (Katz and Thomas, *U. S.* 2,864,780).

A review of recent research on soybean utilization covered polymers prepared from vinyl ethers of soybean alcohol (Cowan and Witham, *Soybean Digest*, 19 [12], 14). Such polymers were prepared from the vinyl ethers of linoleyl alcohol, linolenyl alcohol, or the mixed unsaturated fatty alcohols obtained by the reduction of drying and semidrying vegetable oils (Cowan and Teeter, *U. S.* 2,901,469). These polymers adhered well to metal and were alkali-resistant. They offered promise as can coatings (Teeter *et al.*, *Ind. Eng. Chem.*, 50, 1703). Such a coating composition contained the polymer, a vehicle, a drier, and an oxidation inhibitor (Teeter *et al.*, *U. S.* 2,889,309). Infrared spectroscopy was used to study the composition of copolymers obtained from soybean vinyl ether with each of six low-alkyl vinyl ethers (Glass and Melvin, *J. Am. Oil Chemists' Soc.*, 36, 100).

A review on driers for drying oils discussed the subject from the stand-point of the metal used as well as from the stand-point of the type of oil (Gardner, *ibid.*, 568). A titrimetric method for the determination of the calcium, cobalt, lead, manganese, and zinc contents of driers was based upon the chelating action of ethylenediamine-tetra-acetic acid (Luechesi and Hirn, *Anal. Chem.*, 30, 1877).

Methods of the British Standards Institute for the analysis of oils and fats were published (Brit. Standards Inst., *Brit. Standard 684*, 100 pp.). Reviews on the analysis of drying oils covered general methods (Link, *J. Am. Oil Chemists' Soc.*, 36, 477), research methods (Dutton, *ibid.*, 513), analysis of tall oil products (Herrlinger, *ibid.*, 119), application of infrared spectroscopy to fats (autooxidation, copolymers) (Kaufmann *et al.*, *Fette, Seifen, und Anstrichmittel*, 61, 547), analysis of polymerized fats (Täufel *et al.*, *Deut. Lebensm.-Rundschau*, 5, 235), analysis of coatings (Swann *et al.*, *Anal. Chem.*, 31, 674). Determination of iodine value and water content on a single sample was described (Heidbrink, *Fette, Seifen, und Anstrichmittel*, 61, 194). A symposium on rheology included a paper on the rheology of paints and varnishes (Gotoda, *Yukagaku*, 7, 489). A nomograph giving the viscosities of drying oils at different temperatures was presented (Shakhkel'dyan, *Masloboino-Zhirovaya Prom.*, 25 [3], 38).

The auto-ignition of oils and fatty acids was studied in a Mackey apparatus. Cooking linseed oil or adding driers to it increased its ease of ignition. Ignition time decreased with increase in iodine number (Bergman and Lindberg, *Färg och Fernissa*, 22 [3], 6). A manometric method was devised to detect the onset of autooxidation in substances of low vapor pressure, such as methyl linoleate (Kern and Dulog, *Die Makromolekulare Chemie*, 29, 199). A polarographic method was used to study the oxidation of fish oils. An additional wave, not present in the polarograms of fresh oils, was found in the polarograms of oxidized oils and was apparently due to the presence of an aldehyde group (Kikuchi *et al.*, *J. Tokyo Univ. Fisheries*, 42, 39). A colorimetric method using 2-thiobarbituric acid as the reagent was used in the study of oxidizing changes in fats (Dzikowski, *Roczniki Panstwowego Zakladu Hig.*, 9, 461). An apparatus for determining the drying conditions for protective coatings at elevated temperatures was described (Schwab *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 275).

A method for studying the effect of variables on the levelling of latex paints was described (Garrett *et al.*, *Ind. Eng. Chem.*, 51, 117). An argentometric method for determining epoxides in oils was developed, and the effect of epoxides on the determinations of other analytical values of oils was determined. The determination of hydroxyl value was considerably affected (Krull, *Fette, Seifen, und Anstrichmittel*, 61, 223). A spectrometric method was used to determine the p-tert-butylbenzoic acid content of alkyd resins (Seerest and Kosciesza, *Anal. Chem.*, 31, 1402). Inorganic and organic pigments in paints were

determined by an infrared spectroscopic method (Harkins *et al.*, *ibid.*, 541).

The degradation of drying oil films was the subject of a review (Miller, *J. Am. Oil Chemists' Soc.*, 36, 596). Microbiological deterioration of water-thinnable coatings was divided into two types, spoilage in the container and disfigurement of films. The former was due to bacterial attack on the resins or emulsion stabilizers, the latter to mold growth (Ross and Buckman, *Ind. Eng. Chem.*, 51, 116).

The rheological properties of a dispersion of a finely divided solid, such as paint pigment, were an indication of the degree of wetting action of the liquid for the solid. Good wetting was indicated by low relative viscosity and low rate of settling. Poor wetting was indicated by high viscosity and yield value and by thixotropy (Mardles, *Paint Technology*, 22, 353). A method for grinding a pigment into a drying oil vehicle was patented (Eastman, *U. S.* 2,885,298).

A paper on polyvinyl chloride plasticizers from fats was part of a symposium on fat chemistry (Shigeno, *Kagaku (Kyoto)*, 11, 650). Thirty-one different acyl or aroyl derivatives of hydroxystearic acid were tested as plasticizers in vinyl chloride-vinyl acetate copolymer. Many of them were good primary plasticizers with outstanding low temperature performance (Knight *et al.*, *J. Am. Oil Chemists' Soc.*, 36, 382). Some cyanoethylated ricinoleic acid derivatives which were of potential interest as plasticizers were prepared (Dupuy *et al.*, *ibid.*, 659). Castor oil derivatives evaluated as plasticizers included 4-ricinoleoylmorpholine, hydrogenated, acetylated, and cyanoethylated ricinoleic acid derivatives, cyanoethylated ricinoleyl alcohol and its saturated counterpart. Most of these were satisfactory primary plasticizers for vinyl chloride-vinyl acetate copolymer. Four of them were satisfactory for cellulose acetate (Magne *et al.*, *ibid.*, 635). Highly chlorinated tung oils, containing more than 40% chlorine, lowered the milling temperature of vinyl chloride-vinyl acetate copolymer but did not impart flexibility at room temperature (McKinney *et al.*, *ibid.*, 170). The adduct of methyl vinyl ketone and  $\alpha$ -oleostearic acid, and its hydrogenated, epoxidized and aromatized derivatives were more efficient primary plasticizers for vinyl chloride-vinyl acetate copolymer than was dioctyl phthalate (Placock *et al.*, *ibid.*, 651). Vinyl chloride-vinyl acetate copolymer was plasticized with a mixture of diacetolein and a liquid ester of phosphoric acid (Magne *et al.*, *U. S.* 2,857,318). Other plasticizers for vinyl polymers were the ester prepared from an aliphatic diol and a mixture of a C<sub>2</sub> to C<sub>10</sub> aliphatic monobasic acid, a monobasic aromatic acid, saturated fatty acids, and polyunsaturated fatty acids (Rhodes and Imes, *U. S.* 2,886,545), partially epoxidized linseed or soybean oil (Greenspan and Gall, *U. S.* 2,857,349), and a carbonate ester of a fatty acid (Riedeman, *U. S.* 2,858,286). Nitrocellulose was plasticized with the acetoacetic ester of castor oil (Bader and Vogel, *U. S.* 2,895,844).

Miscellaneous products from fatty materials included: a beverage can coating consisting of vinyl polymers with 0.1 to 0.75% of lecithin (De Christoforo, *U. S.* 2,877,922); a meat can coating consisting of an alkylene bis-stearamide synthetic wax and synthetic rubber (Clark and Raich, *U. S.* 2,884,392), a shell mold binder consisting of a phenol-formaldehyde resin and a fatty alkylolamide (Cooper and Kelly, *U. S.* 2,869,195), a sealing composition containing inorganic fillers, a raw drying oil, a bodying oil, and an aqueous emulsion of a nondrying polymerized fraction from bodied marine oil (Zweifel *et al.*, *U. S.* 2,886,457), an adhesive gel containing a saturated higher fatty acid, an aluminum triacoholate, and microcrystalline wax (Duro, *U. S.* 2,875,081), a fatty acid diester of an alkyl glucoside as a suspending agent for suspension polymerization of vinyl polymers (Lynn and Mohrmann, *U. S.* 2,862,913), foamable styrene particles containing C<sub>12</sub> to C<sub>20</sub> fatty acids or their salts or monoesters (Colwell and Platzer, *U. S.* 2,857,341), the 2,4,5-trihydroxy phenone of a C<sub>14</sub> to C<sub>18</sub> fatty acid as a heat stabilizer in polyesters (Knowles and Moore, *U. S.* 2,856,383). Nonfatty polymeric products included: polyesters prepared from adipic, suberic, maleic, or acrylic acids and 1,4-butenediol, 1,4-pentanediol or 2,5-cyclohexanediol (Kutepow and Himmele, *Ger. 1,014,979*), a molding composition containing an amorphous polymerizable unsaturated chlorophthalic alkyd, diallyl phthalate and an organic peroxide catalyst (Hyland, *U. S.* 2,871,215), oil-reactive o-cresol-formaldehyde resins for paints and varnishes (Kumanotani *et al.*, *Yakagaku* 6, 100), a demulsifier prepared by air oxidation of a gas oil-solar oil fraction in the presence of calcium naphthenate (Masumyan and Danielyan, *U.S.S.R.* 113,860).

## Soaps and Detergents

## MANUFACTURE

## Processes

SOAPS. Continuous saponification procedures continue to be of high interest; one such is described (Algranati, *Seifen-Ole-Fette-Wachse*, 85, 30-31). The Monsavon, DeLaval, and Sharples continuous processes were detailed and were compared as to characteristics of the glycerin lyes obtained, and the energy consumed by each (Anon., *Soap Chem. Specialties*, 35 [2], 133, 135, 137-138). An automatic process utilizing a series of chambers was disclosed in which pre-heated fatty acids and alkalis were reacted under controlled pressures and temperatures (Mazzoni, *Italian* 550,133). Vigorous agitation of spent lye with neutralization by a fatty oil until all free alkali had been neutralized was initiated by including suitable amounts of soap to promote intimate contact (Owen and Hurt, *U. S.* 2,899,450). Lumping of spray-dried soap powders in hot water may be prevented by adding to the slurry a xylene sulfonate and either an alkali metal silicate or carbonate to a coconut-tallow soap slurry (Unilever Ltd., *Brit.* 810,755). The Lever Plodded Bar process, the Mazzoni and Meccaniche Moderne processes of household cooling capable of solidification in about 30 min. were described and compared in detail (Webb, *Soap, Perfumery, Cosmetics*, 32, 477-481, 611-614, 705-707).

The causes contributing to warping, sweating, efflorescing, feathering, and lathering of household soaps were said to be explainable on the 66% rule. This rule, originally applied to glycerin recovery, is that a soap curd consisting of soap hydrate containing 66% of fatty acids and lye is identical in composition with that from which it had separated (Webb, *Soap, Perfumery, Cosmetics*, 32, 256-259).

SURFACTANTS. Details of manufacture, flow sheets, and equipment requirements were described for the following surfactants as manufactured by Process Chemicals: lauryl sulfate, fatty alkanolamide condensates, glyceryl fatty acid esters, polyethylene glycol fatty acid esters and fatty alcohol polyethers, amine polyethers, and quaternary ammonium compounds (Gushce and Scherr, *Ind. Eng. Chem.*, 51, 798-804).

Undesirable free sulfuric acid produced in processing higher alkylbenzenes (AB) can be prevented from causing "frosting" and "salting out" in detergent bars by converting the acid to another organic sulfonic acid compatible with the higher AB sulfonates (Raehlin, *U. S.* 2,893,370). The inoperative gel region between 39 to 57% total solids for the sodium salt of monoglyceride higher fatty acid sulfates can be avoided by using a lower aliphatic monohydric alcohol and water, then concentrating without difficulty (Carpenter and Silvis, *U. S.* 2,879,839).

Continuous manufacture of detergents by the Procter and Gamble process features a combination of pump mixer and heat exchanger as the heart of the system. Flow rates and process variables are adjusted to cope with the tricky laws of chemical equilibrium. Either alkylbenzene or fatty alcohols can be sulfonated, and, for the former, a higher active ingredient process is possible. Blending of the neutralized sulfonates with builders and other ingredients proceeds continuously through spray drier to packaging plant (Pedor, Strain, Theoharous, and Whyte, *Ind. Eng. Chem.*, 51, 13-18).

A new type of continuous sulfonation unit (Chemetron) makes possible high production in small space. Continuous sulfonation of alkylbenzene with oleum involves sulfonation, dilution, separation of excess acid, and neutralization of the concentrated sulfonic acid (Anon., *Soap Chem. Specialties*, 35 [4], 131, 133, 135). Preliminary data were given to show that alkyl sulfates could be produced from hydrogenated, oxidized then reduced, petroleum fractions (Veselov, Kataeva, Orechkin, and Popova, *Masloboino-Zhirovaya Prom.*, 24 [10], 19-22).

Various methods and their economies for hoisting salt and glycerin recovery were discussed in considerable detail (Webb, *Soap Chem. Specialties*, 34 [6], 54-56, 190; [7] 127, 129, 131, 167; [8] 147-148).

Following are surfactant process patents or manufacturing techniques listed by patentee or assignee:

Atlantic Refining Company, nonionic surfactants from 2,2-bis(4-hydroxyphenyl)-propane (Woodbridge and Keenan, *U. S.* 2,859,250)

California Research Corporation, alkylbenzene sulfonates of high sulfonate to sulfate ratio (Lewis, *U. S.* 2,897,156)

Colgate-Palmolive Company, purification of sulfated, partial fatty glyceryl esters (Becher, *U. S.* 2,863,887); monoesters of glycerol monosulfuric acid (Gray, *U. S.* 2,868,812)

Phillips Petroleum Company, glycol thioether converted to corresponding sulfoxide (Louthan, *U. S.* 2,864,866)

Procter and Gamble Company, process for speckled, colored granulated product (Tecklenburg, *U. S.* 2,889,283)

Sugar Research Foundation Inc., process for sugar esters (Hass, Snell, and Osipow, *U. S.* 2,893,990)

Union Carbide Corporation, process for polyethylene glycols, using primary and secondary alkanols (Carter, *U. S.* 2,870,220)

Wyandotte Chemicals Corporation, reaction of polypropylene and ethylene oxides with organic compound with two to six reactive hydrogen atoms (Wyandotte Chemicals Corporation, *Brit.* 800,159).

Statistics concerning anionic detergents and their future were reviewed (Morgan and Wizemann, *Soap*, 49 [9], 51-53), and the need for detergent manufacturers to keep abreast of trends in appliance manufacture to plan their product lines was emphasized (Alaback, *Soap Chem. Specialties*, 35 [7], 54-55, 170-171). An economist's view of the British soapmaking industry included a comparison between retail prices of soap and detergents for 1950-1958 and the relationship between real income and detergent consumption from 1870 to 1957 (Brech, *Soap, Perfumery, Cosmetics*, 32, 159-164).

RAW MATERIALS. Acetaldehyde disulfonic acid from acetylene and sulfur trioxide can be made to react with alkylbenzenes, phenols, and chlorinated phenols to provide surfactant, moth-proofing, and fungicidally active materials (Gilbert, McGouch, and Otto, *Ind. Eng. Chem.*, 51, 925-928). Olefins boiling at 180-320°, synthesized from carbon and hydrogen over Cu-Ni catalysts, can be sulfonated to give satisfactory surfactants (Kheifetz, Milovidova, Zelvyanskaya, Il'in Yudakova, and Rapoport, *Khim. i Tekhnol. Topliv i Masel*, 3 [9], 48-54). Tall oil usage was reviewed; the surfactant usage was as polyoxyethylene products, esters, alcohols, sulfates and sulfonates, and amines (Anon., *Tappi*, 42 [6], 60A, 62A, 64A, 66A). Oxo bottoms consisting principally of ether alcohols were reacted with ethylene oxide to give condensates showing advantages over nonylphenol adducts (Bartlett, Kirshenbaum, and Muessig, *Ind. Eng. Chem.*, 51, 257-258).  $\alpha$ -Branched hydrophobic groups with complex substituents as produced by the Guerbet synthesis are suitable as surfactant components. These result from the condensation of alcohols and aldehydes with alcoholates (Machemer, *Melliand Textilber.*, 40 56-65, 174-179). "Alfols" based on the Ziegler reaction of aluminum metal, ethylene, and hydrogen were described. These alcohols may be used as raw materials to prepare alkyl sulfates, alcohol ether sulfates, dodecylbenzene sulfonates, lauryl trimethylammonium chloride, and ethoxylated lauryl alcohol (Hinds, *Soap Chem. Specialties*, 35 [5], 57-59, 144-145; *Petrochem. Ind.*, 2, 7-9).

Different petroleum fractions were evaluated for Soviet produced ABS (Rabinovich and Skripchenko, *Masloboino-Zhirovaya Prom.*, 24 [6], 26-29). Naphthenes were sulfochlorinated photochemically to produce detergent sulfonaphthenates said to compare favorably with other synthetics (Tyutyunnikov and Volkov, *Khim. i Tekhnol. Topliv i Masel*, 3 [12], 49-52). Another paper dealt with various petroleum fractions useful for alkylation (Rabinovich and Skripchenko, *Masloboino-Zhirovaya Prom.*, 24 [6], 26-29).

## Additives

A review of fluorescent brightening agents was concerned with their historical development, properties, uses, their chemical constitution, and the effect on properties of changes in structure (Adams, *J. Soc. Dyers and Colourists* 75, 22-31). The performance of a single brightening agent (Durig and Kaufmann, *Fette, Seifen, und Anstrichmittel*, 60, 838-843), and the evaluation of these agents and of oxidizing bleaches on cotton were described (Furry, Bensing, and Kirkley, *Am. Dyestuff Repr.*, 48 [8], 59-73). In the latter reference a comparison of values obtained by visual means compared well with reflectometric evaluation. A comparison was made between the Launder-Ometer results and a modified-agitator household washer. Control analysis of fluorescent brighteners was achieved (Weeks, Harris, and Lewis, *Soap Chem. Specialties*, 35 [5], 66-70, 277) by comparative analysis with a standard brightener employing ultraviolet absorption spectroscopy. Suggested as a means for characterization were the functional properties.

## Compositions

LIQUIDS. Heavy-duty liquid compositions have begun to assume some importance and the principles and requirements were outlined (Tillotson, *Soap Chem. Specialties* 35 [2], 49-52,

169). The four essential components were organic active ingredient, alkaline builder, soil-suspending agent, and fabric whitener. Formulation of these liquids is difficult because of settling and phase separation, and the latter was said to be controlled through the addition of alkali metal toluene sulfonate as a solubilizer for the alkylbenzene sulfonate in the aqueous phosphate solution (Thomas Hedley and Company Ltd., *Brit. 807,586*). Homogeneous and stable heavy-duty liquids were claimed through the use of an alkali metal aryl sulfonate and at least one alkylolamide in a liquid containing the potassium salts of alkylaryl sulfonate and pyro- or tripolyphosphate (Carroll, *U. S. 2,859,192*). Suds-controlled heavy-duty liquids were obtained in aqueous suspensions of 2 to 3% potassium dodecylbenzene sulfonate, 3.5 to 5% sodium tallow methyl taurate, 2 to 3% of alkali metal xylene sulfonate, about 1% of coconut fatty acids, about 1% of a condensation product of one mole lauric monoethanolamide and one mole ethylene oxide, about 1% triethanolamine, 0.3% NaCMC and 22.5 to 25% tetrapotassium pyrophosphate (Lamberti and Gray, *U. S. 2,860,107*). A thixotropic liquid consisting of glycol or glycerol as the vehicle, a colloidal dispersion of a polyphosphate having a particle size not greater than about 0.5 micron, and a fully soluble nonsoap detergent having a viscosity ranging from 0.5 to 2.0 poises formed a heavy duty detergent (McCune and Quimby, *U. S. 2,864,770*). A clear, heavy-duty liquid was prepared, containing an alkyl glyceryl ether sulfonate, sodium toluene sulfonate as solubilizer, large amounts of pyro- or tripolyphosphate, and sodium silicate to protect against tarnish or corrosion of aluminum (Henderson and Schramm, *U. S. 2,877,185-6*).

**SOAPS.** Soap compositions in various physical forms containing phenolic bactericides were color- and odor-stabilized by adding minor amounts of azines, nonaromatic hydrazides, or hydrazonium salts of organic acids (Olin Mathieson Chemical Corporation, *Brit. 802,447*). Deterioration of odor can be retarded by using certain hydrazides, incorporated during any stage of manufacture (Unilever Ltd., *Brit. 795,674*). The many problems involving the perfuming of detergent products were reviewed (Fourman, *Soap Chem. Specialties*, 35[8], 43-45, 102-103). A fresh natural odor for toilet soap may be achieved by using 0.02 to 1.5% by weight of dihydroterpinyl acetate (Fiore, Kitchens, and Saunders, *U. S. 2,889,254*).

A soap composition contained germicidal amounts of the reaction product of silver chloride and ethylene thio-urea (Baldwin, *U. S. 2,864,768*). In contrast, the silver salt of an aromatic sulfonic acid has been used (Lutz and Sharpe, *U. S. 2,864,769*).

Addition of 10 to 20% quaternary ammonium compound to soaps prevented hard water precipitation and was apparently compatible (Aylesworth, *U. S. 2,861,955*). Soap may be protected from insoluble salt formation by using 1 part of a fatty acid-protein condensation product and about 3.5 parts of condensed sodium phosphates. All are kneaded to form a tablet (Chemische Fabrik Grunau Akt.-Ges., *Ger. 922,432*). Soaps may be formed in place by mixing 45% of yellow grease (containing at least 5% free fatty acids), 8 to 9% caustic soda, 25% of a 51% sodium silicate solution, and 21 to 22% water softeners such as phosphates, carbonates, and silicates. These are mixed and covered with the saponifiable material (Thurman, *U. S. 2,861,953*) ready for subsequent usage.

**SURFACTANTS.** The 25th anniversary of Dreff's introduction was acknowledged by a review of synthetic detergent developments in this country since that time (Anon., *Soap Chem. Specialties*, 34[9], 47-50, 121), and an attempt was made to visualize the future of synthetic detergents (Beach, *Soap Chem. Specialties*, 34[12], 49-52, 241). The history and prospects for growth of light-duty detergents were reviewed (Bright and McKenney, *Soap Chem. Specialties*, 35[1], 43-46, 107), as were anionic surfactants for either heavy-duty industrial (Davidson, *Soap Chem. Specialties*, 35[1], 47-48) or household usage (Tillotson, *Soap Chem. Specialties*, 35[2], 49-52, 169).

Surfactant usage in cosmetic formulations with good coverage of applicable properties and many recipes were examined by individual surfactant type: sulfated oils (Levy, *Am. Perf. Arom.*, 72[4], 67-68), polyhydric alcohol esters (Kreps and Starkman, *Am. Perf. Arom.*, 72[4], 73-75), alkylolamides (Lennon and Rosenbaum, *Am. Perf. Arom.*, 72[4], 76, 78-80), alkylbenzene sulfonates (Harris, *Am. Perf. Arom.*, 72[4], 62-64), and cationics (DuBrow, *Am. Perf. Arom.*, 72[4], 95-100). A broad review detailed the special requirements for surfactants in toiletries and personal products, including the important factor of toxicity. The amounts of surfactant used in several important product types were given (Longfellow, *Soap Chem. Specialties*, 35[2], 53-56, 101-103; [3], 60-63).

Shampoo formulation with soap and surfactants indicated that many hard water-stable blends may be used (Wells, *Soap Chem. Specialties*, 34[8], 39-42, 178; [9], 161, 163, 165, 207). A liquid shampoo formulation was patented, covering a major proportion of a higher fatty acid monoglyceride monosulfate and minor amounts of water-soluble hydroxypropyl methyl cellulose (Henkin, *U. S. 2,871,193*). A germicidal detergent was claimed for 0.36 parts per 100 parts of water of a mixture of 10 parts 5-chloro-2-hydroxydiphenylmethane in 59 parts isopropanol and 31 parts of an aqueous solution of 20% sodium secondary alkyl sulfate (Steward, *Brit. 806,791*).

**TOILET BARS.** Interest continues in toilet bars. This product is resistant to change but is gradually yielding to the addition of surfactant. This usage is said to represent one of the largest potential outlets for nonionic surfactants (McCutcheon, *Soap*, 49[9], 54-55, 111), but such compositions must meet a number of requirements which were reviewed (McCutcheon, *J. Soc. Cosmetic Chemists*, 9, 270-273). The surfactant bars are already the target for bacteriostats (Vicklund, *Soap Chem. Specialties*, 35[4], 56-57, 159) and other additives common to soap bars. For convenience the patents are listed by name of the assignee or patentee:

- Armour and Company, addition of "Tetronic" for some of coconut oil used (Armour and Company, *Brit. 799,279*)
- Colgate-Palmolive Company, hydratable inorganic salts on outer surfaces partially hydrated to increase briquette strength (Miles, *U. S. 2,875,155*)
- E. F. Drew and Company, reaction product of a hydroxyethylsulfonic acid salt with higher fatty acid (Barsky, *U. S. 2,886,585*)
- C. F. Dupuy, water-insoluble wax added to reduce slushing (Dupuy, *U. S. 2,858,569*)
- General Aniline and Film Corporation, fatty acid taurine or hydroxyalkane sulfonate (General Aniline and Film Corporation, *Brit. 799,909*)
- Thomas Hedley and Company Ltd., soap, solid anionic surfactant, and a binder of gelatinized nonwaxy starch (Thomas Hedley and Company Ltd., *Brit. 796,627*)
- Imperial Chemical Industries, bactericidal bars from alkylphenol nonionic and quaternary bactericidal compound (Imperial Chemical Industries, *Brit. 795,814*)
- Lever Brothers Company, fatty acid isethionates, alkylbenzene sulfonate, soap, and fatty acid as binder and plasticizer (Geitz, *U. S. 2,894,912*; Henderson and Carroll, *U. S. 2,868,731*)
- Unilever Ltd., fatty acylaminomethane sulfonates, potassium soap, and a plasticizer of fatty amide and/or lanolin (Harvey and Small, *Brit. 799,075*)
- United States of America,  $\alpha$ -sulfonated long-chain fatty acids (Weil, Storton, and Maurer, *U. S. 2,867,586*)

New equipment such as driers, amalgamators, and vacuum extrusion presses have made modern European toilet bar processing much more effective (Zilski, *Soap Chem. Specialties*, 34[5], 187, 189, 191, 193; [8], 137, 139, 141). The raw materials used in soap bars have received some attention. The color of the original fat, their fatty acids, and their soaps manufactured by using nonsplit fats and those split catalytically are about the same as the original fat (Zaliopo and Sharov, *Mastobno-Zhirovaya Prom.*, 24[6], 17-19). Soap quality was found to improve with hydrogenated fat with a decrease of iso-acids which promote the wax phase in soap while coconut oil additions do likewise. A relation between soap structure and X-ray data is evident (Kenigsberg, *Trudy Vsesoyuz. Nauch-Issledovatel. Inst. Zhirov.*, 1954[15], 190-201; Referat Zhur. Khim. 1956, Abstr. No. 41510). Dependence of intersurface intervals in crystalline soap lattice (X-ray) from its fat composition was determined. Hydrogenated whale oil was superior to hydrogenated cottonseed oil as a raw material though the former decreased plasticity and contributed to cracking and break-up of soap during usage, overcome to some extent by adding oleic and palmitic acids to the fat stock. Less than 15% of the *trans* isomers of hydrogenated oils could be used though 7% of coconut oil or 15% bone fat on the fat stock decreased defects caused by the *trans* isomers (Kenigsberg, *Trudy Vsesoyuz. Nauch-Issledovatel. Inst. Zhirov.*, 1954, No. 15, 190-201).

**MISCELLANEOUS.** A noncaking, easily soluble machine dish-washing composition was claimed by hydrating the silicate and condensed phosphate mixture before adding any chlorinated trisodium phosphate (Milenkevich and Henjum, *U. S. 2,895,916*).

Enhanced foaming and detergency of sulfated and sulfonated surfactants may be obtained by adding a higher fatty alcohol-ethylene oxide adduct to the composition (Massie, *Brit.*



808,805). Various amides also may enhance the sudsing characteristics of sulfated or sulfonated surfactant compositions (Thomas Hedley and Company Ltd., *Brit. 809,060*), as could mono-ethers of glycerol and monohydric aliphatic alcohols (Fowkes, Sawyer, and Schick, *U. S. 2,900,346*). Addition of an alkyl (10-16) ester of p-hydroxybenzoic acid to a  $C_{10-20}$  alkyl sulfate was said to improve lather (Ashford and Coskie, *Brit. 810,688*).

Bleaching compositions may be obtained by entraining sodium perborate in the porous structure of the granular detergent composition without gravitation separation (Strain, Eaton, and Ericson, *U. S. 2,876,200*), and improved bleaching action with perborate compositions was obtained by addition to the surfactant mixture of acetamide, formamide, or acrylamide (Dithmar and Hoffmann, *U. S. 2,898,181*).

Improved detergency was claimed for compositions of nonionic surfactants by the addition of ammonia or an organic amide and a builder such as the sodium salt of styrene-maleic anhydride copolymer known as Stymer S (Feldmann, *U. S. 2,876,201*). Storage stability, uniformity, nonseparability, caking inhibition, and density-controlled products are desired for package distribution. A nonionic-builder composition remained dry by adding silicon dioxide to the cooled powder (Degussa G.m.b.H., *Brit. 807,640*). Reduction in separation and improvement in uniformity was obtained by adding a small amount of soap to a nonionic-builder mixture before spray-drying (Unilever Ltd., *Brit. 799,421*). Reduction in foaming of a slurry of anionic surfactant-builder mixtures to give a high-density spray-dried product was achieved by adding certain nonionic surfactants (Thomas Hedley and Company Ltd., *Brit. 812,249*). The caking tendencies of sodium alkylbenzene sulfonates may be reduced or eliminated by adding 3 to 5% by weight of boric acid (Lewis, *U. S. 2,875,154*). A free-flowing anionic surfactant composition may be obtained by using Form II tripolyphosphate which, when added to a slurry containing only sufficient moisture to make it pumpable, also minimized polyphosphate reversion (McNaught and Bryant, *U. S. 2,897,155*).

Colored compositions may be produced by using a finely subdivided dye or pigment (Lumsden and Milner, *Brit. 801,018*) or colored detergents which leave no color effect on the fabric are prepared by adding peroxygen compounds and a dye decolorized by them in normal detergent usage (Henkel et Cie. G.m.b.H., *Brit. 811,028*).

The skin-irritating properties of alkyl sulfates or alkylbenzene sulfonates were lessened by adding minor proportions of salts of sulfated fatty alcohol-ethylene oxide (or propylene oxide) products (Thomas Hedley and Company Ltd., *Brit. 797,119*). The addition of at least 0.1% of succinic acid or its salts reduced the skin irritation of mixtures of alkylbenzene sulfonates and higher alkylphenyl ethers of polyethylene glycol (Dvorkovitz, Berst, and Leist, *U. S. 2,878,190*).

Cellulose ethers treated with a mineral-oil sulfonate formed solid, stable, and easily used products (Schlack, *Ger. 949,236*). Alkylaryl sulfonates, alkyl sulfonates, and sulfates had improved detergency and whiteness-retention properties when promoted by NaCMC and a soluble hydroxyalkyl cellulose (Bacon, Smith, and Vaughn, *U. S. 2,886,533*).

Alkali carbonates, because they are said to be synergistic to alkali silicates, were believed superior to alkali pyrophosphates when used in combination with one or more surfactants, fatty alkylolamides, polyphosphates, and silicates (Société Belge de l'azote et des produits chimiques du Marly S. A. and Société carbochimique S. A., *Belg. 564,082*). Tripolyphosphate compositions containing from 10 to 20% of an alkali metal carbonate gave reduced tarnishing of German silver when 2-mercaptothiazoline and tallow methyl tauride (Ruff, *U. S. 2,870,092*) or the thiazoline and coco- $\beta$ -alanine (Ruff, *U. S. 2,870,093*) were used as synergistic tarnish-inhibitors.

Calcium sequestrant compositions were corrosion- and tarnish-inhibited when a phosphated alkyl ( $C_{11-18}$ ) glyceryl ether was added to tripolyphosphate or ethylene diamine tetraacetate and an anionic nonsoap surfactant (McCune, *U. S. 2,892,796*). The addition of an aluminum salt to an alkylbenzene sulfonate-built composition rendered it stable to hard water (Raecke, *Ger. 945,945*).

A pH-controlled product of surfactant (not soap), alkali metal phosphate, and MgO, may be prepared when the powdered MgO is coated with cetyl alcohol (Henkel-Helios, *Brit. 810,151*).

## CHEMICAL ANALYSIS

One extensive review of analytical procedures was made (Smith, *Analyst*, 84, 77-89) in which surfactants were classified as to hydrophobic, hydrophilic, and linking groups. The Ger-

man and U. S. standard procedures for the analysis of petroleum sulfonates were also reviewed (Maass, Buchspiess-Paulentz, and Stinsky, *Seifen-Ole-Fette-Wachse*, 54, 575-578).

Ion exchange as an analytical tool received much attention. An improved saponification number procedure was devised, using a nonaqueous medium and a cation exchanger. The endpoint was much sharper, precautionary measures for carbon dioxide absorption were unnecessary, and information on the nature of the organic acids could be made available (Swann, Zahner, and Milner, *Anal. Chem.*, 30, 1830-1833). Separation of nonionic from anionic surfactants by a columnar, mixed bed ion exchange procedure, followed by elution of anionic surfactant, was applicable to all but acid-cleaved products (Ginn and Church, *Anal. Chem.*, 31, 551-555). Separation of anionic from nonionic products can be achieved by a three-phase ion exchange procedure. The anionic acids are determined potentiometrically, and the nonionic surfactants gravimetrically (Voogt, *Rec. trav. chim.*, 77, 889-901). Separation of nonionic from anionic or cationic surfactants was found possible by ion exchange; the nonionic material was determined gravimetrically from the effluent (Kurata and Inoue, *Yukagaku*, 6, 92-6). Silicic acid was used as an adsorbent for an alkylphenol polyoxyethylene surfactant; the elution curve shape indicated isolation of very pure species (Kelly and Greenwald, *J. Phys. Chem.*, 62, 1096-1098). Separation and determination of alkyl sulfate and fatty acid-alkanolamine condensates in shampoos may be achieved by an ion exchange technique (Newburger, *J. Assoc. Offic. Agr. Chemists*, 41, 664-668).

The assay of alkylbenzene sulfonates in raw water supplies is important, and methods of detection and determination were reviewed (Vaughn, *J. Am. Water Works Assoc.*, 50, 1343-1352). Colorimetric procedures for detection of alkyl sulfates continued of interest, and o-tolidine in buffered systems was used (Graham and Whitney, *Anal. Chem.*, 31, 1673-1676).

A control technique for analysis of sodium tripolyphosphate by reverse flow ion exchange offered rapid, complete recovery of each species of phosphate present (Kolloff, *ASTM Bull. No. 237*, TP 94-100). A modification of downward-flow paper-chromatographic technique to increase accuracy and precision was made by running at 4°C. and using an ascending solvent system (Smith, *Anal. Chem.*, 31, 1023-1025). Another modification of the paper-chromatographic procedure by using a modified acid solvent, and spot measurement by a densitometer was said to be both rapid and accurate (Bernhart and Chess, *Anal. Chem.*, 31, 1026-1028).

Mixtures of nonionic with cationic surfactants may be analyzed by a combination of the ferrieyanide and bromphenol blue or the ferrieyanide and Epton procedures (Kurata and Inoue, *Yukagaku*, 6, 96-100). A variety of surfactants and their analytical control methods was reviewed (Gushee and Scherr, *Ind. Eng. Chem.*, 51, 798-804).

A procedure for the estimation of either hexachlorophene or bithional in soaps was described (van der Pol, *Pharm. Weekblad*, 93, 881-886).

Absorptiometric determination of alkylaryl sulfonates by an ultraviolet method was described (Kelley, Blank, Fine, and Thompson, *ASTM Bull. No. 237*, TP 90-3) while an infrared procedure applicable to the barium salts of 10 organic sulfates and sulfonates promised a means for their identification (Jenkins and Kellenbach, *Anal. Chem.*, 31, 1056-1059).

## PHYSICAL CHARACTERISTICS

The electrical conductivity characteristics of sodium stearate-water-sodium chloride systems were investigated, showing, in the transition from sol to gel, a characteristic hysteresis and deviation from additive conductivity. These lead to the conclusion that the primary effect of NaCl is reduction of the degree of dispersion of the systems by diminution of the specific charge of the micelles. Electrolyte effect was minor at high temperatures but very pronounced in the sol-gel transition area (Angelescu and Radu, *Acad. rep. populare Romine, Studii cercetari chim.*, 6, 403-415). The specific conductivity of the system water-soap-butanol in the presence of free acids and alkalies was increased with the increase in NaOH concentration and decreased with the increase in butanol (Bose and Mehrota, *Kolloid Z.*, 163, 15-17). The surface-tension characteristics of soap-cresol-water systems were investigated. Increasing temperature caused an increase in the surface tension of sodium soap solutions and a decrease with potassium soaps. With over 2% cresol, surface tension increased with increases of cresol up to 7%, minimum surface tension occurring with 1.0% cresol addition, and a specific isomer effect was noted. It was assumed that cresol addition caused both a dispersion and

solvation of the soap particles. Cresol penetrated the oriented hydrocarbon chains to form a compound with the soap carboxy group (Angelescu and Davidescu, *Kolloid Z.*, 163, 132-136; *Kolloid Z.*, 158, 135-144). A dilute soap solution formed a two-component system of solution and micelles; the solid phases were crystals and ice. An "invariant point," i.e., a temperature, not dependent on concentration, at which both crystals and micelles were present together, was determined for two quaternary surfactants by fluorescence measurements after adding a fluorescent dye of opposite charge. The effect of salts on these points was noted (Nash, *Chem. and Ind.*, 1958, 590).

The fine structure of sodium laurate as investigated by high-resolution electron microscopy and electron diffraction showed that soap fibers differ from soap crystals, agreeing generally with that proposed by Bondi (Shuttleworth and Camp, *Nature*, 183, 535-536). Soap crystal structure was discussed as a factor of chain-packing arrangements (Segerman, *Norelco Repr.*, 5, 84-85, 94).

The adsorption of sodium alkyl sulfates and sodium oleate on various textile fibers passed through a maximum, and sometimes subsequently a minimum, as the concentration of surface-active material in the aqueous phase was increased. The transverse swelling of single fibers, constant in dilute solutions of surface-active compound, decreased at the concentration corresponding to maximum absorption. The shape of the adsorption/concentration graph can be explained on the basis of absorption of single ions on a changing surface, and this hypothesis could also explain the dialysis of surface-active compounds. The effects of alkali and inorganic electrolyte on the adsorption isotherms were also discussed (Evans, *J. Colloid Sci.*, 13, 537-552).

Adsorbed layers of soap were studied; it was possible to obtain foams whose chemical composition was independent of composition of the foam solution (Raison, *Rev. Franç. Corps Gras*, 6, 207-223).

Reaction between nonionic polymers and anionic surfactants in water was studied with an oil-soluble dye, using a solubilization technique. Solubilization occurred by solubilization inclusion sites surrounded by dehydrated polymer and surfactant, the degree of synergism depending upon degree of polymerization (Saito, *Kolloid-Z.*, 158, 120-130).

The solubility of calcium soaps was studied by using radio-tagged  $\text{Ca}^{45}$ . Equilibration of the insoluble soaps with water made marked changes in the X-ray diffraction patterns, indicating true hydration of the crystal. The solid phase in equilibrium with the saturated solution was monohydrated (Yoke, *J. Phys. Chem.*, 62, 753-755).

Fatty acids and  $\eta$ -alkanols heated with solutions of various soaps exhibited transition to a liquid crystal at a sharply defined temperature, depending upon the nature of the soap but insensitive to concentration. Phase diagrams were developed (Lawrence, *Discussions Faraday Soc.*, 25, 51-58).

The critical surface tensions (tensions at which surface wetting occurs) for polyethylene and Teflon were tested, using the contact angle method and solutions of anionic, cationic, and nonionic surfactants. Aqueous solution of surface tension lower than 30 dynes/cm. spread on polyethylene, but none would spread on Teflon. This criterion was concluded as an excellent index of wetting ability (Gernett and Zisman, *J. Phys. Chem.*, 63, 1241-1246). Penetration of surfactant solution into filter paper obeyed the Kozeny-Carman equation (Nakasima and Nakao, *Nippon Kagaku Zasshi*, 78, 594-597).

A comparison of the physical and chemical properties of sucrose esters with those of other surfactants was made (Pilpel, *Research*, 12, 68-74). The characteristics of cationics are a positive attraction to negatively charged surfaces. The surface then is altered to reflect the characteristics of the substituent group about the nitrogen atom, contributing hydrophobicity and other properties (DuBrow, *Soap Chem. Specialties*, 34[8], 45-47, 91).

The physicochemical properties of soaps and their solutions were reviewed (Perron, *Parfums, cosmet., savons*, 1, 308-317). The dependence of hydrolytic stability of sodium lauryl sulfate upon maintenance of a pH above 5 was emphasized (Read and Fredell, *Drug and Cosmetic Ind.*, 84, 178, 256-257).

Sodium dodecyl sulfate killed gram-negative and gram-positive organisms only in the presence of a respiratory poison (e.g., KCN). The surfactant solution extracted the lipoproteins from the cell walls of *E. coli*. Specific activity with other organisms was noted (Bolle and Kellenberger, *Pharm. Acta Helv.*, 33, 379-380).

An abundance of foam, or its control continues important. Low or depressed sudsing action was achieved by combining with at least an equal weight of alkali metal polyphosphate a

suds-depressant mixture of at least three compounds with acyl radicals differing from 16 to 3 in carbon atom content as saturated fatty acids, the mixture containing more than 50% of compounds having at least 16 carbon atoms and at least 5% of those having at least 20 carbon atoms (Thomas Hedley and Company Ltd., *Brit. 802,302*). As a suds depressant for an anionic surfactant and alkali metal polyphosphate, a mixture of fatty acids and/or their alkali metals was used in combination with a nonionic, such as alkylphenol and propylene oxide and ethylene diamine (Thomas Hedley and Company Ltd., *Brit. 808,945*). High-foaming phenoxyethoxyethanol was converted to a low-foaming, more versatile surfactant by reaction at high temperatures with acidic catalysts, such as strongly acidic cation-exchange resins and acid-treated clays (Lane, *U. S. 2,850,535*). A higher aliphatic alcohol was used to control the foam of the polyalkylene oxide condensate of alkylphenols and higher monohydric aliphatic alcohols (Buch, *U. S. 2,855,367*). A higher aliphatic alcohol of from 12 to 20 carbon atoms was used as a foam depressant in a ratio of about 25:1 to 4:1 by weight of a nonionic polyoxyethylene condensate (Vitale, *U. S. 2,867,585*).

Lather improvement has received greater emphasis. More persistent surfactant compositions may be made by the addition of N-tris-(hydroxymethyl)-methylamides of several fatty acids (Unilever Ltd., *Brit. 800,710*). Palmitic alkanolamide in from 2 to 10% by composition weight overcame the destructive action of bleach on the sudsing of formulated detergents containing N-substituted  $\beta$ -amino propionates or  $\alpha$ -amino acetates (Ruff and Thornton, *U. S. 2,880,178*). Spray-dried surfactant compositions may have the persistence of their lather increased by adding certain 2-( $\text{C}_{10-15}$ )alkyl-4,4-bis(hydroxymethyl)oxazolines to the slurry before drying (Unilever Ltd., *Brit. 800,291*). Organic sulfate detergent lather may be improved by adding a fatty acid amide and a straight chain  $\text{C}_{10-14}$  saturated p-acyl phenol or a mono-ethylene glycol or diethylene glycol ether of phenol (Stayner, *U. S. 2,863,836*). Monoalkyl  $\text{C}_{10-15}$  benzene sulfonate foam was improved by the addition of 2 to 20% of a N-acyl sulfanilate and 2 to 20% of a saturated aliphatic alcohol or 1,2-glycol (Lew and Stayner, *U. S. 2,874,127*). The foam of N-acyl taurate solutions was improved by 1 to 5% of a  $\text{C}_{12-18}$  saturated normal alcohol (Lew, *U. S. 2,874,125*). Anionic or nonionic light-duty detergent foam was improved by adding  $\beta, \beta'$ -decylaminobisethanolpropionamide (Henderson and Schramm, *U. S. 2,877,187*). A liquid composition had maximum lather when the ammonium salt of the sulfated coconut fatty alcohol had been reacted with 2 to 4 moles of ethylene oxide (Thomas Hedley and Company Ltd., *Brit. 791,704*). Pelargonic diethanolamide added to compositions containing large amounts of inorganic builders, fatty alkanolamides, fatty acid amide detergent, and cocodithanolamide, caused the inorganic builders to remain in solution (Tomlinson, *U. S. 2,870,091*). An abundantly foaming liquid detergent was obtained by using low-molecular-weight alcohol, water, and the salt of a sulfated  $\text{C}_{10-12}$  alcohol-ethylene oxide (1- to 5-mole) condensate (Fernandez, *U. S. 2,861,956*).

A detergent gel was developed by using a water-soluble soap and a liquid polyoxyalkylene condensate in a 4:1 to 1:1 ratio; the total weight was 40 to 60%, the balance water (Dalton, *U. S. 2,875,153*).

The critical micelle concentration (cmc) of surfactants continues under study. Complexes of anionic and cationic materials vary in apparent value as a function of dye concentration (Kondo, *Nippon Kagaku Zasshi*, 78, 1093-1096) while the spectral dye procedure for estimation was shown as being affected by co-solubilization of neutral oil in alkylbenzene sulfonate solutions (Ginn and Harris, *J. Phys. Chem.*, 62, 1554-1557). Methods for measurement not affected by this phenomenon were preferred.

Dimerization of lauryl sulfate ions to form  $\text{LS}^2$  occurred reversibly. It also formed, reversibly again, ion pairs with quaternary ammonium compounds such as (n-propyl) $_4$ NLS. Both reactions were explained on the basis of interfacial energy reduction as the hydrocarbon portions of the two ions amalgamated. Dimerization was shown as a rather general phenomenon in solutions of amphiphathic ions, helping to correlate a number of previously unexplained observations (Mukerjee, Mysels, and Dulin, *J. Phys. Chem.*, 62, 1390-1408). Membrane electrodes were used to determine the activity of counterions in aqueous surfactant solutions and for cmc determination. The degree of association between micelles and counterions determined from experimental activity coefficients indicated that the strong electrostatic field of the charged micelles tended to bind a large fraction of counterions (Botre, Crescenze, and Mele, *J. Phys. Chem.*, 63, 650-653). An in-

vestigation of nonionic surfactants showed that as the hydrophilic portion of the molecule was increased, cmc was increased and the number of molecules in the micelle decreased. These changes were explained as due to the increase in the free energy of the hydrophil portion and the decrease in lowering of interface free energy between hydrocarbon and water (Nakagawa, Kuriyama, and Tori, *Nippon Kagaku Zasshi*, 78, 1573-1577; Nakagawa and Kuriyama, *Nippon Kagaku Zasshi*, 78, 1568-1573).

Mixed solutions of sodium lauryl sulfate and polyoxyethylene lauryl ether contained only one kind of mixed micelles of a low degree of dispersion. At lower concentrations of the ionic surfactant in the mixture, the charge and *zeta* potential of the micelles, and the association number of the ionic surfactant constituent in the micelles decreased while the radius and amount of micelles and the association number of the nonionic substituent of the micelles increased (Nakagawa and Inoue, *Nippon Kagaku Zasshi*, 78, 636-640). Ethanol and ethylene glycol lowered the cmc of sodium oleate solutions (Yurzenko and Storozh, *Kolloid Zhur.*, 20, 550-555). The octyl glycol ether,  $\alpha$ -octyl glyceryl ether, and octyl glucoside gave surface activity and/or cmc values similar to those of ionic surfactants containing the undecyl or dodecyl group as the hydrophobe (Shinoda, Yamanaka, and Kinoshita, *J. Phys. Chem.*, 63, 648-650). Adsorption on sand of an ethylene oxide-propylene glycol-propylene oxide surfactant increased with an increase in concentration while a maximum was reached with an alkyl-aryl polyether alcohol. Since the propylene glycol product exhibited little micelle formation to compete with adsorption process, adsorption continued with concentration increase (Bell, *J. Phys. Chem.*, 63, 299-300). Solubilization as a function of micelle formation was reviewed (Ruyssen, *Chem. Weekblad*, 54, 681-686).

Recommendations were made of detergents to be used for general military hygiene, types of fabrics, and disinfection following chemical, bacterial, and atomic warfare (Kiger, *Rev. corps sante militaire*, 14, 5-62). Metal salts of lauryl sulfate, dioctyl sulfosuccinate, and isopropyl naphthalene sulfonate were tested as antifungants and bactericides (Bone and O'Day, *J. Am. Pharm. Assoc.*, 47, 795-799).

An apparent increase in eczematous dermatitis of the hands of females was noted, but evidence was lacking to attribute this to the new detergent products (Ferguson and Rothman, *A.M.A. Arch. Dermatol.*, 80, 300-310).

Surfactants were used in the textile industry to improve several aspects of viscose manufacture (Alexander and Cross, *Ind. Eng. Chem.*, 51, 535-538), fatty alkylolamides were preferred over polyethylene oxide nonionics for wool scouring because of the greater ease of waste liquor clarification (Fong, *Am. Dyestuff Reprtr.*, 48, 45-50), while protection of wool fiber in the carbonizing bath was highest with alkyl or aryl hydrocarbon nonionics and certain cations, and polypropylene nonionics and anionics were not as effective (Crewther and Pressley, *Textile Research J.*, 29, 482-486). Detergents were shown as effective in textile bleaching (Ward, *Textile Weekly*, 59, 469-470, 473, 534-536).

Water softening improved both soap and syndet usage (Aultman and Montgomery, *J. Am. Water Works Assoc.*, 50, 1353-1364), and sequestration of calcium was demonstrated as effective at low cost by oxidation products of dextrose hydrate and corn starch (Mehlretter and Watson, *Soap Chem. Specialties*, 35 [8], 49-50, 106).

Described were cationic applications (Campbell, *Soap*, 49, [9], 59-60), ampholytes for a variety of uses (Bass, *Mfg. Chemist*, 30, 105-106), surfactants in the petroleum industry (Yamamoto, *Yukagaku*, 7, 125-128), and a high-expansion foam formed over a cotton net useful in control of coal mine fires, lauryl sulfate being superior to other agents (Hartmann, Nagy, Barnes and Murphy, *U. S. Bur. Mines, Rept. Invest.* 5419, 18 pp.).

A comparison of the endogenous oxygen uptake in sewage-seeded B.O.D. dilution water showed an increase for higher fatty acid sucrose esters and almost no uptake for tetrapropylenebenzene sulfonate (Issac and Jenkins, *Chem. & Ind.*, 1958, 976-977).

### Surfactant Reviews

A number of reviews of the various surfactant types were made during the year. A general review of classification, preparation and properties of various surfactants appeared (Gantz, *Am. Perf. Arom.*, 72 [4], 43-48, 50-52). Several reviews of ampholytic surfactants were published (Mannheimer, *Am. Perf. Arom.*, 72 [4], 69-70, 72; Mannheimer, *Soap* 49 [9], 56-58, 206; Andersen, *Am. Perf. Arom.*, 72 [4], 59-60; Bass, *Mfg.*

*Chemist*, 30, 105-106). Known methods for synthesis of cationic products were reviewed (Naumenko and Khaskin, *Maslo-boino-Zhirovaia Prom.*, 25 [1], 33-35). Anionics from the petroleum industry were examined (Koga, *Yukagaku*, 7, 327-331) as were fatty-based products (Woodward, *Soap Chem. Specialties*, 35 [4], 53-55, 60), and aliphatic alkyl sulfates (Goette and Meinhard, *Am. Perf. Arom.*, 72 [4], 90-94). Non-ionic surfactants were considered under the following headings: sucrose esters, Rhodes, *Chem. Prods.*, 21, 320-323), fatty acid amido derivatives (Zussman, *Soap Chem. Specialties*, 35 [4], 51-52, 102-103), alkyl-phenols and -mercaptans (Mayhew and Cloney, *Am. Perf. Arom.*, 72 [4], 83-84, 86, 88) block polymers (propylene and ethylene oxide surfactants) (Stanton, *Am. Perf. Arom.*, 72 [4], 54, 56, 58), and fatty acid esters and ethers (Milling, *Am. Perf. Arom.*, 72 [4], 39-42).

### PERFORMANCE AND USE TESTING

A critical study of photometric measuring apparatus was made, and a color measure of detergent powders and of their action in linen whitening was given as a practical example of their action (Jacquain, *Ind. chim. Belge*, 24, 605-618). Various applications for the radio-tracer technique in detergency studies were outlined (Wagg and Britt, *Perfumery Essent. Oil Record*, 50, 609-610). Screening of skin degerming agents, while usually made with hand-washing tests, may also be tested for actual effectiveness on rabbit skins and on the cheeks (Rubenkoenig and Majors, *Am. Perfumer Essent. Oil Rev.*, 74 [1], 34-36).

Detergency comparison based upon three laundry machines, and the ability to remove fat from glass and metal by gravimetric measurement showed that, of six commercial detergents, lauryl sulfate performed best and that metaphosphate was superior to other inorganic materials (Weder, *Textile Rundschau* 13, 637-642). The detergency of sodium laurate was found similar to that of sodium myristate. The addition of the oleate to other saturated soaps had the effect of decreasing the carbon chain length (Hayashi, Fuchizawa, and Namba, *Yukagaku*, 6, 208-213). A comparison of a film-testing apparatus with the Launder-Ometer was made, and detergent properties were evaluated irrespective of soils, fabrics, stirring, temperature, rinsing, bleaching agents, or optical dyes (Vallee, *Teintex*, 23, 321-336). The "energetics" of washing and washing agents was developed, using comparative cleaning, whiteness, and textile influence (Walter, *Fette, Seifen, und Anstrichmittel*, 59, 966-972). Observation of removal of oily soil from a variety of fibers by solution impingement was followed, using a microscope (Harker, *J. Textile Inst.*, 50, T 189-222).

For a series of saturated  $C_{10-18}$  alkyl sulfates, detergency was better correlated with dispersibility, emulsifying power, solubilization, and redeposition prevention than with surface and interface activity. Increase in alkyl chain length improved the former properties. The latter showed a maximum at  $C_{14}$  (Hayashi, Yamamoto, Fuchizawa, and Namba, *Yukagaku*, 6, 213-217). Detergent efficiency of *p*- $\eta$ -alkylbenzene sulfonates increased up to 18 carbon atoms (Kolbel and Kuhn, *Angew. Chem.*, 71, 211) while passage from the *p*-dihexyl to the *p*-dioctylbenzene sulfonate raised the surface tension and lowered detergency by formation of insoluble calcium salts, but detergency may be raised by using branched-chain alkyl groups. Dialkyl substituents in general are less effective than monoalkyl groups of equivalent carbon chain length (Nevolin, Nikichin, Petrov, Kral-Osinkina, and Vorobiev, *Parfums, cosmét.*, savons, 2, 62-66).

Better foaming and detergency was found for sulfated monoglycerides prepared from  $C_{12-13}$  and  $C_{14-15}$  fatty acid fractions than the surfactant made from lauric acid (Jedliński and Hampel, *Przemysl. Chem.*, 12 [35], 47-51).

Correlations were obtained which indicated that in a detergent system it is desirable that the *zeta* potential of both the soil and substrate become nearly equal to reduce the attractive forces causing adherence. Correlations also exist between *zeta* potential and suspension values, critical micelle concentration, and detergency values (Harris, *Textile Research J.*, 28, 912-928). Further attempts were made to correlate surfactant adsorption in the detergency process with critical micelle concentration, *zeta* potential, and other factors (Harris, *Soap Chem. Specialties*, 34 [11], 40-43, 101; [12], 59-62, 233; 35 [1], 49-52, 108-110; [2], 57-58, 103). In oily soil removal from various fibers it was observed that the more polar the fiber, the more easily oily soil was removed while addition of polar substances to nonpolar soil made it more easily removed (Harker, *J. Textile Inst.*, 50, T 189-222).

The ideal cotton detergent was described as containing both a surfactant and a highly efficient hard water ion sequesterant. The surfactant should have moderate surface-activity (wetting and emulsifying powers), have a hydrophobe length as large as possible commensurate with surface properties, and be anionic (Stayner, *Soap Chem. Specialties*, 35 [5], 64-65, 264-265). Suspending action in detergent solutions may be affected by these factors: mechanical, chemical, and electrical forces, adsorption of surfactant, sedimentation, deflocculation, soil particle size, solvation, and others of lesser potential. A redeposition preventative such as NaCMC was interpreted as acting by adsorption on the cellulose substrate (Harris, *Textile Research J.*, 29, 99-118).

Adsorption of carbon on wool, cotton, and Perlon in tetrachloro-ethylene depended on the moisture in the system, but desorption was little influenced by moisture changes. Surfactant choice may markedly affect soil adsorption or desorption (Wendell, *Kolloid Z.*, 163, 11-15).

The prevention of soil redeposition during the cleansing process, reduction in the retentivity of soil once deposited, and increased ease of soil removal once deposited can be important factors in improved cleansing. A significant series of conclusions concerning surfactants and additives on knitted fabrics follows (Johnston *et al.*, *Am. Dyestuff Repr.*, 47, 933-940): a) surfactants, particularly nonionics, tend to decrease dry-soiling resistance of most fibers; b) colloidal silica, of finishes tested, significantly improved the soil resistance of all fibers except Daeron; c) additives, in general, reduced Daeron's soil resistance; d) most additives had little effect on soil removal during washing. Soil redeposition on cotton during the wash cycle was studied (Stawitz and Hopfner, *Seifen-Ole-Fette-Wachse*, 84, 711-713) as a function of time, with and without NaCMC. Redeposition began simultaneously with removal and continued at the same rate through rinsing. Addition of NaCMC reduced the redeposition rate. Resoiling of swatches following each wash was resorted to, to demonstrate the effect

of NaCMC on redeposition. NaCMC addition to sodium dodecylbenzene sulfonate alone or in combination with soap reduced redeposition probably through a protective coating to weaken the additive forces of soil to film (Szmidtgal, *Fette, Seifen, und Anstrichmittel*, 60, 1132-1139). The suspending and soil removing power of NaCMC was affected by water hardness. Combination with low soap concentrations was most effective (Nieuwenhuis and Tan, *Teintex*, 23, 629-648).

Considerable controversy has existed over the mechanism of NaCMC action. Carbon-14 radiotagged NaCMC was found (Hensley and Luks, *Textile Research J.*, 29, 505-513) to be adsorbed on cotton; the adsorption increased with excess cation concentration and valency. In excess cation concentration and equilibrium adsorption, a zero temperature coefficient was found. Limited measurements with wool, Orion, or acetate showed no adsorption; significant adsorption was found with nylon or rayon, but such adsorption was greatly reduced by addition of alkylaryl sulfonate. Significant soil redeposition preventative action was found for NaCMC adsorbed on cotton. A monomolecular layer of NaCMC on cotton may be of the order of 400-500 micrograms per gram of cotton. Comparison with sulfated pulp showed that NaCMC was superior in preserving color whiteness of cotton or staple fiber fabrics (Nevolin, Kari-Osikina, and Orekhova, *Masloboino-Zhirovaya Prom.*, 25 [1], 25-27) for longer periods of time.

Other materials were recommended to prevent soil redeposition. One was a 200 molecular weight polyvinyl oxazolidone (Vitalis, *U. S. 2,874,124*). In addition to preventing redeposition, polyvinyl pyrrolidone (PVP) is said to reduce skin irritation and the sensitizing effect of chlorinated phenols in germicidal soaps (Azorlosa, *Soap Chem. Specialties*, 35 [8], 51-54, 173). Redeposition in drycleaning systems is a serious problem, and certain solvent-soluble long-chain fatty acid salts, surfactants, oil and petroleum additives, and diphenylamine reduced soil redeposition on wool (Wagg, *J. Textile Inst.*, 49, T 561-T 565).

## Report of Cellulose Yield Committee, 1959-60

**D**URING the past season, 1959-60, three sets of three samples of linters were sent out to nine laboratories equipped to run these analyses. The following table gives the average results for the three tests:

Lab. No.	No. of tests	A Linter	B Linter	C Linter	Over-all avg. for the year
1	3	77.5	75.0	69.5	74.0
2	3	78.1	75.3	69.8	74.4
3	3	77.7	75.1	69.4	74.1
4	3	78.3	75.7	69.8	74.6
5	3	78.1	75.4	69.7	74.4
6	3	78.0	75.4	69.8	74.4
7	3	77.7	75.1	69.3	74.0
8	3	78.0	74.7	69.0	73.9
9	3	78.0	75.4	69.9	74.4
		77.9	75.2	69.6	74.2

As seen from the above table, good checks were obtained during the year. On a few occasions maybe one of the laboratories was off the average but was quickly brought back into line by these regular samples which were sent out for yield analysis.

This ends 23 years of service for the committee without any serious complaint in regard to cellulose yield. No changes are recommended for the method at this time. It is recommended that samples be sent out at least three times during the next year to check laboratory equipment.

E. H. TENENT	W. S. HUDE
W. J. JOHNSON	T. C. LAW
R. E. KNIPPLE	R. C. POPE
P. D. CRETEN	L. N. ROGERS, chairman