

Report of the Literature Review Committee

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

V. MAHADEVAN, University of Minnesota, The Hormel Institute, Austin, Minnesota

INTRODUCTION

As in previous years, this review of the 1963 literature was compiled from current, original publications and from abstracts of publications that were not available in the original. The review attempts to embrace all phases of fats and oils ranging from technology to metabolism and provide a unified source of reference for anyone engaged in any phase of work or study connected with fats and oils.

The outlook for fats and oils seems bright. New research findings and processing techniques have created a wide diversity of products and new markets for fats. The usage of fats in feeds can be expected to increase and competition between animal and vegetable fats for this market is keen. Extensive research work and legislation requiring biodegradable detergents may open new usage potentials for derivatives of natural fats and oils as against petroleum based detergents. The application of physical methods of analysis to problems in lipid chemistry has sharpened the interest in the chemistry and biochemistry of lipids.

SOAPS, SURFACTANTS, AND DETERGENTS MANUFACTURE AND PROCESSES

SULFONATION. A method for sulfonation of mineral oils using gaseous sulfur trioxide was used and widely recommended (Kalashnikov et al., *Novosti Neft. i Gaz. Tekhn. Neftepererabotka i Neftkhem.* No. 6, 11). Sulfur trioxide vapors in air were passed over tetrapropylbenzene. The products so obtained were superior to those obtained by sulfonation in petroleum ether or dichloroethylene (Niewiadomski et al., *Tuszcze i Srodki Piorace* 5, 369). Alkylaromatics such as dodecyltoluene were sulfonated with sulfur trioxide diluted in an inert gas (Bloch and Mammen, *Ger.* 1,152,099). Tetrapropylbenzene and other reactive products were sulfonated with sulfur trioxide in dry air (Colgate-Palmolive Co., *Belg.* 617, 968). Alkylbenzene was sulfonated with sulfur trioxide (Brooks and Brooks, *U.S.* 3,069,243). Various compounds including ethoxylated derivatives are sulfonated with sulfur trioxide in dry air (Sipon Products Ltd., *Fr.* 1,293,265). Polyphosphoric acids were added to alkylarene products during sulfonation with sulfur trioxide (Mammen, *Ger.* 1,126,361). Sulfonation of the distillate from thermal cracking of a petroleum residue was accomplished with sulfur trioxide (Ashimov et al., *Azerb. Neft. Khoz.* 41(9), 37). Fatty acids or esters were successfully sulfonated with sulfur trioxide and dry air (Henkel and Cie. *Belg.* 621,137). Sulfur trioxide with dry air was used for sulfonating fatty acid-polyhydric alcohol esters (Henkel and Cie. *Belg.* 621,140).

Sulfo chlorination with a mixture of Cl and SO₂ was used in preparing alkanesulfonates (Gershenovich et al., *Khim. Prom.* 1962(10), 701). Side reactions occurring during sulfonation were examined and the operation optimized for fatty alcohol sulfates (Varlamov and Ivanova, *Maslob.-Zhir. Prom.* 12, 19). Various fatty alcohols were chlorosulfonated satisfactorily (Brooks and Brooks, *U.S.* 3,069,243). An extensive review of sulfonation appeared (Knaggs and Nussbaum, *Soap Chem. Specialties* 38(5), 237; (6), 165; (7), 145).

SAPONIFICATION. Theoretical principles of continuous soap manufacture include two-stage saponification, first with soda ash, then with caustic soda (Bespyatov, *Obmen Opytom po Nepreryvnomu Proizv. Myla, Gos. Nauchn.-Issled. Inst. Nauchn. i Tekhn.-Inform.* 1962, 11). The major use of computer control in continuous soap making is calculation of the various amt of raw materials required (Anon. *Chem. Eng.* 69(21), 152). Removal of carbon dioxide to complete saponification is achieved in a gas separation, followed by caustic soda introduction (Baikov et al., *USSR* 152,530, addition to 113,241). Soap phase low in water is obtained by continuous counter current extraction (Leuring, *Ger.* 1,148,686). Soap from oxi-

dized tallow causing color is partially decolorized by salt water washing (Lechartier, *Rev. Franc. Corps Gras* 10, 19). Rancidity in toilet soaps was reviewed (Thom, *Tuszcze i Srodki Piorace* 6(2), 85), and antioxidants to prevent rancidity of tallow soap were tested (Houdouin and Loury, *Rev. Franc. Corps Gras.* 9, 532). The cause and prevention of rancidity was reviewed (Soloman, *Ibid.* 10, 49). Refining of cottonseed oil with soda ash and utilization of the refining foots for soap making was reviewed (Bestraten, *Lipidos* 22, 98). Described was a machine for stamping and cutting soap (Pronin, *Maslob.-Zhir. Prom.* 12, 29).

MISCELLANEOUS PROCESSES. Alkyl sulfates and alkyl sulfonic acid esters were obtained by hydrogenation of mineral oil fractions followed by chlorosulfonation in the presence of light (Farbenfabriken Bayer A.-G. *Brit.* 928,548). A mixture of alkylbenzene sulfonate (ABS) and an alcohol sulfate was produced continuously (Brooks and Brooks, *U.S.* 3,058,920). An alkyl benzene sulfonate was produced from tetrapropylene and benzene. The alkyl benzene is sulfonated with oleum

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(Muchinskii and Serebrayani, *Opyt Primeneniya Sintetich. Zhirozamenitelei v Proizv. Myla i Moyushchikh Sredstv*, Moscow, Sb. 1962, 101). Use of hydrogen peroxide in the neutralization step of alkyl benzene sulfonate preparation lightens its color (Groves and Terry, *U.S. 3,068,279*). An automatic device is used to prevent overheating of alkyl benzene sulfonates in storage containers (Erdman, *Tluszczci Srodki Piorace* 6(1), 24).

Industrial manufacture of alkylolamides is described (Sukhaterin et al., *Maslob.-Zhir. Prom.* 29(2), 29), as well as the technology of their production (Ranny et al., *Prumysl Potravlin* 14(2), 94). Sucrose fatty acid esters are decarboxylated by passing them through ion-exchange resins (Kunugi, *Chem. Pharm. Bull. (Japan)* 11(7), 922). Description of the industrial use of the Schotten-Baumann reaction to give acyl taurides is covered (Schenck, *U.S. 3,057,889*), and a continuous process described (*Ibid.* *U.S. 2,903,466* and *Brit. 919,426*).

Alkylsulfonates are color-stabilized by small additions of a number of specified salts (Schenck and Papalos, *U.S. 3,089,882*); as are ester-type alkane sulfonates (General Aniline & Film Corp. *Brit.* 919,426). Descriptive data on spray-drying syndets is given (Milwidsky, *Soap Chem. Specialties* 38(10), 59; (11), 56; (12), 73), and a spray-tower is described and the mathematical theory discussed (Fainberg, *Maslob.-Zhir. Prom.* 28(8), 36).

RAW MATERIALS. Reviewed were raw materials for soap manufacture (Anon. *Lipidos* 22, (Soap Section), 5). Tallow was replaced by synthetic fatty acid of 16-21 carbons length and coconut oil by those of 10-15 in length. Various other formulations and usages were noted (Lesyus, *Opyt Primeneniya Sintetich. Zhirozamenitelei v Proizv. Myla i Moyushchikh Sredstv*, Moscow 1962, 17). Somewhat similar recommendations for synthetic fatty acids were made for household and toilet soap (Kupchinskii, *Obmen Opytom po Nepreryvnomu Proizv. Mula, Gos. Nauchn.-Issled. Inst. Nauchn. i Tekhn. Inform.* 1962, 71). Ease of handling of fatty acids indicates their use in cosmetic soap bases (Molteni, *Am. Perfumer Cosmet.* 77, Sect. 10, 111). Sperm whale skin oil, caustic soda and sodium acetate were used in preparing a white soap, not obtained in the absence of the acetate (Masano et al., *(Japan)* 23,860 ('61). Soap was separated centrifugally from the saponification of crude alcohols (Man'kovskaya et al., *Tr. Nauchn.-Issled. Inst. Sintetich. Zhirozamenitelei i Moyushchikh Sredstv.* 1961, No. 2, 50).

The cracking of solid synthetic paraffins, separation, conversion to methyl esters followed by saponification gave a number of α -dimethylalkanoic acids (Puzitskii et al., *Zh. Prikl. Khim.* 35, 2740). Alkylarenesulfonates were produced from a straight-run fraction of petroleum (Orechkin et al., *Khim. i Tekhnol. Topliv i Masel* 8(1), 27), and olefins from the thermal cracking of paraffin were used in this synthesis (Doladugin et al., *Tr. Vses. Nauchn.-Issled. Inst. po Pererabotke Nefti*, No. 9, 95). Olefins polymerized from propylene-rich feedstocks were used in alkylbenzene production (McLean and Addy, *Brit.* 913,795). A review of the commercial aspects of alkyl benzene included the discussion of the most desirable isomers (Scott, *Hydrocarbon Process. Petrol. Refiner* 42(3), 109). Methods for lengthening the side chain of alkyl benzene were disclosed (Hunter et al., *U.S. 3,051,766*). Alkylarenesulfonates from thermally cracked gasoline in the presence of benzene and toluene were described (Ashimov and Kalaushin, *Azerb. Khim. Zh.* 1961(6), 43). Monoalkylbenzenes were produced in a near-pure form (Esso Research and Engineering, *Fr.* 1,307,798).

The alkylation of phenol for nonionic manufacture was directed to the dodecyl product through propylene polymers (Mixer and Wagner, *Fr.* 1,322,509). Alkylolamides were produced from naphthenic acids (Demchenko and Slavikovskii, *Dopovidi Akad. Nauk. Ukr. RSR* 1963(7), 903), and the use of natural fatty acids for producing these compounds and their applications were reviewed (Osteroth, *Umschau Wiss. Tech.* 63(2), 46).

Surfactants were produced from soybean or wheat protein (Akabori et al., *Japan* 6455('63), while other protein derived detergents were produced as complex amides (Riso, *Soap Chem. Specialties* 39(5), 82). Surfactants were produced by sulfonating a fraction of lignite tar (Gororova, *Akad. Nauk Ukr. RSR, Inst. Teploenerg., Zb. Prats* 1962(25) 62), while peat tars were also used as raw materials (Kazakova et al., *Tr. Inst. Goryuch. Iskop., Akad. Nauk SSSR* 17, 157). The sulfation of vegetable oils was described for surfactant production (Kasiviswanadham and Murti, *Indian Oil Soap J.* 28(4) 115). Solvent naphtha was reacted to form a ketone which was sulfonated (Hiyama et al., *Japan* 208 ('62). Rice by-products were used in the derivation of partial xylitol esters (Yufera et al., *Rev. Agroquim. Technol. Alimentos* 3(2), 147). Fatty alcohols separated from the neutral products of paraffin

oxidation were available for surfactant use (Kobsova and Moshkin, *Tr. Vses. Nauchn.-Issled. Inst. po Pererabotke Nefti-Gaza i Polucheniyu Iskusstv. Zhidkogo Topлива* 1959(8), 186). In the oxidation of paraffin, unsaponifiables are formed from which fatty alcohols are separated (Kudryashov, *Opyt Primeneniya Sintetich. Zhirozamenitelei v Proizv. Myla i Moyushchikh Sredstv. Moscow, Sb. 1962, 78*). Surfactant substances were classified for several chronological periods as to raw material source and other characteristics (Pueschel, *Z. Chem.* 3(9), 338).

SYNTHESIS OF AMPHOTERICs. Reaction of laurylamine with ethylene oxide, followed with monochloroacetic acid in aq. NaOH, gave the poly (oxyethylene) lauryl betaine (Komori and Kashiwabara, *Japan* 3,555 ('62). Six amphoteric containing both quaternary ammonium or imidazole and anionic groups were synthesized (Linfield et al., *JAOCs* 40, 114).

SYNTHESIS OF ANIONICS. An alkylarene sulfonate was synthesized comprising the sodium 2-octylmercapto-6-benzimidazole sulfonate (Szule, *Pol.* 45,710). An essentially salt-free ABS was disclosed (Shell International Research Maatschappij N.V. *Belg.* 618,971). A kerosene fraction was used in the synthesis of sulfanol, an ABS product (Gershenovich, *Opyt Primeneniya Sintetich. Zhirozamenitelei v Proizvodstve Myla i Moyushchikh Sredstv, Moscow* 1962, 118). Alkenylbenzene and -toluene were synthesized for surfactant production (Mamadaliyev et al., *Azerb. Khim. Zh.* 1962(5), 19). An octylphenyl sulfonate surfactant was disclosed (Horvath, *Hung.* 148,277).

Stearate soaps of metal groups III, IV, V, VIA and VIII cations were synthesized (Olson, *U.S. 3,078,288*). Reviewed were the laboratory and commercial methods for metallic soap preparation (Pilpel, *Ind. Chemist* 39, 134). The metallic soaps of various fatty acids were synthesized and the manufacturing procedures given (Reed, *Am. Perfumer Cosmet.* 77, Sect. 2, 105). Alkali metal soaps and their uses were disclosed (Johnson, *U.S. 3,081,190*). The procedure for preparation of aluminum soaps was patented (Tabe, *Japan* 3,909 ('63), as were those of cadmium (Kawasaki and Sato, *Japan* 2,860 ('62), and (Kato and Tachihara, *Japan* 10,435 ('62). Lithium soaps of epoxidized fatty acids were disclosed (Hoesch and Hoesch, *Brit.* 927,965).

Reaction products of isohexadecenylsuccinic acids and maleic anhydride were used in the synthesis of surfactants (Smirnov et al., *Zh. Nauchn. i Prikl. Fotogr. i Kinematogr.* 8(3), 165). α -sulfo fatty acids were claimed as effective surfactants (Gavlin et al., *U.S. 3,104,247*). Hydrocarbons sulfonated by sulfur dioxide and oxygen under the effect of intense γ -radiation gave aliphatic sulfonic acids (Esso Research and Engineering Co. *Ger.* 1,139,116). Sodium 1-acyl-2-hydroxypropane sulfonates were synthesized (Nagayama et al., *Japan* 1,715 ('62). Condensation of a fatty acid with alkyl sulfonates such as $-\text{CH}_2\text{CH}_2\text{OSO}_2\text{Na}$ was claimed (Shell International Res. Maatschappij N.V. *Belg.* 612,097). Oxysulfonates of partially epoxidized fatty acids were synthesized (Dieckelmann and Plapper, *Ger.* 1,137,004). Claimed was the synthesis of sodium 3-tridecyloxy-2-propanol-1-sulfonate (Gaertner, *U.S. 3,082,249*). Synthesized were sulfoalkyl and sulfopolyalkylenoxyalkyl monoesters of alkenylsuccinic acids and their salts (Gaertner, *U.S. 3,086,043*). Glycidyl esters were sulfonated for surfactant use (Borstlap and Kooijman, *U.S. 3,067,220*). Covered were *N*-substituted 3-aminopropane sulfonates or 2-methylaminoethanesulfonates (Gaertner, *U.S. 3,084,187*). High mol wt 2-acyloxyalkane sulfonates were prepared by treating fatty acids with 2-hydroxyalkane sulfonate (Elbel, *Ger.* 1,121,045).

A fatty alcohol poly (oxyethylene) ether was sulfated to give a paste product when neutralized with caustic soda (Neher, *Ger.* 1,141,743), while a compound tertiary amine reacted with ethylene oxide was also sulfated and neutralized (Dupre and Boettner, *U.S. 3,079,416*). Monohydric alcohols reacted with ethylene oxide in the presence of a peroxy catalyst are sulfated (Esso Research & Engineering Co., *Ger.* 1,142,602). Nonylphenoxypolyethoxyethanol is reacted with chlorosulfonic acid to give the sulfonylethylammonium sulfate (Shull et al., *Belg.* 618,393).

Sodium salts of tertiary alkanolic acids were reacted with a halogenated epoxy alkane and sulfonated (Buesink and Kooijman, *U.S. 3,067,221*). Dodecylhydroxyethylsulfone is reacted with sulfamic acid to give the sulfonylethylammonium sulfate (Oda, *Japan*, 4,864 ('62).

Mixtures of surfactants are claimed: Tert-amine-ethylene oxide and tert-amine-ethylene oxide sulfates (Boettner and Dupre, *U.S. 3,079,348*); ABS and/or fatty alcohol sulfates were combined with salts of sulfonated fatty acids (Henkel & Cie. *Belg.* 614,508). Sulfobetaines used with alkylsulfates are compatible (Henkel & Cie. *Belg.* 614,604). *N*-acylphenylalanines were synthesized by the mixed anhydride method (Tsunobone and Yamamura, *Kuyushu J. Med. Sci.* 13, 93). Alkyl

urethanes such as $\text{ROCONR}_1\text{-CH}_2\text{-CH}_2\text{SO}_3\text{Na}$ were synthesized where R is C-8-12 and R₁ is octyl (Orthner et al., *U.S.* 3,086,986). Epoxides of unsaturated long chain hydrocarbons, alcohols, ethers, etc. are sulfonated (Plapper et al., *U.S.* 3,096,357). Polymers of vinyl dodecylether, dimethyl maleate and benzene with a peroxide catalyst are reacted, neutralized to give a polysoap (Murai et al., *Japan* 4,497 ('63). Peroxide-catalyzed addition of diethylphosphate to dioctyl maleate easily gave dioctyl alpha-diethylphosphosuccinate (Yamamoto et al., *Yukagaku* 11, 144). A phosphono ester was produced by blowing oxygen through a mixture of cetylpalmitate and phosphorous trichloride and neutralizing (Sakurai, *Japan* 16,967 ('62). A phosphinic acid chloride from a long-chain olefin was reacted with 2-ethylhexylalcohol (McBride and Mais, *U.S.* 3,092,650). A group of salts of mono-, di- and/or triocetylamine and dioctyl acid orthophosphate were synthesized as oil soluble surfactants (Cantrell and Kuhue, *U.S.* 3,080,222).

SYNTHESIS OF CATIONICS. Prepared were bis-(quaternary ammonium) compounds such as *N*-methyl-*N'*-dodecyl-N,N'-ethylene bis-(dimethylammonium chloride) (Hwa, *U.S.* 3,079,436). New dichlorides of 1,6-hexamethylene bis-(alkyl dimethylamino acetates) (Denisenko et al., *Zh. Obshch. Khim.* 32, 731). Propylene monochloride was reacted with dipropylene triamine, this sulfonated with sodium bisulfite and the sulfonate reacted with an acyl chloride (Weingarten, *Ger.* 1,134,068). Quaternary alkoxy compounds were prepared by reacting a primary monohydric alcohol having a β or γ substituted alkoxy group with formaldehyde and quaternizing with pyridine (Aldridge and Hunter, *U.S.* 3,062,766). An example of a poly (amine acid) quaternary derivative was obtained by polymerizing *N*-carboxy-glycine anhydride in the presence of *N*-dodecyl-beta-alanine (Isemura et al., *Japan* 15,046 ('62). A diamide quaternary salt can be obtained by reacting hydrogenated tallow fatty acids with diethylenetriamine, then with polyethylene glycol chloride (Lee and Svarz, *U.S.* 3,074,815).

A quaternary salt is formed by reacting epichlorohydrin with triethylamine and potassium laurate (Kalopissis et al., *Fr.* 1,313,143). The reaction of a tertiary aminehydrochloride with epichlorohydrin gave a quaternary ammonium compound (Yamamoto et al., *Yukagaku* 12, 29). Polyallyl type cationic surfactants were obtained by quaternizing allylic polymers with *N*-bases, e.g., poly(allylchloride) with *N*-dodecylpiperidine (Narasaki, *Kogyo Kagaku Zasshi* 65, 793). Quaternary compounds are formed by reacting a tertiary amine having little or no steric hindrance with propylene oxide (Yamamoto et al., *Yukagaku* 11, 464). Alkylamine salts, reacted with a variety of anions, were treated with ethylene oxide (Yamamoto et al., *Ibid.* 12, 415), to form quaternary compounds. Long-chain oxazolines were prepared by condensing fatty acids with β -amine alcohols and were converted to soluble salts by reaction with organic acids (Kimura et al., *Kogyo Kagaku Zasshi* 63, 582). Quaternary hydrazinium chlorides prepared from long-chain tertiary amines and NH_2Cl are fused with sodium soaps to give hydrazinium salts (Rudner, *U.S.* 3,070,600). Cationic compounds were prepared by reacting naphthyl methyl bromide with pyridine (Romanov et al., *Izv. Akad. Nauk Turkm. SSR, Ser. Fiz.-Tekhn., Khim. i Geol. Nauk* 1962 (6), 114). Dimethylethorophosphite was reacted with a secondary amine to form phosphoramidates having cationic properties (Cheymol et al., *Fr.* 1,239,989). Tertiary phosphine oxides of many kinds were synthesized and used for the improvement in properties of detergent compositions including cold water solubility (Laughlin and Yoke, *Belg.* 615,204). Poly(sodium dodecylvinylether comaleates) were synthesized using various amines for half amination (Sakai, *Kogyo Kagaku Zasshi* 65, 961).

SYNTHESIS OF NONIONICS. Monoglyceride surfactants were prepared by hydroxylation of allyl esters of hydroxy fatty acids (Kaufmann and Baltes, *Ger.* 1,148,224). Epoxy triglycerides were converted to epoxymonoglycerides by heating glycerol with a tert-aromatic nitrogen base (Swift & Co. *Brit.* 908,500). Acylamides of α -amino acid salts were prepared from alkali metal salts of lower α -amino monocarboxylic acids and higher fatty acid anhydrides (Lorentzen, *U.S.* 3,074,980). Biodegradable detergents were produced as amine oxides by treating tertiary amines with hydrogen peroxide (Hoh et al., *JAOCs* 40, 268). Mono- and dioctylphenol were converted to surfactants by treatment with ethylene oxide (Sonawane and Rao, *Indian J. Technol.* 1(1), 36). Surfactants were produced from naphthenic acids or alcohols by condensation with ethylene oxide (Romanov and Niyazov, *Izv. Akad. Nauk Turkm. SSR, Ser. Fiz.-Tekhn., Khim. i Geol. Nauk* 1962(5), 34). Aldox C₁₂ alcohol was treated under nitrogen with sodium methylate and ethylene oxide giving a liquefied polyether alcohol (Esso Research & Engineering Co. *Brit.* 913,001). Tetramethyldecylol was reacted with ethylene oxide using

Et₃N as catalyst (Air Reduction Co., Inc. *Brit.* 893,431). Abitol and a mixture of abietyl, dihydroabietyl and tetrahydroabietyl alcohols were reacted with ethylene oxide and this converted to benzyl ethers (Harris, *Brit.* 908,010). Symmetrical tertiary acetylenic glycols were synthesized (Russell and Leeds, *U.S.* 2,997,447).

Sucroglycerides prepared by transesterification of glycerides with sucrose were condensed with ethylene oxide (Ledoga S.p.A. *Belg.* 616,658). Sucrose esters such as laurates are prepared by reacting methyl laurate with sucrose in *N,N*-dimethylbenzylamine (Sakama and Kikuchi, *Japan* 18,710 ('62). Transesterification was used to produce linoleate esters of sucrose with dimethylformamide as a solvent (Bobalek et al., *I & EC Product Res. & Dev.* 2, 9). Methyl α -D-glucopyranoside was reacted by transesterification with fatty acid methyl esters in dimethylformamide or formylmorpholine to give monoesters; the short-chain esters are surfactants. These in turn, when reacted with ethylene oxide, give surface active agents (Okhara et al., *Kogyo Kagaku Zasshi* 64, 177). A saccharide such as sucrose may be reacted with propylene oxide to give a useful product for foam reduction and cleaning operations (Farbenfabriken Bayer A.-G. *Brit.* 928,906). Starch treated with polyols such as ethylene glycol undergo transglycosidation to form polyol glycosides and these are then treated with ethylene oxide and these further with fatty acids to form emulsifying agents (Otey et al., *JAOCs* 40, 76). Mannitol urethans were prepared by heating a solution of DL-mannitol with long-chain isocyanates to give surface active compounds (Ulsperger and Jacobi, *Fette, Seifen, Anstrichmittel* 64, 1093). Mono- or polysaccharides are treated with halomethyl alkyl ethers to give products not saponified in alkaline media as are conventional ester type carbohydrate surfactants (Rosen and Kaye, *U.S.* 3,092,618).

Products were prepared, for example, from phenol condensed with propylene oxide, and these in turn with ethylene oxide (Jackson and Lundsted, *Ger.* 1,132,730). Conjugated poly(oxypropylene)-poly(oxyethylene) compounds were synthesized (Patton, *U.S.* 3,101,374). Fatty acids are reacted with maleic anhydride and this reacted with poly(ethylene glycols) to give surfactants (Creelius et al., *Belg.* 622,310). A polyethylene glycol substituted polyester may consist of a dibasic acid, a diol and a polyethylene glycol monoether (Stuart et al., *U.S.* 3,083,187). A polyglycol substituted linear polyamide may be prepared from a polyethylene glycol, a dibasic acid and a polyamine (Stuart et al., *U.S.* 3,083,188). A mixture of lauric acid, vinyl acetate and benzoyl peroxide gives a polymer which is reacted with diethanolamine (Konishi, *Japan* 8,812 ('63). A copolymerized surfactant was made of vinyl acetate and an unsaturated dicarboxylic acid (Hattori and Ishikawa, *Japan* 11,282 ('63). Nonionic polysoaps were prepared by oxyethylating nonylphenol-formaldehyde and nonylphenol-*p*-cresol-formaldehyde resins (Narasaki, *Kogyo Kagaku Zasshi* 66(3), 391). Copolymers of two different alkylene oxides were treated with a polysiloxane to give block polymers useful as surfactants in polyurethan foams (Haluska, *Belg.* 620,800). Poly(oxyethylene) and poly(oxypropylene) glycols, esters, ethers and other derivative preparations were reviewed, including patents and development (Lamendin, *Chim. Ind. (Paris)* 87, 240). Ethylene oxide nonionics (Weiss, *Rev. Arg. Grasas y Aceites* 4, 7) and oxyethylation product synthesis were reviewed (Gerault, *Bull. Soc. Pharm. (Marseilles)* 11, 7). Nonionic polysoaps were prepared as acrylic acid esters of poly(oxyethylene) lauryl ether and the allyl ether of poly(oxyethylene) octylphenyl ether but all had low-water solubility due to hindrance of hydrophilic groups in the polymer (Yamashita et al., *Kogyo Kagaku Zasshi* 65, 2050). Reviewed were new detergents based on sugar (Simonis, *Zuckerind.* 13(8), 461). Surfactants containing saccharides in their molecules were reviewed (Komori, *Yuki Gosei Kagaku Kyokai Shi* 21, 19).

COMPOSITIONS

ANTISEPTIC. A halogen-substituted thiocarbanilide was used with an anionic or nonionic surfactant (Beaver and Stoffel, *U.S.* 3,103,467). A synergistic mixture of di- and trihomomonosaliacylanilides was used in soaps and cosmetics (Stecker, *Soap Chem. Specialties* 39(5), 75). Sensitization by tetrachlorosalicylanilide was tested, and some positive patch test reactions were found with bromosalicylanilides (Wilkinson, *Brit. J. Dermatol.* 74, 295). 8-Quinolol was used with a mixed soda-potash tallow-coco soap (Roman, *U.S.* 3,088,916). 8-Hydroxyquinoline, preferably the sulfate, was added to an anionic surfactant solution and the pH adjusted with phosphoric acid to 4.5-5.5 (Vodros, *Hung.* 147,545). Addition of hexachlorophene to a potash soap solution reliably reduced the number of skin organisms (Privora and Synek, *Akoslov. Epidemiol., Mikrobiol., Immunol.* 12(4), 249). Hexachlorophene was used in a mixture of nonylphenol ethylene oxide

adduct, an anionic surfactant, a water soluble lanolin derivative, therapeutically effective neomycin, in aqueous solution (Blodinger, *U.S.* 3,069,358). Mixed with a water soluble soap was hexachlorophene and dihydroxydimethyl dichlorodiphenyl sulfide (Noel and Casely, *U.S.* 3,081,266). A mixture of quaternary surfactants was found effective against several vegetative forms of bacteria, to be used in detergent mixtures (Shura-Bura et al., *Gigena i Sanit.* 27(8), 101). A built detergent composition for woolen-type fabric disinfection comprised a nonionic or cationic ethylene oxide adduct, and a mixture of quaternary ammonium, phosphonium and arsonium compounds (Fussgaenger and Taeuber, *Ger.* 1,145,292).

A solid cresol triethanolamine soap containing ethylenediamine sodium tetraacetate was useful as a disinfectant (Ito, *Japan* 3,907 ('63). Used as a germicide in soap or soap-detergent mixtures was pyridinethiones (Schramm, *Belg.* 616,540). Reviewed were iodophores as detergent-sterilizers (Davis, *J. Appl. Bacteriol.* 25(2), 195).

Disinfectant activity was claimed for combinations of anionic and nonionic surfactants employing pyro- or polyphosphates and phenylmercuriborate (Ranny et al., *Czech.* 102,442). Phenylmercuriborate was the active disinfectant in a liquid mixture of anionic and nonionic surfactants (Nigrin et al., *Czech.* 102,457). Alkylarenesulfonic acids or dry sodium salts with dry acidic materials to reduce the pH to 2.5-2.9 were claimed for their sterilizing effect (Pennsalt Chemicals Corp., *Brit.* 917,432). Mixtures of anionic or nonionic surfactants with a haloalkyl pentachlorophenyl carbonate were claimed for disinfectant garment washing (Monsanto Chemical Co., *Brit.* 914,891).

Color stabilization of a detergent composition was claimed by adding a dicarboxylic acid to a soap containing a bacteriostat such as $(HO)C_6H_4-S-C_6H_4(OH)Cl_2$ (Mitoray and Bauer, *U.S.* 3,085,066). Modern trends in deodorant soaps were reviewed, those containing hexachlorophene, bithionol, tetramethylthiuram disulfide and trichlorocarbanilide being mentioned specifically, and synergistic action by their combinations being described (Linfield and Casely, *Am. Perfumer Cosmet.* 77, Sect. 2, 103). Quaternaries in floor cleaning compositions were discussed (Walter, *Mfg. Chemist* 34(4), 170). Disinfectants containing ampholytic surfactants were described (Schmitz, *3rd Intern. Congr. on Surface Active Materials*, Cologne, 1960, 4, 264).

BAR AND TABLET. Soap-synthetic and all synthetic bar compositions were discussed (Price, *Am. Perfumer Cosmet.* 77, Sect. 2, 99). A process was described for introducing gas into a plasticized mass of soap or syndet to provide floating bars (Poek, *Soap Chem. Specialties* 38(11), 135). Bars are claimed in which salts easily melting or dissolving in their water of crystallization are mixed with a surfactant, heated and formed under pressure (Slob, *Belg.* 617,684). A mixture of potassium alkyl sulfates, fatty alcohols and magnesium alkyl sulfates were worked to translucent flakes and these extruded to form bars (Soc. Belge de l'Azote et des Produits Chimiques du Marly, S.A. and Soc. Carbochimique S.A., *Brit.* 858,074). Molded bars are claimed by reaction of liquefied polyalkylene glycol solution of a sulfonic acid and an alkali followed by neutralization with an alkaline builder such as sodium tripolyphosphate (Basol Ltd. and Chinnick, *Brit.* 934,682). A non-soap anionic bar is produced from selected surfactants, corn starch, tetrasodium pyrophosphate and aluminum sulfate being used to impart desired physical properties for manufacture in conventional soap-manufacturing equipment (Wittwer, *U.S.* 3,055,837). Similar anionic surfactants are used, but the ingredients are mixed in water to uniformity as a slurry and water reduced to 5% when bars are formed (Wittwer, *U.S.* 3,057,805).

Soap syndet bars containing nonionic surfactants and tallow-coco soap were disclosed (Ward, *Ger.* 1,151,340). Bars were obtained by mixing alkaline earth salts of ABS with soap (Ward, *Ger.* 1,142,983). Alkaline earth fatty acid amide alkane sulfonic acid salts were mixed with soap to form bars (Ward, *Ger.* 1,144,428). Bars of improved physical properties and use characteristics were formed by mixing a potassium alkyl sulfate with soap, a hydrated magnesium soap and a salting-out electrolyte (Chaffee, *U.S.* 3,070,547). Bars containing less of an anionic surfactant and more soap were claimed to have superior characteristics (Anstett, *U.S.* 3,076,766). Conventional soap manufacturing equipment was used in forming bars of salts of primary alkane sulfonic acids and water-soluble soap (California Research Corp., *Brit.* 905,952). Soap bars for oily skins were prepared from soda soap, 1.5% grit-free water insoluble sodium metaphosphate, a halogenated phenolic bactericide, menthol and water (Farrar and Schluerud, *U.S.* 3,105,051).

Tablets were formed from a nonionic surfactant, an anionic surfactant, usual additives and all mixed with a sodium silicate solution; tale was added and the mix poured into molds. The

tablets were sprayed with a solution of polyvinyl alcohol containing polyvinyl acetate and dried (Farrar et al., *Belg.* 615,884). A powdered mixture of sodium tripolyphosphate and anionic and nonionic syndets was mixed, pressed into a tablet of specified characteristics and the tablet surface sprayed with water to hydrate the tripolyphosphate and form a protective surface (Laskey, *U.S.* 3,081,267). Powdered anionic surfactant, sodium tripolyphosphate and other builders and additives were mixed and pressed into tablet form. These tablets were encased by spraying them with nonaqueous solutions of polyvinyl alcohol (Sullivan, *Belg.* 617,018).

Transparent soap was obtained by treating soap with a polyhydric alcohol, free fatty acid and salt in specified proportions (Unilever N.V., *Fr.* 1,291,638). Calcium and magnesium salts of pentapropylenebenzenesulfonic acid were added in 20-30% amt to an 80-20 tallow-coco soap (Kelly, *Belg.* 616,497).

BLEACH. Listed here also would be antiseptic agents based on available chlorine or oxygen.

Hydrogen peroxide was mixed with ABS, a fatty alkylamide, acid pyrophosphate, normal sodium and potassium pyrophosphates to give stable compositions (Kali-Chemie A.-G., *Belg.* 614,204). A granular detergent was claimed, based on hydrogen peroxide addition to sodium tripolyphosphate and a detergent mixture of sodium silicate and ABS, and other constituents (Dugan, *Ger.* 1,144,866). Inorganic peroxy compounds are used in compositions with an activator containing one or more nitrogen atoms and at least two acyl groups attached to it (Maddox et al., *Brit.* 907,356). Potassium persulfate may be substituted for sodium perborate because of its greater release of oxygen (Baranowska, *Tluszcze i Srodki Piorace* 6(3/4), 143). A peroxybenzoic acid is used with one of several anionic surfactants to form a stable composition (Brocklehurst and Pengilly, *U.S.* 3,075,921). Liquid detergent compositions containing polyphosphates, ABS and the like are combined with organic peroxy compounds in which both oxygen atoms are attached to a carbon atom as in benzoyl peroxide (Henkel & Cie., *Belg.* 615,369).

A powder is obtained with soap and builders by adding a portion of the sodium perborate and drying. To the resulting light powder the balance of the perborate was added (Slowinski, *Pol.* 44,089). Urea hydroperoxide was found to bleach fabrics satisfactorily but could not be used in dry compositions as could sodium perborate (Kajl and Pasternak, *Tluszcze i Srodki Piorace* 5, 95). Soap or a syndet, an inorganic peroxide and an ester of phenol, or of a substitution derivative of phenol with an α -chlorinated lower aliphatic carboxylic acid are mixed. These peroxidated compounds become activated by the above esters and release oxygen (Procter & Gamble, *Belg.* 621,901). A detergent and water softener is composed of chlorinated trisodium phosphate and an anionic surfactant to increase solubility (Shere and Carrera, *Belg.* 619,321). The odor of chlorinated trisodium phosphate was masked by the addition of a fractional percentage of a polyethenoxy nonionic surfactant (Karabinos and Ballun, *Soap Chem. Specialties* 38(12), 63).

Dry compositions containing a dry water soluble hypochlorite, ultramarine blue and a fluorescent brightening agent are claimed (Wixon, *Belg.* 623,267). A bleaching composition comprising a hypochlorite, a detergent and an organic nitrogen-containing compound having at least one NH group was reactive with hypochlorite to form an N-Cl group; the Cl acceptor prevents conversion of the NH group in textiles to NCl groups (Gagliardi and Pollock, *U.S.* 3,099,625). A liquid automatic dishwashing compound was claimed, consisting of an alkali metal hypochlorite, sodium or potassium tripoly or pyrophosphate, trisodium or potassium orthophosphate, meta-silicate, potassium hydroxide and water (Lintner, *U.S.* 3,058,917).

Chlorites can be activated to increase rate of bleaching by adding substances of formula RS_2O_2X . R is an alkyl, cycloalkyl or aryl, or aralkyl group whose benzene nucleus can be substituted by at least one S_2O_2X group, X = H or Na (Farbwerke Hoechst A.-G., *Belg.* 616,623). A bleaching agent is covered as a nucleus with a coating of a water soluble soap or syndet containing sodium tripolyphosphate, silicate, methyl cellulose and other usual additives (Speak and McConnell, *Belg.* 612,158). Reviewed were household inorganic and organic chlorine- or oxygen-releasing compounds and optical brighteners in washing powders (Milwidsky, *Mfg. Chemist* 34(7), 302).

BUILDERS AND ADDITIVES. Replacement of soda ash by sesquicarbonate in wash baths was recommended (Tomaszewski and Pischinger, *Tluszcze i Srodki Piorace* 5, 235).

Cleaning efficiency was improved by building with sodium tripolyphosphate blended with excess sodium sulfate (Schmidt and Hohfeld, *E. Ger.* 21,995). Viscosity of syndet slurries are avoided by using completely anhydrous form II sodium tripolyphosphate (Martin, *U.S.* 2,961,409). Form II sodium

tripolyphosphate is used in syndet mixes, ca. 60% being converted to form I and during spray drying to 95% form I (Shen and Metcalf, *Belg. 622,142*). Foaming and detergency of polyoxyethylene nonylphenyl ether surfactants were improved by using polyphosphates which were more effective than silicates, carbonate or neutral salts (Kame et al., *Yukagaku 12*, 108). The synergistic power of polyphosphates for use with syndets was discussed (Colas, *Chim. Ind. (Paris) 87*, 128). Sodium tripolyphosphate was found effective in improving the detergency of ABS syndets (Ashimov et al., *Azerb. Khim. Zh. 1962*(4), 27).

Combinations of tetrapotassium pyrophosphate with nitriloacetic acid were shown quite effective in improving the detergency of ABS compositions (Alier and Bonilla, *Afnidad 20* (224), 75). Heptonic acids from invert sugars are claimed effective sequestering agents for multivalent metals (Karabinos and Quinn, *U.S. 3,106,822*). Sodium glycoheptonate was used in paper mill cleanup (Kunklin and Moudry, *U.S. 3,071,504*). Discussed were builders for detergent manufacture (Nevolin, *Opyt Premeneniya Sintetich. Zhirozamanitelei v Proizv. Myla i Moyushchikh Sredstv, Moscow, Sb. 1962*, 3). Soluble silicates were described as anionic surfactant builders (Warren, *Soap Chem. Specialties 39*(3), 50). Builders were discussed (Smith, *Am. Perfumer Cosmet. 77*, Sect. 2, 107; Gomez, *Grasas y Aceites* (Seville, Spain) 13, 247). The role of alkalies in the washing process was discussed (Stache, *Seifen, Oele, Fette, Wachs 89*(12), 367). Phosphates in detergency were discussed (Colas, "Le phosphore dans la detergence" Paris: *Progil. 1962*, 20 pp).

Antiredeposition agents such as sodium carboxymethyl cellulose (NaCMC) and sulfate cellulose in their effect on soil redeposition prevention were discussed as to effect of degree of polymerization (Zhgach et al., *Opyt Primeneniya Sintetich. Zhirozamanitelei v Proizv. Myla i Moyushchikh Sredstv, Moscow, Sb. 1962*, 131; 133). Prevention of shrinkage of bars was experienced when NaCMC was added during manufacture (Herrera and Ayerbe, *Grasas y Aceites 13*, 161). NaCMC added to olive oil soap reduced bar shrinkage (Gomez and Ramos, *Grasas y Aceites* (Seville, Spain) 13, 161). A process for evenly dispersing NaCMC in cold water was obtained by first wetting with a soap solution (Unilever, Ltd. *Brit. 927,542*). Soil redeposition preventive agents were synthesized from water dispersible cyanoalkylated polysaccharide (Rutenber and Wurzburg, *U.S. 3,061,551*). Improvement in ABS compositions was claimed for polyvinyl alcohol addition (Inamorato, *Ger. 1,145,735*). Increase in soil removal by immersion of soiled garments in an aqueous solution of a suitable high polymer was achieved (Matsukawa, *Kogyo Kagaku Zasshi 62*, 1584). The foaming and detergent properties of nonylphenol ethylene oxide adducts were improved by adding polyphosphates, more than other builders (Kame et al., *Yukagaku 12*, 108).

Addition of polyethylene glycol to nonylphenyl EO adduct had no effect on cloud point or foaming properties. Addition of nonylphenol had no effect on wetting but marked effect on foaming and cloud points (Oneda, *Yukagaku 12*, 48).

DRYCLEANING. Added to drycleaning solvents was a polyhydric alcohol, or ester polymers thereof, for its improvement in the fabric appearance (Edwards, *U.S. 3,091,508*). As drycleaning detergent, the products obtained by reacting oleic acid with di- or triethanolamine and this with alkylbenzene sulfonic acid was claimed as an effective detergent (Piepmeyer, *Brit. 912,489*). Used in an organic solvent was the calcium salt of alkylarenesulfonate and a nonionic surfactant (Jacard, *Belg. 621,107*). Added to a drycleaning solvent was a mixture of triethanolamine oleate, -stearate, ammonium stearate, alkane sulfonate and water (Matusiewicz et al., *Pol. 44,740*). A product capable of binding water in a drycleaning solvent was comprised of an alkylaromatic compound and a hydroaromatic compound and cyclohexanol, with a mixture of alkylarenesulfonate and a petroleum sulfonate in the presence of finely dispersed copper or ferrous salts, subsequently removed by centrifugation (Gilbert et al., *Czech. 103,715*). A drycleaning agent is required to disperse water within the solvent and the solvent-insoluble dirt within the water: Syndets are said to have certain advantages over soap for this purpose (Davidsohn, *Am. Perfumer Cosmet. 77*, Sect. 2, 115). High operating efficiency in drycleaning is maintained by monitoring the level of surfactant and water in the solvent, electrical conductance being employed (Warren et al., *U.S. 3,101,239*).

HEAVY DUTY DETERGENTS. Potassium silicate and tetrasodium ethylenediamine tetraacetate are added to saturated solutions of sodium silicate to give detergents stable to crystallization (Mounier, *Fr. 1,323,416*). Sodium metasilicate with alkylarenesulfonates, NaCMC, carbonates, metaphosphate, an antimony or bismuth salt of a strong inorganic acid and other normal additives are claimed (Zajdler et al., *Pol. 44,942*).

Hard surface detergents are claimed comprising a mixture of alkali metal phosphates and carbonates or sesquicarbonates prepared by reaction of phosphoric acid and the carbonate. Also used in the mixture are silicates and a surfactant (McKenna et al., *Belg. 621,716*). A composition with wide solution temp stability was prepared from a nonionic surfactant, a fatty alcohol, a polyalkoxydihydric alcohol to which builders may be added (Michaels, *U.S. 3,067,144*). A composition to remove silicone grease contained a monobutyl ether of an oxyethylene propylene diol, a fatty acid soap and sodium silicate (Mankowich, *U.S. 3,069,360*). Granular products for hard surface cleaning were prepared by pulverizing a mixture of orthophosphate, carbonate or pyrophosphate, one of which is hydrated, a surfactant and an aqueous solution of an organic adhesive (Procter & Gamble, *Belg. 621,577*). Mechanically stable spray-dried hollow beads were obtained using a formulation of sodium sulfate, tetrasodium pyrophosphate, a surfactant, a bleaching agent and a carboxylic polymer as binder (Shields and Patterson, *Belg. 622,138*). An abrasive nonrusting composition such as pumice, an alkali builder, ABS or other anionic surfactant and a nonhygroscopic inorganic dust inhibitor was disclosed (Fries and Sinner, *U.S. 3,079,344*).

LIQUID. Superior foaming properties are claimed for compositions consisting of ABS, sec-alkyl sulfates and ethylene oxide adducts of alkylphenols (Shell Internationale Res. Maatschappij N.V. *Belg. 623,881-2*). A coned liquid was comprised of ABS, alkylphenylethoxy ethanol sulfate, sodium silicate, sodium xylene sulfonate, fatty acid diethanolamide, ethanol and water (Wixon, *Belg. 615,983*). A stable, pourable heavy-duty liquid was obtained because of the sequence of ingredient mixing. NaCMC was stirred into water, and tetrapotassium pyrophosphate added. ABS and color were dissolved in water, heated and a fatty acid isopropanolamide melted and added (Wixon, *U.S. 3,075,922*). A stable liquid composition was obtained using an alkali metal alkylmononuclear aryl sulfonate and potassium polyphosphate, an alcohol and water (Wixon, *U.S. 3,101,324*). An anionic liquid detergent contained ABS, alkyl ether ethylene oxide sulfate, fatty acid alkylolamide, a hydrotropic solubilizer and water (Aubert and Devlin, *Belg. 617,969*).

A creamy high-foam liquid detergent contained tetrapotassium pyrophosphate, a silicate, ABS, NaCMC, mixture of sulfated monoesters of lauric and myristic acid and 2-amino-2-methyl-1,3-propanediol and water (Tidridge and Cohen, *U.S. 3,072,578*). An opaque liquid contained sodium or ammonium soaps, a nonionic surfactant and a complex phosphate (Carroll and Sepulveda, *Belg. 621,529*). Lower viscosity compositions are obtained when formulated with a low concn of calcium ion in typical formulations containing ABS, sodium sulfate, sodium silicate, magnesium silicate and methyl cellulose (Knapsack-Griesheim A.-G. *Belg. 614,765*). A stable heavy-duty liquid composition was comprised of an alkylamine alkylarylsulfonate, a fatty alcohol sulfate and conventional builders, lithium hydroxide and potassium CMC (Dasch and Cutter, *U.S. 3,066,104*). An opaque toilet liquid was obtained by mixing glyceryl ether sodium or potassium sulfonates, alkyl glyceryl ether sodium or potassium sulfonate, an amine oxide and a water-soluble polyacrylamide or an ethylene oxide polymer (Pileher and Eaton, *Fr. 1,299,244*). A foaming liquid contains an alkylarenesulfonate, a nonionic ethylene oxide adduct and fatty acid ethanolamide, the latter two providing synergistic foaming action (Blakeway and Burgess, *Brit. 921,036*). A hard-surface liquid cleaner was prepared from an alkaline phosphate, soap and a nonionic fatty acid alkanolamide of alkylphenol ethylene oxide adduct (Unilever N.V. *Fr. 1,292,330*).

3,5-dimethyl-1-hexyn-3-ol is used as a volatile surfactant either alone or in combination with other products in isopropyl alcohol solution (Tinnon and Leeds, *U.S. 3,095,381*). Hard-water stable dishwashing detergents were prepared from mixtures of polyethoxy and propoxy adducts and their phosphate esters (Goette and Kirstahler, *Ger. 1,093,607*). Liquid medium and heavy-duty detergents are formulated from dimethyldodecylamine oxide, triethanolamine salt of ABS, potassium pyrophosphate, potassium toluenesulfonate, sodium silicate and water (Steer and Smith, *U.S. 3,085,982*). An aqueous liquid gel was prepared from a nonionic surfactant, alkaline polyphosphates, silicates and their mixtures, all with a cross-linked polymer (Ginn, *U.S. 3,060,124*). Low viscosity abrasive compositions, stable against sedimentation were obtained using NaCMC and a polyphosphate with up to 30-40% of an abrasive (Unilever N.V. *Belg. 620,087-8*). Reviewed were liquid soaps and detergents, the role of NaCMC and other additives, giving typical formulations (Milwidsky, *Soap Chem. Specialties 39* (4), 53). Clear, transparent gels were obtained using the sodium salt of oleyl sulfate and water (Weiss and Schmidt, *Ger. 1,133,062*).

LOW SUDSERS. A low-sudsing detergent composition con-

tained a fatty acid ethylene oxide adduct, a portion of the same adduct reacted with propylene oxide and sodium sulfate (Goette and Kirstahler, *Ger. 1,135,122*). The reaction product of ortho-cresol and ethylene oxide is further treated with propylene oxide to give a low-foaming detergent (Distillers Co. Ltd. *Belg. 616,761*). An alkali metal soap is mixed with a nonionic surfactant to which is added a readily soluble sulfate or sulfonate anionic surfactant to make a low-sudsing composition (Stayner, *Ger. 1,123,784*). A foam-preventing agent is comprised of aluminum soaps, spindle oil, lecithin, nonionic emulsifier and a C₇-7 alcohol (Ezstajn et al., *Pol. 45,112*). A nonfoaming surfactant comprises water and a mixture of nonionic surfactants of several types (Wedell, *U.S. 3,086,944*). A rinse additive for mechanical dishwasher use consists of a lowfoaming polyethylene oxide nonionic and a small amt of polyoxyalkylene glycol mixture (Temple and Martin, *U.S. 3,083,172*).

METAL CLEANING AND CORROSION. Amphoteric amino-carboxylic surfactants were used in soap-type cleaners for nonferrous metal cleaning. Compositions were prepared capable of removing asphalt and mineral oil soils (Mankowich, *U.S. Dept. Com., Office Tech. Serv., PB Rept. 171,128*). Sanitary equipment is cleaned by a mixture of fatty alcohol sulfates or a condensate of fatty acids and polypeptides, also containing a quaternary antiseptic. Acidity is controlled and an abrasive material added (Korda and Bryja, *Pol. 46,209*). Useful for removal of aluminum chloride-hydrocarbon complexes is an aqueous solution containing an alkylphenol ethylene oxide product (Dravnieks, *U.S. 3,061,548*). Tank protective oils contain a petroleum sulfonate and a partially ammoniated fatty acid (Schiermeier, *U.S. 3,090,690*). Acid cleaning was accomplished with a foam from HCl containing abietylamine and sodium N-methyl-N-oleyltaurate (Brenner and Engle, *U.S. 3,037,387*). Effect of household laundering compositions on copper strips was determined. Based upon previous literature, current detergents are believed no more corrosive to tinned copper than older ones containing sodium carbonate (Lindner, *Seifen-Oele-Fette-Wachse 89(2), 25*). Discussed the removal of tin from tinned copper vessels (Fries, *Fette, Seifen, Anstrichmittel 64, 1054*).

Cationic surfactants were used as pickling or acid-cleaning inhibitors. Dodecyl dimethylethanol ammonium compounds were evaluated, the halogenated quaternaries reducing corrosion by H₂SO₄ in the order I > Br > Cl > F (Yamamoto et al., *Yukagaku 12, 365*).

GLASS CLEANING. Bottle washing compositions which sequester the hard water elements are comprised of the alkaline hydrolytic products of glucose or other hexose sugars (Karabinos et al., *U.S. 3,062,878*). Several formulas were given for glass cleaning compositions using ABS and secondary alkyl sulfates as the active ingredients (Rabinovich, *Voprosy Eksploat. Ponarei i Okon v Prom. Zdanijakh (Moscow) Sb. 1962, 82*). A bottle washing technic was described using caustic ABS solutions, followed by stepwise rinsing at increasing or decreasing temp (Stepaniv, *Spirit. Prom. 29(2), 5*). Rinsing formulations for dishwashing purposes used monosaccharides treated with butylene oxide, followed by reaction with an organic dicarboxylic acid (Crecelius and Brunelle, *U.S. 3,098,065*). Fogging of glass or glass-like surfaces was prevented by cleaning with fibrous material impregnated with an alkylphenol polyoxyethylene glycol sulfate, nonionic surfactant and an alkyl sulfate in water and alcohol solution (Elias, *U.S. 3,075,258*). Adequate cleaning of dairy equipment was encountered in soft water when using a composition of sodium silicate, soda ash and ABS, but deposits occurred in hard water (Major, *Queensland J. Agr. Sci. 19, 107*). Optical lenses can be cleaned of pitch, wax or abrasives by using a chlorinated hydrocarbon such as tri- or perchloroethylene containing a small percentage of a cationic surfactant (Sherlicker and Ellis, *U.S. 3,085,918*). A composition especially useful for glass or dish cleaning comprised of nondiscoloring mixtures of chlorides of polyethoxylated phenols, and polyethoxylated alcohols blended with alkali metal hydroxides and silicates (Scheneck et al., *U.S. 3,061,552*).

SKIN CLEANERS. Used with syndets of the alkyl sulfate or alkylarylsulfonate type were lipoprotein complexes or degraded proteins, useful in bathing compositions (Morelle, *Fr. Adm. 79,425 to 1,260,505*). Cleansing agents for mucous tissues or wounds contain salts of ascorbyl and/or isoascorbyl fatty acid esters (Janistyn, *Ger. 1,142,217*). A nonfoaming, nongreasy, shaving composition usable without water contains NaCMC, a partially acetylated ethylene oxide derivative of lanolin alcohols and hydroxy esters, lanolin, sucrose, a cationic surfactant, menthol and perfume (Mueller, *U.S. 3,072,535*). A skin protecting agent was comprised of ABS and tertiary-amine oxides (Drew and Voss, *Ger. 1,138,497*). Citric acid or alkali metal citrates added to highly alkaline liquid detergents makes them nonirritating to the skin (Hagan Pneutronics

S.A. *Fr. 1,300,699*). A detergent composition was disclosed comprising non-soap anionic or nonionic surfactants, a water soluble formaldehyde carbocyclic aryl sulfonic acid or its salts and a hydroxy organic acid (Harding, *U.S. 3,083,166*). Cosmetic applications of sucrose esters and sucroglycerides were reviewed, with examples of formulations (Colson, *Riv. Ital. Sostanze Grasse 9, 472*). Beauty creams containing sucrose esters were discussed and formulations given (Rovesti, *Riv. Ital. Sostanze Grasse 9, 468*).

TEXTILE. Soap or non-soap syndets are used with a water soluble N-vinyl-2-oxazolidinone polymer for textile cleaning (Wallis et al., *U.S. 3,067,143*). Knitted cotton or woolen fabrics are washed with a composition comprising a formaldehyde-arenesulfonic acid condensate, citric, lactic or tartaric acid, anionic or nonionic surfactants and a fluorescent brightener (Harding, *U.S. 3,083,166*). Waterproofed textiles such as those impregnated with silicones or acrylic resins are washed with a mixture of sodium sulfonate in alcohol to which is added a liquid silicone (Tintoria Como di Lino Albionico, *Ital. 593,787*). Methods for cleaning wet press cloths were discussed and formulas for some chemical agents were given (Senchea, *Celuloza Hirtie (Bucharest) 11, 414*). Dyed fabrics can be laundered together with white fabrics when protective colloids such as vinylmethyloxazolidinone or polyvinylpyrrolidone are used with the detergent (Wallis et al., *U.S. 3,067,143*).

SHAMPOO. A liquid shampoo was comprised of a N-acyl sarcosinate, an alkyl sulfate or alkyl ethoxylated ether sulfate, acyl monoethanolamide and solvent (Anderson, *U.S. 3,085,067*). A shampoo reducing static electrification of dry hair was comprised of an acyclic hydrophobic radical with a water solubilizing anion, an intermediate member, e.g., amine, ether, etc., and an amine oxide (Lang, *U.S. 3,086,943*). Another product was claimed, containing a salt of N-acyl-N-methyl taurine, alkyl sulfates, a fatty alkylolamide, and an alkyl with a terminal hydroxyl group (Laiderman, *U.S. 3,072,580*). A mixture of an amphoteric surfactant and quaternary amines were disclosed as shampoos and washing agents (Freese, *Ger. 1,130,956*). Various water-dispersible amido-quaternary ammonium compounds were used in shampoos (Lee and Svarz, *U.S. 3,072,690*). Disclosed as foaming agents and shampoos were tris(hydroxyethoxy ethyl) amines and their phosphate or sulfonate products (Debydag Deutsche Hydrierwerke, *Belg. 620,530*). Quaternary ammonium salts having lower eye irritation were used for shampoo formulation (Kalopissis et al., *Fr. 1,313,143*). Used to emulsify mineral oil for hair application were fatty alkylolamides and aliphatic ether ethylene oxide adducts (Siegal et al., *U.S. 3,101,300*). Clear transparent aqueous gels were prepared from mineral oil, water, fatty alkylolamides and aliphatic polyoxyalkylene glycol phosphates (Siegal and Petgrave, *U.S. 3,101,301*). Reviewed were sulfosuccinates, fatty alcohol or fatty acyl alkylolamide derivatives, which are claimed as exceptionally suited to the skin and eyes (Dutton and Reinisch, *Mfg. Chemist 34(1), 4*).

MISCELLANEOUS COMPOSITIONS. Other compositions not easily classified follow. Improved cloud point compositions were claimed when polyethoxylated derivatives of polyhydroxy compounds such as glycerol, hexanetriol and the like were added to compositions such as alkyl sulfates and inorganic salts such as sodium sulfate (Moser and Teichmann, *Ger. 1,140,302*). A detergent paste or cream was obtained by mixing a light mineral oil with ammonium hydroxide or triethanolamine (Sobrero, *Fr. 1,311,280*). A solid shaped body is formed by reacting an organic diisocyanate with an ethylene oxide-containing surfactant (Shelanski and Levenson, *U.S. 3,098,048*). A dentifrice contained as detergent materials a sulfonated nondrying fatty oil, a sulfonated fatty alcohol or fatty acid with a hydroxy group, a sulfonated drying oil and a lower alkyl ester of a nondrying fatty oil (Morris, *U.S. 3,081,235*). Water-dispersible lecithin compositions were obtained using as surfactants a condensed sulfonic acid Na salt, nonylphenol ethylene oxide adduct (Cogwell, *U.S. 3,069,361*). A detergent was obtained using sisal juice, ABS and ethylenediamine tetraacetic acid (Rubin, *U.S. 3,075,924*). A solid laundry detergent was disclosed containing a dye reductable to the colorless form by adding an oxygen-yielding compound to the composition (Sinner and Fries, *U.S. 3,058,916*). A stain remover for leather and plastic films contained a synergistic combination of quaternary ammonium salts of hydroxyalkylbenzene with low-boiling solvents (Baumbach, *Ger. 1,144,427*). A powdered foam formaldehyde-urea resin was used as a carrier for surfactant and a solvent (Aschert, *Austrian 224,605*). Foam-improved ABS compositions are obtained by adding an alkylsulfonate and an alkylphenoxypolyglycol ether (Spitzer et al., *Ger. 1,150,171*).

ANALYSIS

MIXTURES. Types of nitrogen compounds in mixtures of surfactants were separated by paper chromatography. Differen-

iated were quaternary ammonium compounds, tertiary amines and ampholytes (Neu, *Seifen-Oele-Fette-Wachse* 88, 535). A scheme for qualitative separation of surfactants distinguished soaps, sulfonated oils or esters of unsaturated or phosphoric acids, protein fatty acid condensates or succinic esters, alkyl sulfates or alkylarenesulfonates, and condensates of fatty acid or ethylene oxide or alkyl sulfonates. Special tests identify individual members (Linsenmeier and Morgenroth, *Melliand Textilber.* 43, 1320). Separation of anionic from nonionic surfactants by ion-exchange and determination of soaps, primary alkyl sulfates, hydroxy- or amino-alkane sulfonates, and alkylarenesulfonates was detailed (Blumen, *Schweiz. Arch. Angew. Wiss. Tech.* 29(5), 171). Paper chromatography was used for separating and identifying anionic, cationic and nonionic surfactants (Drewry, *Analyst* 88, 225). UV absorption spectra were used for determining ABS, cationic and nonaromatic surfactants (Izawa, *Yukagaku* 11, 627).

Up to 20 ppm anionic or cationic surfactants in aqueous solution can be detected and determined by a liquid extraction-colorimetric procedure (Burger, *Z. Anal. Chem.* 196, 15). Also using a selective liquid-liquid partition technic made it possible to separate and quantitatively determine fatty acids, alcohols, amines, and amides and alkylated phenol ethoxylated adducts (*Ibid.* 22). A bromophenol blue-dichloroethane titration procedure was used for the titration of cationic surfactants in ternary cationic-ampholytic-nonionic systems by pH control (Izawa et al., *Yukagaku* 11, 309). The total active ingredient content of a cationic-ampholytic-nonionic ternary system can be determined by Kieselbach's liquid-liquid extraction method and the cationics determined as noted above. Nonionics were determined by a semi-micro cation-exchange UV absorption spectrophotometric method, and the ampholyte was determined by difference (*Ibid.* 364). Differential determination of cationics and nonionics in mixtures are determined with sodium tetraphenylborate and a differential indicator absorptiometric procedure (Uno and Miyajima, *Chem. Pharm. Bull.* (Tokyo) 11, 193). The *p*-toluidine titration method was used to determine anionic surfactants in their mixtures with soap (Bespyatov et al., *Maslob.-Zhir. Prom.* 29(4), 29). Anionic and cationic ore-floatation surfactants were determined in trace amt by means of the polarographic oxygen max (Dolezil and Kopanica, *Chemist-Analyst* 52, 76).

ANIONICS. Alkali metal soap and alpha-sulfo fatty acids were determined by titration with hydrobromic acid in glacial acetic acid using crystal violet as indicator (Haerberer and Maerker, *JAOCs* 40, 274). A rapid procedure for determination of fatty acids in toilet soap involves precipitation of the soaps as calcium salts and the excess calcium chloride is titrated with Trilon B with Chromagen Black indicator (Bartashevich and Kopysev, *Maslob.-Zhir. Prom.* 28(9), 34). Water in soap may be determined electrometrically, the procedure being based upon the dielectric constant (Cechnicki and Oleksiak, *Pluszcze i Srodki Piorace* 6(1), 16). IR spectroscopic and X-ray diffraction methods were used in examining the constituents of greases containing soaps (Dunken and Bottner, *Freiberger Forschungsh.* A251, 113). The thermal behavior of some aluminum soaps were investigated by thermogravimetric analysis (Rai and Mehrotra, *J. Indian Chem. Soc.* 40, 359).

Fatty alcohol sulfates were determined by flocculation analysis (Ullmann and Thoma, *Arch. Pharm.* 296(5), 344). Neutral red, which forms sparingly soluble products with sulfate or sulfonate type anionics, was used to determine sodium lauryl sulfate by forming the complex, extracting with dichloroethylene and determining the absorbance of the solution (Uno et al., *Yakagaku Zasshi* 82, 1017). The polarographic waves of *m*-nitrobenzene-sulfonic acid formed on the dropping mercury electrode are changed by fatty alcohol sulfates and this deviation was used in determining such compounds (Peter et al., *Magy. Kem. Folyoirat* 69(6), 255). Minute samples of alkylarylsulfonates may be desulfonated, and by GLC and mass spectrometry the structure of the sample can be determined (Setzborn and Carel, *JAOCs* 40, 57). Identification of alkylarenesulfonates may be achieved by alkali fission and phenol determination by paper chromatography (Borecky, *Microchim. Acta* 1962, 1137). Detergent alkylate mixtures were analyzed by a quantitative rearrangement phenomenon and employing sensitivity data independent of volume or pressure measurements and using the mass spectrometer (Boyer et al., *Anal. Chem.* 35(9), 1168).

UV spectrometry was used in determining ABS (Weber et al., *Anal. Chem.* 34, 1844). Dodecylbenzenesulfonates were examined by UV spectrometry and the various max for the product and unsulfonated residues given (Arpino and DeRosa, *Riv. Ital. Sostanze Grasse* 8, 386). The IR spectra of a number of ABS products were investigated and data covering various homologs and isomers given (Mironova et al., *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 26, 1317). Unsulfonated alkylates

in ABS were determined by IR spectrometry and the limit of detection was $\pm 0.1\%$ (Blakeway and Puttnam, *Anal. Chem.* 35(6), 630). IR spectrometry for estimation of ABS in water was considered complex and expensive for sewage plant or water works control. Instead, a modification of the methylene blue method employing a chromium-sulfuric mixture was used for precipitation of the ABS, and the hexavalent chromium was reduced to the trivalent state before developing the methylene blue color (Hill et al., *Am. Chem. Soc. Div. Water Waste Chem., Preprints* 1961, 6). Complex formation of sodium dodecylbenzenesulfonate with magenta with extraction of the complex with chloroform can be used to determine concentrations as low as 10^{-6} molar (Cropton and Joy, *Analyst* 88(1048), 516). The limitations of the methylene blue method for ABS determination were investigated and a detection of one ppm was found, error depending on ABS concn (Wayman et al., *U.S. Geol. Serv. Profess. Papers No. 450-B*, 117). The amt of sodium dodecylbenzene sulfonate remaining on tableware and vegetables washed in aqueous solutions of the surfactant was determined by radiotracer technic. Rinsing procedure affects results. Values for retained ABS were given, in the case of cabbage being 0.1-0.2 mg/100 g cabbage (Shinoda et al., *Shokuhin Eiseigaku Zasshi* 3(4), 387). ABS in tooth paste was alcohol-extracted and after hydrolysis of any sodium alkyl sulfate a methylene blue estimation was made (Sakuma et al., *Yukagaku* 12, 198).

Mixtures of toluene- and xylenesulfonates with ABS are separated by a column cation exchange process, using ammonium sulfate for elution purposes, the eluents being monitored by UV absorption measurements at 222 $m\mu$ (Anon. *Chem. & Eng. News* 41(11), 42). IR spectrometry was used in analyzing toluene- and xylenesulfonates, the method measuring the intensity of the S-O stretching vibration centered at 1175 cm^{-1} , and is applicable to ABS (Kullbom and Smith, *Anal. Chem.* 35, 912). Ammonium dodecylbenzenesulfonate is determined in commercial products by dissolving in absolute ethanol, cooling, filtering and titrating at 60C with sodium hydroxide (Espector, *Centro Quim. Ind.* (Buenos Aires) 1962, 42). An ion-exchange procedure was described for the determination of the mean mol wt of alkylarenesulfonates, alkanesulfonates and alkyl sulfates. Passage through a cation-exchange column gives strong acids. By knowing the concn of the sodium salt in water and the amt of potassium hydroxide for neutralization of the acid, the mol wt may be determined (Desnitskii, *Maslob.-Zhir. Prom.* 28(9), 31).

The exotherm, obtained by the titration of ABS with a specified cationic, was measured and used to determine ABS with a max relative error of 2% (Jordan et al., *Anal. Chem.* 35(10), 1534). The determination of small concn of surfactant such as potassium oleate was made by reaction of crystal violet with the surfactant using aeration, and the residual dye in the lower layer determined for absorbance at 590 $m\mu$ (Tomlinson and Sebba, *Anal. Chim. Acta* 27, 596). Alkyl sulfate or sulfonate surfactants can be determined by colorimetric titration using neutral red and a cationic surfactant (Uno and Miyajima, *Chem. Pharm. Bull.* (Tokyo), 10, 467). Anionic surfactants were estimated by a method based on the reduction in height of the polarographic step of methylene blue when anionic surfactant is added (Buchanan and Griffith, *J. Electroanal. Chem.* 5, 204). Trace amt of anionic surfactants were determined in water through the determination of organic nitro, nitroso and azo compounds with copper (Frankhouser, Univ. Microfilms (Ann Arbor), *Dissertation Abstr.* 23, 4512). The active ingredient in a liquid detergent is determined by titration with a quaternary ammonium salt in a 2-phase system. The migration of the dye from the aqueous to the organic phase is used to detect the end point (Cullum, *J. Soc. Cosmetic Chemists* 13, 348). A basic titration standard for estimation of surfactants by the Epton method is phenoxy-propane- ω -sulfonates, especially suitable being 2,4,6-tribromo and 4-benzyl derivatives which do not foam (Heinroth, *Fette, Seifen, Anstrichmittel* 64, 841).

The chloroform separation in the two-phase method for anionic determination is facilitated by using a shaking rack (Niemitz and Fuss, *Gas-Wasserfach* 104, 117). Automatic shaking for the Longwell and Maniece procedure is described (Brink, *Analyst* 87, 828). Sulfonated oil analytical methods were reviewed (Farran, *Lipidos* 22, (Jabones Section) 2). The contamination of fruits and vegetables was determined using solutions of S^{35} -tagged sodium dodecylbenzenesulfonate. Differences in amt retained were determined (Sasaki and Ito, *Yukagaku* 12, 228).

CATIONICS. Alkyl halide was used to remove tertiary amine interference in the potentiometric titration of long chain amine oxides (Metcalfe, *Anal. Chem.* 34, 1849). A precipitation reaction involving a titrant of sodium lauryl sulfate is used for cationic surfactant estimation, but not applicable to short-chain compounds such as choline or its derivatives (Thoma

et al., *Arch. Pharm.* 296(7), 417). A comparison of the bromophenol blue titration with a biological showed the former more sensitive for estimating quaternary ammonium compounds in milk (Lacrose, *Intern. Dairy Congr. Proc.*, 16th, Copenhagen 1962, Sect. C, 496).

NONIONICS. The hydroxyl equivalent wt of polyoxyalkylene compounds were determined by a phenyl isocyanate method (Reed et al., *Anal. Chem.* 35, 571). Identification of alkylphenols in their ethylene oxide condensates proceeds through hydrogen iodide reaction, decolorization with sodium thiosulfate, extraction with benzene and paper chromatography.

The spots are developed with potassium ferrocyanide or ferric chloride (Borecky, *Mikrochim. Acta* 1962(5), 824). Using silicic acid column chromatography with chloroform-acetone as eluant, the reaction products formed from ethylene oxide and nonyl phenol were separated (Ishiwata et al., *Bull. Chem. Soc. Japan* 36, 129). Surfactants of the nonylphenol ethylene oxide type are determined by complexing with dichlorofluorescein in acetic acid at pH 4 and measuring the absorbance at 490 m μ (Steward, *Analyst* 88(1047), 468). Nonionic surfactants were characterized by nuclear magnetic resonance (NMR) measuring the proton signal intensity in high resolution NMR spectra. Determined were the hydrophile to hydrophobe ratio without reference to standards (Greff and Flanagan, *JAOCs* 40, 118). Relative amounts of protons in propylene oxide and ethylene oxide condensates were determined to characterize the hydrophobe and find the hydrophobe to hydrophile ratio using high resolution NMR spectrometry (Flanagan et al., *Anal. Chem.* 35, 1283). Nonionic ether linkages are split with hydrogen bromide; the split products were purified and determined by gas chromatography. Good results were obtained also with alcohol ether sulfates (Bore and Gataud, *Rev. Franc. Corps Gras* 10(7), 399). The determination of ethylene oxide content of nonionic surfactants was accomplished with sodium tetraphenylborate as titrant and Congo red with barium chloride as indicator (Uno and Miyajima, *Chem. Pharm. Bull.* (Tokyo) 11, 75). This method was compared with others as to reliability (*Ibid.* 80). Pyrolysis and gas chromatography were used in determining the composition of various ethylene oxide-propylene oxide copolymers and various ethylenbutene copolymers (Neumann and Nadeau, *Anal. Chem.* 35, 1454). Minute amounts of nonionic surfactant could be detected through adsorption-controlled catalytic oxygen evolution at a graphite electrode (Elving and Smith, *Microchem. J., Symp.*, Ser. 2, 829). Trace detection and determination of surfactant polyethylene glycols was possible through the formation of an orange-red precipitate with potassium bismuthiodate plus barium chloride in dilute acetic acid. The precipitate was centrifuged and the height of the precipitate column used for estimation in 0.1-10 ppm levels (Burger, *Z. Anal. Chem.* 196, 251). TLC was used in the determination of mol wt distribution and degree of oxyethylation of polyethylene oxide compounds (Burger, *Ibid.* 259).

A colorimetric method for the determination of polyoxyethylene-type surfactants in low concn depended upon the determination of tungsten in the bariumphosphotungstic complex. The method was poorly reproducible, not sensitive and subject to interference (Ritter, *Chem. Ind.* (London) 1962, 1832). Polyethylene glycol in polyethylene oxide surfactants was determined by estimation of the total ethylene oxide and the total of hydroxyl groups, then relating the two values by calculation (Elworthy, *J. Pharm. Pharmacol.* 15(3), 216). The distribution of free polyethylene glycols in oxyethylenated amines was carried out by adsorption of the amines on strongly acid cation exchanger. Reaction of the ethylene oxide groups with hydrogen iodide and titration with sodium thiosulfate was used to determine the polyethylene glycols in the eluate (Obruba, *Collection Czech. Chem. Commun.* 27, 2454). TLC or silica gel was used to separate the polyethylene glycols from the nonionic surfactants (*Ibid.* 2968). A detailed description of all major analytical methods for determination of sucrose esters and sucroglycerides was given (Roussos, *Riv. Ital. Sostanze Grasse* 9, 451).

BUILDERS. Colorimetric and paper chromatographic techniques were employed in estimating the total orthophosphate content of detergents (Hagony and Jaky, *Fett, Seifen, Anstrichmittel* 65, 235). Paper chromatography was used in the quantitative and qualitative determination of phosphates in detergents (Kuebler, *Textil-Rundschau* 17, 683). A direct and rapid procedure involving the stability constants of the proton and some metal complexes formed by pyro- and orthophosphoric acids was evaluated from potentiometric titration measurements (Johansson and Wamminen, *Talanta* 10, 769). The concn and mean chain length of condensed phosphates was determined by titration of the acids liberated when the diacid form is treated with silver ion before and after acid hydrolysis. Flame photometry is a rapid method for sulfate determination (Cullum, *J. Soc. Cosmetic Chemists* 13, 348). Active total

oxygen in washing powders from compounds such as perborate or percarbonate is determined by iodometric titration. A colorimetric method using titanium chloride which does not react with persulfate is used for perborates plus percarbonates. Persulfate is determined by difference (Pokorny et al., *Papers of the Inst. of Chem. Tech. Prague 4-I*, 299).

MISCELLANEOUS. Lignoine and alcohol used in alkyl sulfate purification were determined; lignoine by distillation from a flask containing an oxidizing agent to avoid interference from alcohol. The oxidized mixture was titrated with Morh's salt to determine alcohol content (Babaev et al., *Maslob-Zhir. Prom.* 28(12), 28). An extensive review of surfactant analysis was made (Uno, *Yukuzaigaku* 22, 223). The applications of IR spectroscopy, and gas and ion-exchange chromatography in detergent analysis were reviewed (Bey, *Fette, Seifen, Anstrichmittel* 64, 900).

PROPERTIES

ADSORPTION. The max adsorption of nonylphenyl ether on wool was slightly lower than that of sodium dodecylbenzenesulfonate, the wool whiteness being proportional to greater detergency and increased adsorption (Kame et al., *Yukagaku* 12, 223). Radio-tagged hexadecyl and tetradecyl sulfates adsorbed on nylon film showed abrupt increase near the critical micelle concentration (CMC) and the desorption rate in water rose abruptly at a concentration corresponding to CMC, the effect of sodium chloride being small (Hayashi, *Acta Med. Nagasakiensis* 5(4), 197). Quaternary ammonium salts containing various anions were obtained by reaction of the corresponding amine salt with ethylene oxide. Arrangement of the salts of the hydrogen halides in order of increasing adsorption for cotton, rayon, nylon, orlon, tetron and wool were F, Cl, Br and I (Yamamoto et al., *Yukagaku* 11, 646). Adsorption of radiotagged ABS on kaolinite was studied using a tracer-membrane dialysis technique (Wayman et al., *U.S. Geol. Surv., Profess. Papers No. 450-E*, 181). Adsorption of radiotagged ABS on montmorillonite was studied, the longer chain ABS being adsorbed to greater extent, initial adsorption being hastened by orthophosphate ion, acidic pH 4 solutions with 1000 ppm di- or trivalent salts being optimum (*Ibid.* 475-B, 213).

Adsorption of dodecylammonium benzoate on carbon blacks in hexane was studied, most blacks showing a Type I adsorption (Kobayashi and Kitahara, *Nippon Kagaku Zasshi* 83, 1158). The adsorption of anionic, cationic and nonionic surfactants and their emulsified mixtures with nonpolar oils on coking coals exhibited a linear function of concn up to 2% (Beilin and Emal'yanov, *Izv. Vysshikh Uchebn. Zavedenii, Gorn. Zh.* 6(1), 185). The anionic adsorption values for sediments, clays and humic acid were studied by determining residual unadsorbed sodium dioctylsulfosuccinate, and the values related to humic acid (Lenhard et al., *Hydrobiologia* 21(1-2), 177). Selective adsorption studies at the air/solution interface of aqueous solutions were made with radiotagged sodium soaps and dodecyl sulfate, the measurements being made on equal volumes of collapsed foam and bulk solution. The difference in the ratio of radioactivity of C¹⁴ and S³⁵ (alkyl sulfate) indicated the competitive adsorption values (Shinoda and Kinoshita, *J. Colloid Sci.* 18, 174). The differential capacities of the electric double layer between mercury and aqueous saline solutions of sodium octyl sulfate were measured by the impedance bridge method. The peculiarities of the data are discussed (Eda, *Nippon Kagaku Zasshi*, 80, 343, 349).

Interfacial tension and mercury electrode capacity were determined as a function of concn of sodium benzene disulfonate. The adsorption data were fitted to a Temkin isotherm (Perry and Parsons, *Trans. Faraday Soc.* 59, 241). The adsorption isotherms for tetrabutyl ammonium cations adsorbed on mercury were developed and discussed (Damaskin et al., *Zh. Fiz. Khim.* 36(10), 2530).

ANIONICS. Proton resonance adsorption curves for higher sodium alkane carboxylates and water systems were prepared (Noguchi, *Nippon Nogei Kagaku Kaishi* 34, 416). Hydrated water in these same systems by dielectric constant measurement indicate that soap with a high degree of crystallinity is hydrated (*Ibid.* 420). Soaps both moisture-free and normal were investigated for hydrated water by IR absorption spectra, dielectric constant and X-ray diffraction (*Ibid.* 694). Electrical resistance measurements of commercial soap with less than 30% water show one or more inflection points apparently connected with phase transitions due to interaction of soap molecules and water. Unsaturated soaps generally lower the transition temp (Ezaki et al., *Kogyo Kagaku Zasshi* 62, 534). Electron diffraction patterns were obtained for sodium laurate and stearate (Grothe and Schimmel, *Naturwiss* 49, 535). Fatty acid soaps with two to three side chains were synthesized and evaluated. Foaming and wetting properties of solutions increased with increasing mol wt whereas branched

chains decreased these properties (Petrov et al., *Tr., Vses. Nauchn.-Issled. Inst. Zhirov* 1960(20), 278).

Kettle wax phase occurring in the sodium palmitate-water-electrolyte system at 90°C was subjected to an X-ray diffraction study, showing lack of a simple phase, but was a mixture of curd, neat and lye (Vincent and Skoulios, *JAOCs* 40, 20). The viscosity of ammonium lauryl sulfate solutions was measured at 20-70°C using various applied shearing stresses. Behavior of Newtonian or pseudo-plastic fluid was apparent (Mateo, *Afnidad* 19, 453). Changes in the crystal and the crystal-to-liquid-crystal state can be established by IR spectrometry for the clarification of phase structure of soaps as grease components (Trzebowski and Kaseh, *Freiberger Forschungsh. A251*, 143).

The association of aluminum trisoaps of several saturated fatty acids in five solvents was determined using a high precision differential ebullioscopic technic (Rudakoff and Knispel, *Fette, Seifen, Anstrichmittel* 64, 1046). The structural viscosity of aluminum distearate in benzene was measured by capillary viscometry (Nagasaki et al., *Yakagaku Zasshi* 83, 185). Mol wt of some aluminum soaps were measured in various organic solvents. The trisoaps were monomeric, the alkoxy soaps dimeric and mono- and dichloride soaps trimeric in solution. Probable structures were suggested (Mehrotra and Rai, *J. Inorg. Nucl. Chem.* 24, 961). Cadmium soap structures of the mesomorphic phase at elevated temp were described as corresponding to the packing of cylindrical structural elements according to a two-dimensional hexagonal array (Spegt and Skoulios, *Acta Cryst.* 16, 301).

The properties of organic solutions of heavy-metal soaps were reviewed (Pilpel, *Chem. Rev.* 63, 221). The solubilities of magnesium soaps of linear carboxylic acids were given (Irani, *J. Chem. Eng. Data* 7, Pt. 2, 580). The surface activity of poly (sodium dodecylvinyl ether comaleates) was determined, the solubilizing power for *n*-octanol being higher than for monosoaps, surface tension decreasing with increasing lipophilic character, with poor but stable foaming power, and a CMC at 0.2 wt % (Sakai, *Kogyo Kagaku Zasshi* 65, 961).

CATIONICS. Mixed colations of cationic polysoaps and polyallyl-type cationic surfactants were evaluated for viscosity, surface tension, foaming, wetting and solubilizing power (Narasaki, *Kogyo Kagaku Zasshi* 65, 796). Cationic surfactants with two hydrophilic groups/molecule were prepared and good wetting properties were found (*Ibid.* 799). Mixtures of *N*-dodecylpyridinium bromide and nonionic surfactants were measured for CMC, wetting, foaming, emulsifying and solubilizing power. Used were nonionics such as nonylphenyl ethylene-oxide adducts, sorbitan monolaurate and polyethylene oxide sorbitan monolaurate. These mixtures caused marked synergistic effects on wetting, foaming and solubilizing power (Narasaki and Suzuki, *Ibid.* 801). Organic acid salts of *N*-*n*-alkylethylene diamines were prepared and optimum surface activity was found for *N*-*n*-dodecyl or tetradecyl salts (Kimura et al., *Yukagaku* 12, 105). Polyvinyl pyridines of different degrees of polymerization were evaluated. Surface activity as evidenced by wetting, aggregation, surface tension, foaming, dispersing and solubilizing action increased with decreasing degree of polymerization (Narasaki, *Kogyo Kagaku Zasshi* 65, 1282).

The foaming, dispersing and bacteriostatic properties of quaternary ammonium salts such as $(C_{12}H_{25}N(CH_3)_2C_2H_4OH)X$, where X was any of a number of anions and quaternary ammonium chlorides, were measured. Bacteriostatic properties were little affected by type of anion (Yamamoto et al., *Yukagaku* 12, 415). Various types of cationics were evaluated as to adsorption, foaming and corrosion-inhibiting properties. Adsorption on a variety of powdered substrates was only partially reversible and is a function of pH and nature of the alkyl group. In the presence of anionic compounds, adsorption rises steeply to a max at unit mole ratio of cationic: anionic (Mueller and Krempl, *Fette, Seifen, Anstrichmittel* 65, 532).

COMPLEXES. Various dyes and anionic, cationic and nonionic surfactants were paper-chromatographed and R_f values determined. Much data were developed and discussed on the basis of a theory in which formation of association complexes between dyes and surfactants was assumed (Gotoh and Hayama, *Nippon Kagaku Zasshi* 84, 104). Interaction of dyes with anionic and cationic surfactants was studied photometrically (Haque and Malik, *J. Phys. Chem.* 67(10), 2082). Meta-chromatic changes in formation of complexes of dodecyl sulfate-dodecyl alcohol occurred at 1:2 ratio (Maruta and Takiwa, *Nippon Kagaku Zasshi* 82, 1657). Dodecyl sulfate showed a marked rate of desorption in mixed films with gelatin, evidence of an interfacial compound (Kretzschmar, 3rd. *Intern. Congress on Surface Active Materials, Cologne* 1960, 2, 344).

An anionic surfactant increases the viscosity of gelatin solutions, the increase being dependent on pH and structure.

Nonionic surfactants had no effect on viscosity. The effects on other surfactants were studied (Kalinkina et al., *Yadern. Fotogr., Akad. Nauk SSSR, Tr. Tret'ego. Mezhduar. Sovesh.*, Moscow 1960, 116). Formation of precipitates or soluble complexes between solutions of zinc chloride and surfactants was investigated by pH and conductivity titrations. The effects produced by various surfactants are described (Vold and Singh, *JAOCs* 39, 424). By studies of pH, light transmission and diffusion coefficient, dimethyldodecylamine oxide and sodium dodecylbenzenesulfonate have been found to interact (Kolp et al., *J. Phys. Chem.* 67, 51). Adsorption spectra of toluidine blue and conductivity measurements were used to follow the complex formation between sodium dodecyl sulfate and long alkyl chain compounds (Murata, *Nippon Kagaku Zasshi* 83, 788). The effects upon solubilization of yellow OB were used to show interaction between several types of surfactants with polyvinyl pyrrolidinone (Murata, *Ibid.* 786). A further study with other polymers was made (*Ibid.* 858). Addition of sodium oleylmethyltaurate to milk increased rennet coagulation time and decreased the optimum temp (Rotini and Ferrera, *Intern. Dairy Congr. Proc., 16th, Copenhagen* 1962, Sect. B, 473).

DETERGENCY. Fat-derived amphoteric surfactants possessing both a quaternary ammonium group and an imidazoline and an anionic (sulfate, etc.) functional group were studied. Detergency of single-chain compounds was superior to that of double chained and the latter showed better fabric softening; ABS types and soap were incompatible with these amphoteric, nonionics being more compatible (Linfield et al., *JAOCs* 40, 114). The relationship between detergency of an alkylphenyl nonionic and its other surface active properties was investigated in comparison with ABS and lauryl sulfate. Soil character strongly affected detergency of the two types, the nonionic surfactants being soil selective (Kame et al., *Yukagaku* 12, 173). The whiteness of wool washed with ABS and poly (oxyethylene) nonylphenyl ether adduct was almost proportional to the amt adsorbed, the nonionic being less effective (*Ibid.* 223). Poly (oxyethylene) nonyl phenyl ethers of varying ethylene oxide contents were evaluated, showing that surface tension increased and wetting, soil redeposition and detergency on wool, silk and capron decreased as the number of moles of ethylene oxide increased. Foam formation increased and foam stability decreased as the temp increased (Polyakova et al., *Maslob.-Zhir. Prom.* 28(10), 22). The detergency of propylene glycols reacted with ethylene oxide varied widely with the nature of the fabric being cleaned (Nevolin et al., *Ibid.* 29(7), 23). High detergent activity and complete assimilability by bacteria were evident for hydroxylated esters of saccharose and fatty acids (Simonis and Ismail, *Angew. Chem.* 75(16/17), 791). The detergency of α,α -dimethyl alkanolic acids began to appear with salts of C_{14} acids, while satisfactory foam properties occurred with C_{17-18} acids (Puzitskii et al., *Zh. Prekl. Khim.* 35, 2740).

Glass plates soiled with tallow, olive oil and violet brown and washed with cationic, nonionic and anionic surfactants were cleaned satisfactorily by laurylpyridinium chloride, especially when mixed with alkylphenyl ethylene oxide adduct (Kajl and Cybulska, *Thuzsze i Srodki Piorace* 5, 310). A kinetic approach to detergent synergism in removal of baked milk films by NaOH, a nonionic surfactant or their mixtures was developed. Synergism of the two component system occurred below the cloud point temp, but was lost above that point (Jennings, *JAOCs* 40, 17). The stability of oil droplets and gas bubbles on liquid surfaces was used to study the mechanism of dirt removal. The effects produced by builders and the like are discussed (Rosano and Montagne, *Rev. Franc. Corps Gras.* 10, 9). The shape of the cleaning curve, obtained with radiotagged tristearin and sodium hydroxide, led these investigators to suggest the existence of two species of soil (Bourne and Jennings, *Nature* 197, 1003). The effect of temp, detergents, electrolyte, agitation and fabric structure on the removal from cotton of octadecane, tripalmitin, stearyl alcohol and radiotagged stearic acid was studied. Mechanisms found were rolling up, mesomorphic phase formation, soap formation and break-up of polycrystalline aggregates. The magnitude of electrolyte effect was measured (Scott, *J. Appl. Chem.* (London) 13(3), 133).

ELECTRICAL. Surface compression and surface potential properties of monolayers of stearic acid were examined on solutions of pH 2-11.1. Marked changes in electrical characteristics and cohesion of the monolayer occurred at pH 9. Related changes and speculation concerning the monolayer structure and the effect of sequestering agents are discussed (Goddard and Ackilli, *J. Colloid Sci.* 18(6), 585). Contact potentials for the adsorption of dodecyltrimethylammonium bromide and sodium dodecyl sulfate at *n*-heptane/sodium chloride interfaces agreed with values predicted from a theory based on film ionization (Heydon, *Kolloid Z.* 185(2), 148).

The surface potential vs. conen curves of polyethylene oxide dodecanols and octadecanols in 0.001 M HCl solution were determined as a function of ethylene oxide chain length. The data developed indicate that the amphiphathic molecules orient above the air/water interface and the ethylene oxide chains form coils in the aqueous phase (Schick, *J. Colloid Sci.* 18, 378). Surface pressures and potentials of spread monolayers of sodium octadecyl sulfate at the air/solution interface were measured and the variations with respect to surface area and electrolyte conen in the sub-solution were analyzed in terms of current theories of the ionic double layer (Mingins and Pethica, *Trans. Faraday Soc.* 59(488), 1892). A rapid method for classifying surfactants was based on the linear relation between the polar valence of a surfactant as indicated by its HLB and the log of its dielectric constant (Gorman and Hall, *J. Pharm. Sci.* 52, 442). The electrokinetic properties of the rutile/dodecyl sulfate solution interface were influenced by pH, adsorption of dodecyl sulfate anions decreasing with pH increase, though flotation simultaneously decreased (Graham and Madeley, *J. Appl. Chem.* (London) 12, 485). Electrophoretic mobility of polystyrene latex particles stabilized by sodium lauryl sulfate was measured by the moving boundary method. Z potentials were calculated, adsorption, and CMC measured (Sawyer and Rehfeld, *J. Phys. Chem.* 67(10), 1973).

EMULSIONS. Ammonium oleates and stearate can produce either water-in-oil or oil-in-water emulsions, the latter giving somewhat more viscous products (Wood, *Am. Perfumer Cosmet.* 77(10), 117). Emulsions prepared with triethanolamine soaps are distinguished by small particle size, ease of preparation, noncorrosiveness, formula flexibility and stability (Failla, *Ibid.* 77, Sect 2, 95). The interaction of oil- and water-soluble emulsifiers was measured with respect to stability and emulsion type where a more than additive increase was observed in all cases (Sonntag and Klare, *Z. Physik. Chem.* (Leipzig) 223(1/2), 8). Reviewed was the hydrophobe/lyophobe balance method for preparing emulsions (Wachs, *Adhaesion* 6, 553). Also reviewed was the effect of electrolytes on emulsions stabilized by anionic soaps (Bohn, *Finska Kemistasamfundets Medd.* 72(1), 40).

FOAM. Foam-formation and stability of polyoxyethylene tridecanols, tert-octylphenols, nonylphenols, dodecanols and octadecanols were determined as a function of ethylene oxide chain length. The most stable foams were comparable to that of sodium dodecylbenzenesulfonate without added foam stabilizer. Foam formation and stability pass through a max in which nonylphenol products were much higher than the dodecanol series (Schick and Beyer, *JAACS* 40, 66). Foam properties of ABS and nonionic surfactants failed to form stable foams at 2-3 ppm conen, while Hyamine 1622 required conen of greater than 8-10 ppm. Foams of ABS and nonionics were more stable than that of cationics. Nonionic stability increased as the ratio of hydrophobic to hydrophilic groups was increased. The relation between surfactant conen and foam stability was nonlinear and stability increased with decreases in temp. Effect of bacteria on surfactant foam was discussed (Wayman et al., *U.S. Geol. Surv., Profess. Paper No. 450-D*, 188). The foaming properties of quaternary ammonium chlorides prepared by reaction of amines with ethylene oxide were affected little by the cationic constituent but much by anions. The perchlorate, benzoate and *p*-toluene sulfonate products were superior (Yamamoto et al., *Yukagaku* 12, 415). The effect of keratin hydrolyzate upon the foam of ABS, lauryl sulfate and a nonionic was determined (Oneto, *Soc. Hydrotech. France, Compt. Rend. Journees Hydraulique, 7emes, Paris, 1962, 1*, 202). The foaming properties of mixtures of nonylphenyl ethylene oxide adducts with sodium laurate, myristate and palmitate were measured. The foaming properties of the surfactants were decreased by small additions of soap (Yano et al., *Yukagaku* 11, 304).

Foam fractionation was used to separate the various ethylene oxide fractions of an octylphenol 1:9 ethylene oxide M ratio adduct. A separation over 44 hr gave 37 stable fractions. Hydrophilicity decreases with increasing temp and/or decreasing number of ethylene oxide groups. (Prins, *Rec. Trav. Chim.* 82(4), 329). An apparatus was detailed for the quantitative separation of surfactants from dilute aqueous solutions (Skomoroski, *J. Chem. Ed.* 40(9), 470). Falling velocities of glass spheres in water and in sodium dodecyl sulfate solution confirmed that air bubbles rise as spheres within which circulation of the contained air is suppressed by adsorption of the surfactant (Okazaki, *Kolloid-Z.* 185(2), 154). Bubbles in this soap film are ruptured in doughnut-shaped depressions where radii are less than the range of the α particles from a Po^{210} irradiation source. Foam rupturing ability of the particles appears to increase as their energy decreases (Kato and Kono, *J. Appl. Phys.* 34, 708).

Foams stabilized by anionic surfactants were broken faster by spraying with a foam stabilized with a cationic surfactant than by spraying with the unfoamed cationic though both foams were destroyed (Sebba, *Nature* 197, 1195). The foaming properties of aliphatic alcohol and alkylphenol ethylene oxide derivatives were measured by the Ross-Miles and a semi-micro method, the latter proving unsuitable (Tagawa et al., *Kogyo Kagaku Zasshi* 65, 949).

The foaming properties of ethylene oxide derivatives of fatty acids, fatty acid amides and aliphatic amides were similar to the results obtained above (*Ibid.* 953).

MICELLES. Ampholytic surfactants form micelles in aqueous solution and exhibit well defined CMC. The log of CMC decreases linearly with the number of carbon atoms in the alkyl group. The shape of log CMC vs. carbon number is steep and nearly equal to that of nonionics whereas the CMC values are far larger than that of nonionics with the same alkyl chain length. The CMC values approach those of anionics. Many other pertinent conclusions are drawn (Tori, *Shionogi Kenkyusho Nempo* 12, 77). The CMC of alkyl betaines were determined with Sudan III (Tori and Kanagawa, *Kolloid-Z.* 187(1), 44). Color changes of water soluble dyes with alkyl betaines, an anionic, nonionic and cationic surfactant were studied. Rough CMC values could be determined empirically from the inflection point on the absorbance vs. conen curve (*Ibid.* 191(1), 42). Studied were the CMC values and micellar wt of two alkyl betaines, using several measurement methods (Tori et al., *Ibid.* 191(1), 48). The CMC values for three alkylbetaines were determined conductometrically. The area/molecul, surface excess concentration and heat of micelle formation were also obtained. Determined were the effects of added salts, temp and solubilization (Tori and Nakagawa, *Ibid.* 189(1), 50). Attempts were made at micellar size determination by the polymerization of all molecules in a micelle, though not highly successful (Hyde and Robb, *J. Phys. Chem.* 67(10), 2089). Manometric and radiotracer methods were used in studying sodium dodecyl sulfate solutions and several low mol wt alkanes. Data were said to support the hydrocarbon-liquid model of the micellar interior (Wishnia, *J. Phys. Chem.* 67(10), 2079). The dependence between interfacial tension, foam formation, foam stability and CMC was studied for alkyl sulfates. Surface tension and foam formation were conen dependent, CMC being determined from the break in the surface tension-conen curve. Foam formation changed irregularly but at conen below CMC (Bespyatov and Leshchenko, *Maslob. Zhir. Prom.* 28(9), 20). The effect of bivalent metals on alkyl sulfate micelle formation was determined by conductivity measurements, finding that a common CMC occurred (Satake et al., *Bull. Chem. Soc. Japan* 36(2), 204). Orientation of micelles differs in the outer and inner layers of soap, causing cracking of commercial soaps (Nakaido, *Kogyo Kagaku Zasshi* 62, 1835). Addition of surfactant builder electrolytes to sodium laurate and naphthenate were most effective in decreasing CMC, trisodium phosphate being most effective, and sodium chloride least. This suggested that mixtures could be obtained, equivalent to longer carbon chain compounds (Demchenko et al., *Ukr. Khim. Zh.* 28, 611).

Experiments were made in micellar-mol wt (MMW) determinations using the Archibald centrifugal method in a Hitachi analytical ultracentrifuge (Kakiuchi et al., *Bull. Chem. Soc. Japan* 36(10), 1250).

A micellar wt of 4500 was obtained for cupric oleate in benzene using magnetic susceptibility, absorption spectra in near UV, solubilities, viscosities and mol wt of the solution (Satake and Matsuura, *Mem. Fac. Sci., Kuyushu Univ. Ser. C*, 5(1), 13). The CMC values for sulfated nonylphenyl ethylene oxide adducts were determined by surface tension measurements. Though the ethylene oxide chain length effect on CMC followed a linear expression similar to that of nonionics, the influence of temp on cloud point suggested a basic difference between the two types of surfactants (Milcovic, *Helv. Chim. Acta* 46, 188). Studies by pH, light transmission and diffusion coefficient for dimethyldodecylamine oxide and sodium dodecylbenzenesulfonate showed interaction in several ways. The CMC of the 2:3 mole ratio system of anionic to amine oxide was lower than that of either surfactant alone, while the M ratio in the mixed micelles is ca. 1:2 (Kolp et al., *J. Phys. Chem.* 67, 51). Dilute solutions of dodecyltrimethyl ammonium bromide in various salt solutions were examined by light scattering, counterion effects on the CMC and aggregation number only roughly followed the anion isotropic series (Anacker and Ghose, *J. Phys. Chem.* 67(8), 1713). The Ferguson principle is applicable to the relation between the bacterial activity of quaternary ammonium salts and CMC (Ecanow and Siegel, *J. Pharm. Sci.* 52(8), 812). Slow equilibration of micellar cationic surfactant solu-

tions was measured by several methods (Peper and Taylor, *J. Colloid Sci.* 18, 318).

Dissolved urea was suggested as a probe for studying water-structure contributions to micelle formation and hydrophobic bonding with a cationic surfactant by UV spectrometry (Mukerjee and Ray, *J. Phys. Chem.* 67, 199). The CMC's of nonionic ethylene oxide surfactants in water and aqueous electrolyte solutions were determined from the conen dependence of surface tension at 1.0–55°C. For comparison, sodium *n*-dodecyl ether alcohol sulfates, sodium dodecyl sulfate and *n*-dodecyltrimethyl ammonium bromide were included. The thermodynamics of micelle formation were then discussed (Schick, *J. Phys. Chem.* 67(9), 1796). Light scattering, solubilization and viscosity measurements were used at different temp to study changes in micellar properties of nonionic surfactants as their lower consolute temp was approached. Micellar wt increased exponentially with temp increase. Micellar size increase had little influence on solubilization, but viscometry indicated that particle asymmetry increased with mol wt increase (Balmbra et al., *Trans. Faraday Soc.* 58, 1661). The effect of sucrose addition to lauryl alcohol ethylene oxide adduct was used to show that electrolyte effect on CMC was not due to changes in the solvent (Becher, *J. Colloid Sci.* 18, 196). MMW of dodecyl ethylene oxide adducts were determined in the ultracentrifuge. The data showed that MMW on the aggregation number is highly dependent on chain length, micelle formation being related to the steric effect as well as the hydrophilic properties of the ethylene oxide chain (Tokiwa and Isemura, *Bull. Chem. Soc. Japan* 35, 1737). A mechanism of interaction similar to mixed micelle formation occurs with a nonionic and cationic surfactant and could affect drug solubility (Hurwitz et al., *J. Pharm. Sci.* 52(9), 893). The CMC values of nonylphenyl ethylene oxide adducts were determined by their spectral behavior with pinaeyanol chloride (Nevolin et al., *Mastob.-Zhir. Prom.* 28(10), 22). On the basis of kinetic wetting isotherms for a number of surfactants, including an anionic and a nonionic alkyl phenyl product, the critical initial and final conen for CMC were measured (Levitskii et al., *Dokl. Akad. Nauk SSSR* 149, 633). Partial molal volumes of sodium alkyl sulfates and sodium alkane sulfonates in the micellar, singly dispersed and hydrated forms were determined by dilatometry. The values of partial molal volume are used to calculate pressure dependence of CMC, or solubility (Shinoda and Soda, *J. Phys. Chem.* 67(10), 2072). Diffusion coefficients of surfactant micelles were determined using surfactant solutions, dyes soluble in micelles but water-insoluble and fritted glass disks. These were impregnated with surfactant solution with and without dye tracer, separated and dye transfer measured (Mysels and Stigter, *U.S. Dept. Com., Office Tech. Serv.*, PB Rept. 158,770). A dialysis cell was described, used in demonstrating that the activity of the surfactant monomer increases with increasing conen even above CMC, contrary to the usual view that monomer and micelles are in phase equilibrium (Mysels et al., *J. Phys. Chem.* 67, 1943). The CMC values, area/molecule and area/OCH₂CH₂ unit were determined for ethylene oxide derivatives of CH₃(CH₂)₁₅OH (Elworthy and Macfarlane, *J. Pharmacol. Suppl.* 14, 100).

MISCELLANEOUS PROPERTIES. The significance of the relationship between the linearity constants of the detergency-micellar solubilization function and surfactant HLB boundary tensions, and soil dipole moment was extended by showing their existence in systems of four homologous surfactants with one soil, or four soils and one surfactant (Mankowich, *JAOCs* 40, 96). Potentiometric measurements of nonionic surfactants on the pH of strong acids, strong alkalies and buffer solutions were made (Donebrow and Rhodes, *J. Pharm. Pharmacol.* 15, 233). Combined film balance and electron microscope technics were used to study monolayers (Reis, *Proc. Am. Petrol. Inst. Sect. III*, 42, 152). A new interfacial balance constructed of nylon was used to measure spread films at the oil/water interface (Jones et al., *J. Colloid Sci.* 18, 485). A strain gauge attached to continuous recording equipment was used to study the tensions of isolated detergent films. Studied was the system sodium dodecyl sulfate/dodecanol (Grabenstein and Corkill, *J. Colloid Sci.* 18, 401). Compression of the surface was shown to produce reduction in surface tension and increase the possibility of foaming, as applied to river and stream effects (Lange, *Kolloid-Z.* 188(1), 44).

The nature of interfacial hydrolysis for a system of high area: volume ratio was studied for various surfactants (Eagland and Franks, *3rd Intern. Congr. on Surface Active Materials, Cologne, 1960*, 3, 539). Reviewed were phase diagram, triple point and Krafft point of anionic surfactants (Dervichian, *Ibid.* 1, 182). Coacervation in cationic surfactant systems was studied (Vassihades, *Dissertation Abstr.* 23, 3154). Mass-

transfer coefficients for the process of solid dissolution varies with solute purity. Surfactants may increase or decrease the transfer rate or leave it unchanged, behavior depending upon solute purity and surfactant ionic nature (Ghosh and Perlmutter, *A.I.Ch.E.J.* 9(4), 474). The coalescence of two mercury spheres as a function of kind and conen of surfactant was studied in an apolar medium (Sonntag, *Z. Physik. Chem. (Leipzig)* 221, 365).

Griffin's HLB was discussed, the equation based on the balance described and its occasional unsuitability noted, though other methods fail to attain the same degree of application (Racz, *Gyogyaszervet* 7(2), 43). Cracking or breaking of silica-alumina hydrogel beads was markedly decreased by gel immersion in a surfactant solution before drying (Ukihashi and Furuichi, *Ind. Eng. Chem., Prod. Res. Develop.* 2(3), 232). The thermodynamic foundations for the influence of surfactants on crystal growth were studied (Engelhardt, *3rd Intern. Congr. on Surface Active Materials, Cologne, 1960*, 2, 202). A method was developed and applied to the study of soap transport phenomena in latex by a dialysis technic. It is possible to measure surfactant migration rate, CMC, effect of alkyl chain length and sorption and desorption in latexes (Bobalek and Bell, *Offic. Dig., Federation Soc. Paint Technol.* 35(460), 423). Viscoelastic dependencies were investigated for coned solutions of two nonylphenol ethylene oxide adducts, using a phase-difference method with an oscillational rheometer. The experimental results are discussed in relation to the structure of such solutions (Kuroiwa et al., *Kogyo Kagaku Zasshi* 65, 2032). Studied similarly were ethylene oxide dodecyl ether sodium sulfate and sodium dodecyl sulfate (*Ibid.* 66(2), 212).

Water evaporation control by monolayers of *l*-hexadecanol was studied (Kromoyan and Pogosyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* 16(2), 97). The increase in conen of sodium dodecyl sulfate at the air/solution interface was followed by tagging with S³⁵. The rate of surfactant buildup at the interface during evaporation is essentially diffusion controlled (Jackson and Krause, *J. Phys. Chem.* 67(11), 2355). A composition to inhibit water evaporation was comprised of various waxes, a mineral lubricating oil to impart flexibility, a relatively light hydrocarbon to improve fluidity and an ester type of oxidate of deoiled macrocrystalline wax (Eckert and Hall, *U.S. 3,095,263*). Measured under varying conditions were the contact angles in quartz/dodecylammonium acetate/nitrogen system (Smith, *Proc. S. Dakota Acad. Sci.* 41(26), 150). Wettability and surface tension of sodium decyl, dodecyl and tetradecyl sulfates were measured, the wetting isotherm being valid also for fatty acid homologs (Tsunoda and Sasaki, *Bull. Chem. Soc. Japan* 36, 450). A review lecture discussed many phases of the physical chemistry of detergents (Garrett, *Chem. Ind. (London)*, 1963, 1606). The nature of a clean surface was discussed (Dillon, *Ann. N.Y. Acad. Sci.* 101, Art. 3, 634).

MIXTURES. Alkylamides added to alkylarenesulfonates in 10% amt increased detergency 1.4–3.7 times (Oreckin et al., *Mastob.-Zhir. Prom.* 28(10), 27). Fatty acid monoethanoldamides increase the detergency and foam action of suds (Varlanov, *Opyt Primeneniya Sintetich. Zhirozamenitelei v Proizv. Myla i Moyuschikh Sredstv*, Moscow 1962, 135). Synergism in detergency was obtained by using binary mixtures of surfactants (Nevolin, *Ibid.* 126). Viscosity and surface tensions of solutions of sodium dodecyl sulfate and dodecyl alcohol were measured, and the effects of polymers such as NaCMC, polyvinyl alcohol, starch and polyvinyl sulfate studied (Maruta and Tokiwa, *Nippon Kagaku Zasshi* 83, 732). Soaps of low turbidity point were obtained by mixing a tallow-coco-palm oil soap with ABS and sodium EDTA (Prosch, *Ger.* 1,141,040). The equivalent conductance and kinetic viscosity of mixtures of sodium dodecyl sulfate and dodecyl alcohol lowered conductance, explained on the basis of the formation of a complex (Tokiwa, *Bull. Chem. Soc. Japan* 36, 281). Emulsifying and water-insoluble material dispersing action was obtained by mixing an alkali metal alkyl sulfate with the water-soluble condensate of hexitol anhydride and an alkylene oxide (Surgant, *U.S. 3,095,353*). Dodecyl ethylene oxide ether properties were measured and compared with those of mixtures with polyvinyl pyrrolidone and polyvinyl alcohol, but no special interaction was noted (Maruta, *Nippon Kagaku Zasshi* 83, 851).

NONIONIC. The effect upon properties of varying ratios of ethylene oxide to nonylphenols was determined. Surface tension was less with 10 mole ethylene oxide than for 13 or 30, wetting power was in the reverse order, while detergency was equal to that of ABS. Electrolytes had little or no effect on these properties (Nevolin et al., *J. Prakt. Chem.* 15, 206). The properties of straight chain alkylphenols was not determined solely by HLB, but by the position of the phenyl

group (Frank and Denk, *Fette, Seifen, Anstrichmittel* 65, 46). The properties of purified nonylphenol ethylene oxide adducts were not affected in foaming or cloud point by added polyethylene glycol, but did affect wetting. Added nonylphenol did not affect wetting but markedly affected foam and cloud points (Onada, *Yukagaku* 12, 48).

Sucrose esters and related compounds and their properties were reviewed (Nobile, *Riv. Ital. Sostanze Grasse* 9, 439). (Passedouet, *Ibid.* 464). Addition of low mol wt hydrocarbons to ethylene oxide-nonionic surfactants lowered the cloud point by as much as 20-30C, while paraffin waxes increased cloud point. Fatty alcohols produced the opposite effect, and no effect on cloud point was found when total concn of surfactant and hydrocarbon was varied 10% (Fugazza, *Ibid.* 11, 567). Small amt of added nonionic ester sulfate significantly increased cloud point of nonionics. ABS will also raise cloud point, but with up to 0.25 mole the foam values also increased (Karabinos and Colaric, *Soap Chem. Specialties* 38(11), 50). Single species of *p*-tert-octylphenol ethylene oxide adducts were obtained by molecular distillation and the properties measured. A preferential adsorption of shorter ethylene oxide chain length compounds was found at the air/water interface, while preferential adsorption of the longer chain compounds was found at the isooctane/water interface (Crook et al., *J. Phys. Chem.* 67(10), 1987). Fractions of octyl- and nonylphenol and oleyl alcohol ethylene oxide products were obtained by centrifugal molecular distillation. Foam heights and stability were at a max with increase/mole of ethylene oxide units, the optimum number of ethoxy units being 7-9 for foam height and stability and wetting properties (Tagawa et al., *Kogyo Kagaku Zasshi* 65, 1844). In addition to the nonionics mentioned above, those of stearic acid were included (*Ibid.* 1260).

Poly (oxyethylene) derivatives of monoglycerides were prepared by addition polymerization of ethylene oxide to monoglycerides and the properties of these compounds compared with commercial products. Products with 20 mole ethylene oxide showed superior surface-active properties (Miyagawa et al., *Yukagaku* 12, 295). Surface-active properties of nonionic surfactants derived from higher glyceryldiethers of formula $R_0CH_2(R'_0CH_2)CH(OC_2H_4)_nOH$ were determined. Twelve to 14 carbon atoms in the $R + R'$, branched alkyl hydrocarbon chains and 60-5% poly(oxyethylene) were superior for wetting and foaming and 16-20C in $R + R'$, for emulsification, and ~ 16C in $R + R'$ for detergency (Kuwamura and Kameyama, *Kogyo Kagaku Zasshi* 65, 1265). Even with increase in concn, ethylene oxide derivatives of octyl- and nonylphenols and lauryl alcohol had no effect on wool felting. Other data on shrinkage as a function of nonionic type, concn and temp are given (Sakai and Komori, *Yukagaku* 12, 299). Ethoxylation of nonylphenol-formaldehyde resins and nonylphenol-*p*-cresol-formaldehyde resins gave nonionic polysoaps. The properties of these were compared with the monosoap, i.e., nonylphenyl ethylene oxide ether. Solubilization, detergency and foaming powers of the polysoaps were poorer than for the monosoap (Narasaki, *Kogyo Kagaku Zasshi* 66(3), 391). The wetting properties of ethylene oxide derivatives of fatty acids, fatty alcohols, alkylphenols, fatty acid amides and fatty acid amines were measured by a semimicro canvas disk procedure. Derivatives of fatty alcohols and alkylphenols were good wetters (Tagawa et al., *Ibid.* 65, 949).

SOLUBILIZATION. Higher alkyl sulfates of L-lysine were found more efficient emulsifiers and solubilizers for fat-soluble vitamins than sodium alkyl sulfate (Utsumi and Harada, *Eiyogaku Zasshi* 20, 142). NMR techniques were used to study the structure of cetylpyridinium chloride micelles. Aromatic solubilizes are found to a large extent at the micelle-water interface (Eriksson, *Acta Chem. Scand.* 17(5), 1478).

The solubilizing power of several metal alkyl sulfates for an aliphatic and several aromatic hydrocarbons was determined. An approx linear relation between the amt of hydrocarbons solubilized and surfactant concn was found (Satake and Matsuura, *Bull. Chem. Soc. Japan* 36, 813). The solubilization of isopropyl- and *p*-diisopropylbenzene in four isooctylarene-sulfonates was determined refractometrically. Solubilization of the alkylbenzenes increased with increasing surfactant concn and was influenced by the surfactant nature and hydrocarbon to be solubilized. Addition of sodium carbonate increased solubilization extent (Serban and Nicolescu, *Analele Univ. "Cl. Parhon," Ser. Stiint. Nat.* 10(30), 141). A turbidimetric method was used to determine the solubilization by mixed primary and secondary alkyl sulfates of oleic acid, a motor fuel, alcohols from paraffin oxidation and the motor fuel mixed with the alcohols (Bespyatov and Leschenko, *Maslob.-Zhir. Prom.* 29(1), 23). The solubilizing power and solubility of sodium *o*-ABS was much greater than the *p*-compound (Kimura et al., *Yukagaku* 11, 532).

Acrylate polysoaps containing increasing amt of α -heptyl-acrylic acid and α -undecylacrylic acid had higher solubilizing powers up to 20% content, but this was considerably lower than that of the monosoaps of the same acids (Yamashita et al., *Kogyo Kagaku Zasshi* 65, 2050). The solubilities in chloroform of several different metal soaps of fatty acids were increased by adding various amines (Chatterjee and Palit, *J. Indian Chem. Soc.* 39, 571). The solubilizing power of aqueous solutions of sodium dodecyl sulfate containing water-insoluble polymers such as polyvinyl acetate, polyvinyl formal and polyvinyl butyral against yellow OB was greater than for the sulfate alone (Maruta, *Nippon Kagaku Zasshi* 83, 395). The solubilizing effect of polyethylene glycols and their nonionic surfactant esters for a number of pharmaceuticals was determined (Kuttel, *Gyogyszereszet* 7(4), 131) and *Pharm. Zentralhalle* 102(3), 116). Some water-insoluble lipophilic drugs can be solubilized by using nonionic surfactants (Kedvessy and Regdon-Kiss, *Pharmazie* 18(2), 131).

The solubilization and viscosity of polyethylene oxide dodecyl ethers were studied as a function of chain length (Tokiwa, *Bull. Chem. Soc. Japan* 36, 222). Three different methods were used to solubilize lanolin in detergent compositions containing 1-3% of the oil, which had little effect on cloud point and did not depress foam volume (Hoch and Russell, *Proc. Sci. Sec. Toilet Goods Assoc.* 38, 51).

SURFACE AND INTERFACIAL TENSION. The interfacial tensions of six nonylphenol ethylene oxide adducts and 29 oil phases and six lauryl alcohol ethylene oxide adducts and 11 oil phases gave the following classes. Class I showed high interfacial tensions at very low and very high ethylene oxide content, with a min at moderately low ethylene oxide content. Class II showed high interfacial tension at low ethylene oxide content, declining smoothly with its increase. (Becher, *J. Colloid Sci.* 18(7), 665). Surface tension measurements were made of octyl- dodecyl-phenol and octylcresol ethylene oxide adducts, surface tension isotherms and ethylene oxide dependence being determined (Popescu and Gobijila, *Zh. Prikl. Khim.* 36, 227). Surface tension vs. concn data were developed for solutions of the ethylene oxide adducts of tridecanols, dodecanols, octadecanols, nonylphenols, and tert-octylphenols. Effect of electrolytes on the surface tension of the nonionic solutions was determined as a function of lyotropic number of the ions (Schick, *J. Colloid Sci.*, 17 801). Three nonionic surfactants comprising polyethylene esters of polypropylene glycols were evaluated. Surface tension decreased and wetting power increased as surfactant concn increased (Nevolin, et al., *Maslob.-Zhir. Prom.* 29(7), 23).

The dynamic and static surface tensions of solutions of two sodium dialkylsulfosuccinates in varying water hardness were determined (Thomas and Potter, *Ann. Rept. Agr. Hort. Res. Sta., Long Ashton, Bristol* 1961, 124). The surface excess of ABS was calculated using the Gibbs absorption equation from surface tension values (Wayman, *U.S. Geol. Surv. Prof. Papers No. 450-E*, 184). Surface tension data for solution mixtures of potassium laurate and potassium lauroylmethyl-taurate, and interfacial tension of the laurate against di-n-heptyl ether were made (Vader, *Trans. Faraday Soc.* 59, 1225). A Cassel-type max-bubble-pressure type tensiometer was used in measuring the surface tension of ABS and nonionic surfactants in the presence of bacteria. The pH effect was also determined (Wayman et al., *U.S. Geol. Surv. Prof. Paper No. 450-D*, 190). Dynamic surface changes in froth-forming aqueous solutions were measured (Van Duyne, *Dissertation Abstr.* 23, 178). Studied were capillary pressure, capillary rise and ultrasonics for surface tension measurement (Schatt and Pietsch, *Chem. Tech. (Berlin)* 15(5), 284). The effects on surface tension produced by surfactants were measured (Roussos, *Soc. Hydrotech. France, Compt. Rend. Journees Hydraulique, 7emes, Paris* 1962, 1, 195).

SUSPENSIONS. The influence of solutions of alkylarenesulfonates and electrolytes upon the heat of wetting of clay was studied and its increase with increasing solution concn was explained by the dispersive capacity of the surfactant investigated (Aleksandrova et al., *Uch. Zap. Azerb. Gos. Univ., Ser. Fiz.-Mat. i Khim. Nauk* 1960(4), 103). The effect of sodium salts of aliphatic monobasic acids, of aliphatic and aromatic amino acids and oxy acids on shear stress and filtration speeds of clay and bentonite were studied. Salts of high mol wt aliphatic acids at high concn prevent coagulation and salts of amino acids are strong stabilizers (Miskarili and Bairamov, *Kolloidn. Zh.* 25(3), 341). Addition of 100-200 ppm ABS to water containing up to 4 g montmorillonite, illite or kaolinite/100 ml lowers solution viscosity at low pH but increases it at high pH (Wayman et al., *U.S. Geol. Surv. Prof. Paper* 475-B, 209). Suspension isotherms of zinc oxide, calcium carbonate and $(BiO)_2CO_3$ in several anionic surfactants were determined. For zinc oxide and the bismuth

salt systems max suspendability occurred at conen below CMC, extending over a short conen range. Limited suspendability of calcium carbonate occurred in all three surfactants (Moore and Lamberger, *J. Pharm. Sci.* 52, 223). Flocculation in sulfamerazine suspensions is principally due to a chemical reaction between dioctyl sodium sulfosuccinate anions and trivalent cations of the flocculating agent (Wilson and Ecanow, *J. Pharm. Sci.* 52(8), 757).

TOXICOLOGICAL. Fluorescent analysis of 25 kinds of toilet soap and seven of washing soap was studied. About two-thirds showed fluorescence both on skin and cloth, and in half the cases the fluorescence remained on the skin after washing once with water (Mori, *Kyoto Furitsu Iku Daigaku Zasshi* 70, 453). Data on five synthetic soaps as to rabbit eye irritation were reported (Jaag, *Parfum., Cosmet., Savons* 5, 445). Sulfosuccinic esters of undecylenic acid monoethanolamide were claimed to be antiseborrhoeic and antiallergic in nature (Hoffman, *Seifen-Oele-Fette-Wachse* 88, 613).

Intrathecal injections of a cationic surfactant and two detergent compositions were made on dogs producing significant proliferative lesions on the meninges and degeneration of arterial media only in conen greatly in excess of those normally used (Smith and Conner, *Anesthesiology* 23, 5). Thirteen commercial surfactants were tested for oral toxicity using rats and skin and eye irritation tests with rabbits. All were low to moderate in acute oral toxicity. Least likely to be skin irritants were ethylene oxide adducts of nonylphenol, the alkali metal triethanolamine salts of didecylated diphenyl ether disulfonate (Olson et al., *J. Soc. Cosmetic Chemists* 13, 469). In the pH range 8.5-10.5, sodium laurate does not significantly penetrate the skin. Between 7.0-8.5 penetration may be attributed to lipid solubility. Above pH 10.5, penetration occurs because of alteration in the major barrier. In patch tests erythema and pruritis develop in normal skin with Na laurate buffered at pH 7.5 but not at 9.5, the higher pH reducing irritation by rendering the skin less permeable (Blank and Gould, *J. Invest. Dermatol.* 37, 485). Patch tests showed potassium laurate significantly more irritating to normal skin than potassium octanoate or palmitate (Bettley, *Brit. J. Dermatol.* 75, 113). Sodium dodecylbenzenesulfonate caused chronic toxicity in rats as shown by storage in organs and excretions using S³⁵ (Ikeda et al., *Shokuhin Eiseigaku Zasshi* 3, 399). Patch test studies were made of patients with photodermatitis apparently attributable to the halogenated salicylanilide (Wilkinson, *Brit. J. Dermatol.* 74, 302). Toxicological studies of optical brighteners showed that none of a series of stilbene derivatives was toxic upon topical application, none produced skin tumors and none was a sensitizer (Snyder et al., *Toxicol. Appl. Pharmacol.* 5, 176). Spectrographic analyses showing the presence of chromium in detergents was suggested as possibly responsible for skin allergies (Nater, *Dermatologica* 126, 160). Reviewed were surface active agents in dermatology (Emond, *Arch. Belges Dermatol. Syphilig.* 18(4), 310).

PERFORMANCE AND USE TESTING

Foam height as a function of time was measured using a constant rate of air or nitrogen addition to a surfactant solution in a chromatographic column (Wayman et al., *U.S. Geol. Surv., Prof. Papers No. 450-C*, 100). Critically surveyed was a mixer method for determination of sudsing power (Ramakers, *3rd Intern. Congr. on Surface Active Materials, Cologne, 1960*, 3, 134). A method was developed to measure the dispersing power of a surfactant for an azo pigment on a semi-micro basis (Imahori and Kimura, *Yukagaku* 11, 134). The procedure was improved by examining the filtrate electrophotometrically (*Ibid.* 470). A clay-oleic acid soil was used to soil cotton fabric for detergency evaluation (Davis, *Soap Chem. Specialties* 39(8), 47). A method for evaluating detergent performance was based on a procedure using several soil types, a series of washing and soiling cycles, and reflectance measurement (Schwartz and Berch, *Ibid.* 39(5), 78). Measurement of reflectance to obtain degree of soil removal must be done in isolation from fluorescent emission of optical brightener at 460 and 620 m μ (Kling, *Fette, Seifen, Anstrichmittel* 65, 258). A mixer is used to which melted tallow is added to detergent solution for dishwashing performance estimation (Howells, *Soap Chem. Specialties* 39(9), 61). A method was developed using dried milk films on microscope cover glasses, exposed to trisodium phosphate with or without sodium hypochlorite for cleansing, and determining residual film by micro-Kjeldahl determination (Merrill et al., *J. Dairy Sci.* 45, 613). The corrosivity of detergent solutions was measured by flushing the metal test pieces in a vertical column in wash and drain cycles, a 15-in. internal pressure being maintained (Whittlestone, *Australian J. Dairy Technol.* 18(2), 100). Stainless steel loss caused by detergent corrosion is

based on the analysis of the solution using the diphenyl carbazide procedure for chromium analysis (Merrill et al., *J. Dairy Sci.* 45, 796). An artificial soil approximating that that found on automobile bodies was sprayed onto metal strips and these used in the Gardner washability tester to evaluate painted surface cleaners (Aapino and DeRosa, *Riv. Ital. Sostanze Grasse* 40, 55). Emulsion stability was evaluated quantitatively by an ultracentrifugal method (Vold and Groot, *J. Phys. Chem.* 66, 1969). A synthetic cake soap was tested by eczema patients (Capalle et al., *Arch. Belges Dermatol. Syphilig.* 16(1), 118). A calorimeter with short heat conductors was used for measuring the wetting rate of textiles by water, recording the heat of adhesion as a function of time (Kretzschmar, *Kolloid-Z.* 189(1), 66). A simple aerosol system was devised for testing the suitability of surfactants as emulsifiers in propellant systems (Sanders, *Soap Chem. Specialties* 39(9), 63). A method for evaluating the usability of hydrogenated fats for soap manufacture was developed. The melting point, freezing point and content of *trans*-isomers were determined for hydrogenated oils. The difference between freezing point of the fatty acids and the corresponding fats decreases during hydrogenation (Pokorny and Vavra, *Pluszeze i Srodki Piorace* 4, 155). A laboratory sulfonation procedure was devised for evaluating alkylbenzenes for detergent production (Liddicoet and Olund, *JAOCS* 40, 5). A consumer panel test using balanced incomplete block design was used to yield accurate and valid data on acceptance of liquid dishwashing compositions (Johnson and Andrews, *Soap Chem. Specialties* 39(9), 57). A monograph was developed for relating the water, caustic and fatty acid content of finished soap to the saponification value of the fat and the caustic conen used for saponification (Clara, *Afnidad* 19, 458). Differences in performance resulting from condition changes during testing or use were discussed (Nuessle, *Am. Dyestuff Repr.* 52(15), P565). Measurements of oil droplets and air bubbles in detergent solutions lead to the conclusion that surfactants function primarily as emulsifiers, not wetting agents (Rosano and Montagne, *Rev. Franc. Corps Gras* 10, 9). The critical conen for max washing activity was examined by conductivity measurement (Sonntag and Oehler, *J. Prakt. Chem.* 15, 334).

BIODEGRADATION

The tests included direct biochemical and volumetric oxygen consumption in the presence of inorganic nutrients and at an O to N consumption ratio of 100:5. A methylene blue test was used on sulfated or sulfonated anionic surfactants. The results of these tests with a variety of branched and straight chain anionics are given. It was concluded that only straight chain normal paraffinic or olefinic compounds were suitable as starting materials for biodegradable alkyl sulfates or ABS (Petter, *Chem. Prumysl.* 13(6), 284). A closed bottle method said to be simple and quantitative was described (Fischer, *Fette, Seifen, Anstrichmittel* 65, 37). The biodegradability of four anionic surfactants (ABS and lauryl sulfate) was studied in a test based on plant activated sludge as the bacterial source (Borstlap and Kooijman, *JAOCS* 40, 78). Technics described for testing biodegradability were dilution method, Warburg and river die-away. A better procedure operated continuously on a pilot scale, one simulating the activated sludge process, the other the trickling filter (Eldib, *Soap Chem. Specialties* 39(6), 59). The ability of bacteria to degrade various sulfonated surfactants was studied using a continuous, three-stage process designed to simulate commercial operations, the results roughly paralleling those of static testing (Anon, *Chem. Eng. News* 41(25), 50). The West German method for testing biodegradability was described. Briefly the synthetic effluent is metered into an aeration tank, is degraded, settled sludge is pumped back to the aeration tank and clarified effluent flows to a collecting tank. After an initial eight-day treatment, the treated and untreated effluents were tested for detergent content for 21 days (*Chem. Eng. News* 41(7), 65).

Two unidentified bacterial strains were used to test degradation of dodecyl sulfate and dodecylbenzenesulfonate. Effects of various isomers are recorded (Payne and Feisal, *Appl. Microbiol.* 11(4), 339). Mechanism studies showed initial microbial attack of ABS to occur at the methyl group furthest from the aromatic ring. Subsequent oxidation formed a terminal carboxyl group and the side chain degraded by conventional β -oxidation (*Chem. Eng. News* 41(25), 50). River water biodegradation of straight chain ABS is characterized by buildup of a few transient intermediates detected by desulfonation and gas chromatography. The four-step β -oxidative attack is then outlined (Swisher, *Soap Chem. Specialties* 39(2), 58; *Ibid.* 39(8), 57).

Syndets were removed to better than 80% efficiency by

adsorption on activated charcoal, coagulation, soft coal slag and foaming (Kresta, *Chem. Prumysl.* 13(6), 281). Effluent containing nonbiodegradable ABS can be reduced 80-90% by treatment with hydrogen peroxide and ferrous iron (Anon. *Chem. Eng. News* 41(15), 102). Fine bubble aeration of ABS in sewage effluent removed more than 80% of the ABS when surface stripping of the froth was achieved (Klein and McGahey, *J. Water Pollution Control Federation* 35, 100). Removal of ABS from ewage effluent was accomplished by forming insoluble precipitates through cationic surfactant addition, followed by conventional coagulation and flocculation procedures (Samples, *Ibid.* 34, 1070). Primary and secondary effluents, containing ABS and phosphate from both trickling filter and activated sludge plants, were given a tertiary treatment for removal by passage through separation beds and activated carbon columns (Culp, *Ibid.* 35, 799). Biodegradability and fish toxicity studies were made with ABS with side chains 8-16 carbon atoms in length; two isomers of each chain were tested, one with the ring at the C-2 position and the other at mid chain. C-2 isomers were more easily degraded and less toxic, toxicity increasing in either case with longer chain length (Anon. *Chem. Eng. News* 41(22), 70).

The biological degradation of tetrapropylene ABS was studied with percolating filters and activated sludge basins on a laboratory scale. Extent of breakdown depended upon origin and condition of the sludge and increased with sludge conen, the ABS being strongly adsorbed by the sludge (Schoenborn, *Gas-Wasserfach.* 103, 1133). Biological investigation of alkylarenesulfonates in sewage treatment was described (Bock, *Ber. Intern. Vortragstag. PRO AQUA*, Basel 1961, 247). The effects of anionic, nonionic and cationic surfactants on their adsorption and effect on multiplication of mycobacteriophages were studied (Kawahara, *Karume Med. J.* 9(2), 140). Addition of 750 ppm ABS to an experimental digester caused rapid decline in gas production, lower dosages as in practice lying below this critical point (Klein, *Water Sewage Works* 109, 373). The adaptation period and degradation rate of ABS and other anionic surfactants was determined. Alkyl-naphthalenesulfonates are less easily degraded than benzene derivatives (Winter, *Wasserwirtsch.-Wassertech.* 12, 265). No detectable effect of surfactants on the dewaterability of crude sludge was discernible in laboratory tests (Swanwick et al., *Water Waste Treat. J.* 997, 314). Abnormally high biodegradable conen of straight chain ABS in plant trickling filters and activated sludge plants showed no effect upon operation (Jendreyko and Ruschenburg, *Gas-Wasserfach* 104, 391). Adsorption by dewatered, digested sewage sludge reduced by 20-60% the ABS content of laundry wastes (Feng, *Water Sewage Works* 109, 183). ABS was removed rapidly by soil, but continued passage reduces rate, bacterial clogging occurring in the direction of water flow. Fine grained soils were severely clogged by bacteria (Page et al., *U.S. Geol. Surv. Profess. Papers No. 450-E*, 179). ABS caused severe growth inhibition in water culture of sunflower and barley, only sunflower was affected in soil tests (Klein et al., *J. Water Pollution Control Federation* 35, 636).

The possibility of reducing foam on rivers by use of small turbines with axial entry and radial water ejection parallel to the river water level was discussed (Balle, *Soc. Hydrotech. France, Compt. Rend. Journees Hydraulique*, 7 emes, Paris, 1962, 1, 188). Easy degradation occurred in river water with sulfonated esters or higher fatty alcohols (Goewa, *Tr. Leningrad Sanit.-Gigien. Med. Inst.* 68, 121). The effect of 1-4 ppm ABS on the fauna and flora of the River Lee was the absence or scarcity of some species normally found (Hynes, *Ann. Appl. Biol.* 50, 779). Removal of phosphorus from sewage by chemical coagulation was studied. Indications are that removal occurs by adsorption. Discussed were other sources of phosphorus including detergent phosphates (Henriksen, *Schweiz Z. Hydrol.* 24(2), 253). Studies indicated that human wastes contributed about 65% and detergents 35% of the phosphorus in lake water (Voss, *Gas-Wasserfach* 104, 397). Sugar esters of ricinoleic or mono-, di- and trihydroxystearic acid were effective easily degraded nonionic surfactants (Anon. *Chem. Eng. News* 4(8), 55). Desired for their biodegradability are glucose esters of fatty acids (Brunelle et al., *Belg.* 622,311). Easily degraded alkylarenesulfonates are claimed by alkylating aromatic hydrocarbons with dimerization products of olefins with subsequent sulfonation and neutralization (Rohlfis and Herold, *Ger.* 1,142,166). Biodegradable ABS products in which the alkyl chain may be 1-butyl-1-methylheptyl or 2-butyloctane (Mirviss et al., *Belg.* 616,990). Biodegradable straight chain ABS was obtained through straight chain olefins from cracked waxes or by Ziegler process (Sherwood, *Ind. Eng. Chem.* 55(4), 33).

Review articles were: Status (Speel, *JAOCs* 40(7), 12). A survey (Truedale, *Effluent Water Treat. J.* 1(4), 218).

Clarifying waste-water polluted with dyes and detergents (Kehren, *Seifen-Oele-Fette-Wachse* 88, 909). Garbage, detergents and sewers (Bowerman and Dryden (*J. Water Pollution Control Fed.* 34, 475). The problem in the USA, England and Germany (Raphael, *Mfg. Chemist* 34(8), 379). Soft detergent production (Husmann, *J. Soc. Cosmetic Chemists* 13, 416). Legislative and technical aspects (Perlman, *Soap Chem. Specialties* 39(9), 68).

MISCELLANEOUS

Nonionic surfactants were useful in the treatment of crude oil emulsions and in the clarifying of oil-bearing strata (Voicu, *Petrol Gaze, Bucharest* 14(3), 126). Nonionic surfactants as stabilizers, emulsifiers and solubilizers for a variety of pharmaceutical preparations were discussed (Mandak, *Congr. Sci. Farm., 21e, Conf. Comun.*, Pisa, 1961, 681). Lauric acid monoethanolamide was used with clay to give stiff gels for a variety of purposes (Sawyer, *U.S.* 3,049,498). Certain nonionic surfactants in neutral or slightly alkaline condition in the presence of electrolyte control clay welling and stabilize the rheological properties of drilling muds (Gelpi, *Soc. Hydrogech. France, Compt. Rend. Journees Hydraulique*, 7emes, Paris 1962, 1, 211). A toxicant emulsifier is comprised of an alkylarenesulfonate and a nonionic surfactant (Aetscher and Groll, *U.S.* 3,071,550). Mixed nonionic and slightly hydrophilic surfactants are used in insecticides and plant protection products (Neel, *Ibid.* 206).

Several surfactants were tested to ascertain their effect on the coagulation of calcium phosphate and ferric phosphate under alkaline conditions in a sludge blanket clarifier in decontamination of radioactive waste water (Frost, *J. Am. Water Works Assoc.* 54, 1082). Surfactants totalling 152 were tested as combustion catalysts for composite rocket propellants including lithium perchlorate, of which five proved of value (Kumao and Arakawa, *Intern. Symp. Rockets Astronaut.*, Proc., 3rd, Tokyo 1961, 301). Surfactants were used to facilitate peptization of carbon black and to stabilize the suspensions (Chupeev et al., *Lakrokrasochnye Materialy i ikh Premeniye* 1963(3) 77). Discussed briefly were the types and applicability of surfactants used in virus and vaccine production (Vallee, *Rev. Franc. Corps Gras* 10(4), 183).

Reviewed were the following: Economic trends and survey of the knowledge of certain properties and materials in detergent usage and production (Raphael, *Mfg. Chemist* 34(3), 116). Attempts are under way by the ASTM to develop detergent bar specifications (Anon. *Soap Chem. Specialties* 39(4), 49). Ionic surfactants (Konishi and Iwana, *Yuki Gosei Kagaku Kyskai Shi* 21, 2). Polymeric surfactants (Yamashita and Koichi, *Ibid.* 28). Surfactant synthesis (Oda, *Ibid.* 37). Radioactivity and surfactants (Sasaki, *Ibid.* 41). Present and future technology and economics (Mayolle, *Rev. Franc. Corps Gras.* 9, 473). Review (Raphael, *Mfg. Chemist* 34(3), 116).

PRODUCTS (EXCEPTING DETERGENTS)

EDIBLE, PHARMACEUTICAL AND COSMETIC FAT PRODUCTS

Nonfat dry milk was successfully enriched with vitamins A and D₂ by either the wet-stage process or the dry-stage process using coconut fat as a carrier for the vitamins (Bauernfeind and Allen, *J. Dairy Sci.* 46, 245). Certain glyceride preparations and Tweens and Spans, lecithin, buttermilk solids and skim milk solids were shown to be effective in improving the spreadability and decreasing the hardness of butter (Kapsalis et al., *J. Dairy Sci.* 46, 107). GLC of butterfat triglycerides showed they possess a non-random fatty acid distribution (Kuksis et al., *JAOCs* 40, 530). The presence in butterfat of non-volatile keto acid esters in trace amt was demonstrated by identification of six pyrazolones formed when butterfat was treated with Girard-T reagent (Van der Ven et al., *J. Lipid Res.* 4, 91).

The properties of margarine formulations and novel fat blends were shown to be predictable from studies of the melting behaviour of binary mixtures of palmito-oleo-triglycerides included in these compositions (Moran, *J. App. Chem. (Lond.)* 13 (2), 91). Rheological measurements were used to demonstrate that crystal lattices of fat crystals are responsible for the consistency of shortenings and margarines (Haighton, *Fette Seifen Anstrichmittel* 65, 479). Spray-dried milk containing solubilized albumin-casein was used as emulsifier for margarine emulsions characterized by high stability and good technological properties for use in confectionery and bakery goods (Kozin et al., *Maslob.-Zhir. Prom.* 12, 17). Margarine from Soviet factories was shown to contain 5.24-13.53% linoleic acid, an unsaturated fatty acid content in fair agreement with that of foreign margarines (Khomutov et al., *Maslob.-Zhir. Prom.*

12, 15). Use of liquid shortenings by the various food industries was reported to be increasing (Lawson, *The Bakers' Digest* 36 (4), 60). Advantages of fluid shortenings over plastic shortenings were presented in a review of the development and uses of fluid shortenings (Ellinger, *Bakers' Digest* 36 (6), 65). Other reviews discussed the use of fat products in the bakery industry (Ellinger and Hoer, *JAACS* 40 (6), 4A), and problems in research on fats in the baking industry (Terada, *Yukagaku* 12, 450). Flour lipids and their involvement in the baking process were reviewed (Glass, *Bakers' Digest* 36 (6), 40).

Two methods for measuring the oil binding characteristics of flour were described and related to the protein content of the flour (Sheuy et al., *Cereal Chem.* 40 (1), 71). Rheological studies of the role of lipids in dough showed lipids have a protective action against the improving effect of oxygen (Narayanan and Hlynka, *Cereal Chem.* 39 (5), 351). Fat content and fatty acid composition of some commercial mixes for baked products were determined (Ostwald, *J. Am. Dietet. Assoc.* 42, 32). A patented method for preparing bread comprised incorporating into the baking mix up to 3% by wt of a diglyceride having one acyl radical derived from lactic acid (Kuhrt and Swicklik, *U.S.* 3,068,103). A titrimetric procedure was described for determination of lactic acid in lactylated monoglycerides and shortenings (Pohle et al., *JAACS* 40, 549). Surfactant activity and emulsion stabilization of stearyl monoglyceridyl citrate were utilized to extend baking tolerances (Geminder, *Bakers' Digest* 2 (4), 60). Methods of measuring the consistency of dough, margarine, butter and other food products were reviewed (Janer, *Grasas y Aceites* 13, 216).

Patents were issued for a plastic shortening containing 8–10% of an interesterified soybean oil hard stock and 85–92% soybean oil base stock having an iodine value of 80–95 (Thompson, *U.S.* 3,102,814); for a shortening agent produced by an ester interchange between glycerides of an edible fat, propylene glycol and glycerine (Allen et al., *U.S.* 3,097,098); and for an aerated shortening production process in which a pressurized aerated shortening was suddenly depressurized and subjected to partial recrystallization with agitation at approx atmospheric pressure (Kearns, *U.S.* 3,095,305). A procedure for preparing a cake batter comprised cooling a liquefied mixture of liquid shortening and normally solid monoglyceride to reprecipitate the monoglyceride in an active form and incorporating the resulting activated composition into the batter within about 45 min of reprecipitation (Handschumaker and Hoyer, *U.S.* 3,069,270). Whipping and powdered shortening compositions containing edible fat, mono- and diglycerides, glycerol lacto palmitate and glycerol lacto oleate were described (Noznick and Tatter, *U.S.* 3,098,748). A study of glycerol lacto palmitates as emulsifiers in shortening showed max effectiveness is obtained when there are two free hydroxyl groups in the lactic acid portion of the molecule (Felt, *JAACS* 40, 81). Up to 0.5% of a non-emulsifying and non-surface-active fatty acid ester of a carbohydrate was incorporated into a plastic glyceride fat composition (Eckey and Alderson, *U.S.* 3,093,481).

Problems encountered in deep fat frying were reviewed (Ota, *Yukagaku* 12, 436). A study of the extent of polymerization in frying fats and in fats extracted from fried foods showed up to 2.5% polymeric fatty acids may be present (Sahasrabudhe and Bhalerao, *JAACS* 40, 711). Determination of the fatty acid composition of various cooking oils and fats, using GLC, showed the polyenoic acid content may decrease by as much as 30% during heating at 495F (Fleischman et al., *J. Am. Dietet. Assoc.* 42, 394). Consumer acceptance of doughnuts was shown to depend upon the amt of fat absorbed and the flavor and other properties imparted by the frying medium. Ways of controlling these factors were investigated (Downs, *Bakers' Digest* 2 (4), 66). Foaming tendencies of frying oils were shown to be related to the amt of polar fraction present (Ota et al., *Yukagaku* 12, 409). GLC of lard methyl esters gave qualitative evidence of the presence of 29 fatty acids ranging in chain length from 10–20C atoms (Herb et al., *JAACS* 40, 83). The distribution of fatty acids in fractions of lard obtained by crystallization was also investigated (Arnold and Milloy, *JAACS* 40, 298). Quantitative comparison, by chromatography, of the fatty acid composition of commercially rendered lard, laboratory rendered lard and solvent extracted lard from the same batch of pig tissue showed that the minor components were not artifacts produced in rendering (Madigman et al., *JAACS* 40, 86). Digestibility and caloric availability of fatty acid esters of carbohydrates, distearin adipate and glycerol adipate were investigated to establish the usefulness of these new fats as pan greases and surface coatings for foods (Booth, *JAACS* 40, 551). Melting phenomena in fats and fatty materials were reviewed and evaluated as criteria for the specification of manufactured products (Meskens, *Lab. and Tech.* 6, 287). A quick and simple method was described for

studying crystallization behaviour as a means of evaluating the consistency of commercial fats (Wilton and Wade, *JAACS* 40, 707).

Mowrah fat, Shea butter, Dumori butter, Njave butter, Baku butter, palm oil, Kepayan oil and Phulwara butter were listed as possible components of a cocoa butter substitute (Sinnema, *U.S.* 3,084,049). Another cocoa butter substitute comprised a mixture of cocoa butter with the monounsaturated triglyceride fraction obtained from Mowrah fat by low-temp crystallization from acetone (Sinnema, *U.S.* 3,070,445). The presence of hydrogenated fats in cocoa butter was detected by analysis of the *trans* fatty acid content (Pokorny et al., *Papers of the Inst. of Chem. Tech. Prague 4-II*, 313). Pressed cocoa butter and hexane extracted cocoa butter were differentiated by differential thermal analysis of samples as small as 0.3 g (Mathieu et al., *Rev. Franc. Corps Gras* 10 (3), 123). Simple hydrogenation of coconut oil, palm oil or palm kernel oil was shown to be insufficient to produce a satisfactory cocoa butter substitute (Janicek and Pokorny, *Papers of the Inst. of Chem. Tech. Prague* 3, 301). A cocoa butter substitute was obtained from a fraction of a semi-solid fat crystallizing from acetone at 10–35C (Arnold, *U.S.* 3,093,480). A method was described for pretreating cocoa butter in order to obtain a reliable melting point by the capillary method (Shimatani and Iwasaki, *Yukagaku* 11, 357). Peanut lipoprotein was shown to be suitable as a substitute for or as an additive for lipoproteins in processed foods (Waltdt et al., *Food Technol.* 17, 107). A method was described for determination of peanut lipoproteins in comminuted meats (Suffis et al., *Food Technol.* 17, 149). Cottonseed stearine was combined with 20–50 parts of hydrogenated interesterified base fat to form a nutritious fat composition (Gooding, *U.S.* 3,099,564). Volatile water extractables from corn cobs were used to impart flavor to edible oils and greases (O'Brian et al., *U.S.* 3,106,472). Herb-flavored edible oils were prepared by blending together the heated oil and powdered and flaked herbs (Stohr, *U.S.* 3,071,475). An ester-interchanged lauric-type fat and C-18 type fat were blended with at least 15% of a selectively partially hydrogenated C-18 type fat to form a confectioners' fat (Gooding and Cravens, *U.S.* 3,085,882). A lecithinated, spray dried, free flowing powder was prepared by combining 30–60% lecithin, 10% edible shortening oil and 30–60% of a protein coating material—consisting of milk solids, sodium caseinate or mixtures of these in combination with carbohydrates (Obenauf and Tatter, *U.S.* 3,060,030). A process for refining solid fats and oils by deacidification comprised stirring the molten mass of fat with sodium hydroxide solution under specified controlled conditions (Eger and Schwartzhopff, *U.S.* 3,085,101). The nutritive value of raw and blended passion fruit seed oil was investigated (Pruthi, *Indian Oilseeds J.* 7 (1), 60). Synthetic β -apo 8'-carotenal was evaluated and found to be satisfactory as a coloring material for foods requiring a light to dark orange shade (Bauernfeind and Bunnell, *Food Tech.* 6, 76). Improvement of the quality of edible oils was reviewed (Yasuda and Watanabe, *Yukagaku* 12, 431). The lipid composition of nine brands of mayonnaise was reported (Eastwood et al., *J. Am. Dietet. Assoc.*, 42, 518). Stability against freezing conditions was imparted to an emulsified salad dressing by incorporating a freeze resistant starch in an amt sufficient to imbibe the moisture in the salad dressing (Partyka, *U.S.* 3,093,485). An edible oil, an emulsifier and a modified freeze resistant starch were combined to form an emulsified salad dressing stable to freeze-thaw conditions (Krett and Gennuso, *U.S.* 3,093,486). Emulsified oily foods, including mayonnaise and related products, were reviewed (Oshida, *Yukagaku* 12, 468).

Vitamin A esters were prepared by treating the acid with lithium aluminum hydride and decomposing the complex with an acylating agent (Matsui et al., *U.S.* 3,086,981). A stable, aqueous vitamin A oil emulsion composition included methyl cellulose and sufficient gelatine to suppress color development under normal storage conditions (Czarnecki, *U.S.* 3,089,823). A stable, heat sterilizable, aqueous solution of vitamin D and a nontoxic calcium salt suitable for parenteral injection utilized a fatty acid ester of a polyoxyalkylene compound as a solubilizing agent (Schenk, *U.S.* 3,089,822). A condensation product of ethylene oxide and castor oil was used as solubilizing agent in a parenteral aqueous solution of fat-soluble vitamins (Mullins and Macek, *U.S.* 3,070,499). Other patented fat-soluble vitamin compositions included: a normally solid wax-like material having a melting point of at least 45C, a fat-soluble vitamin containing material, an edible surface-active agent, an edible antioxidant and a hygroscopic polysaccharide (Hochberg and Ely, *U.S.* 3,067,104); and a fat soluble vitamin, a hydrophilic polysaccharide carrier produced by controlled polymerization of corn sugars and zein (Ratish and Hochberg, *U.S.* 3,067,105). An excipient for dermatological use comprised a mixture of perhydroqualene and hydrogenated tallow (Monot, *U.S.*

3,069,324). A therapeutically useful ointment was prepared by thermally blending Japan wax, sesame oil and a minor proportion of a therapeutically active ingredient (Otsuki and Otsuki, U.S. 3,086,909). A surface active agent such as an alkali metal soap and an oleaginous retardant such as a vegetable oil were included in a skin treating composition containing a major proportion of an active phenolic compound (Brown, U.S. 3,067,106). Stable alcoholic emulsions of therapeutic value were prepared by stirring glycerine difatty acid phosphoric acid amino alcohol esters into a boiling aqueous alcoholic solution of grape sugar until an emulsion was formed (Buer, U.S. 3,070,500). A fatty acid monoglyceride containing not more than 10% polyglycerides was mixed with dicalcium phosphate to form a medicant tablet (Goldman, U.S. 3,054,723). A capsule containing radioactive iodine comprised a mixture of a digestible, nontoxic wax-like material and up to 50% of a radioactive iodinated fatty material (Numerof and Knoll, U.S. 3,061,510). A patented injectable medicinal composition consisted of a non-gelled physiologically compatible vegetable oil, vitamin A, guaiaicol, eucalyptol and an antibiotic (Lobel, U.S. 3,105,793). An oil in water emulsion for oral administration was described as containing an aqueous dispersion medium containing a protective colloid, an internal phase containing up to 35% of an edible unsaturated oil and an additional internal phase containing up to 17% of emulsified sitosterol (Wruble et al., U.S. 3,085,939).

Fats, oils and chemicals for the pharmaceutical industry were reviewed (Molteni, *JAOCs* 40 (8), 4A). A procedure for purifying phosphatides comprised treating the alcohol soluble fraction of commercial lecithin with a water soluble basic calcium compound to precipitate the salt of phosphatidic acid, removing this insoluble salt and treating the remaining solution to isolate a phosphatide emulsifying agent (Elenbogen, U.S. 3,081,320). Seasonal variations in cod liver oil were discussed (DeWitt, *J. Sci. Food Agr.* 14, 92). A dentifrice was patented containing a polishing agent, glycerine, sulfonated non-drying glyceride fatty oil, sulfonated alcohol or sulfonated hydroxy fatty acid, sulfonated drying oil and a lower alkyl ester of a nondrying fatty acid (Morris, U.S. 3,081,235). Cosmetic uses of fats and oils were reviewed (Hintz, *JAOCs* 40 (9), 4A; Colson, *Riv. Ital. Sostanze Grasse* 9, 472; Rovesti, *Riv. Ital. Sostanze Grasse* 9, 468). Another review discussed perfume chemicals and essential oils (Aretander, *JAOCs* 40 (3), 4A). Optimum conditions were discussed for analysis of peroxides in cosmetic creams containing up to 25% of vegetable oils (Pokorny et al., *Papers of the Inst. of Chem. Tech. Prague 4-II*, 297). A semimicro colorimetric method using titanium chloride as the color forming agent was proposed for the analysis of active oxygen in cosmetic products (Pokorny et al., *Papers of the Inst. of Chem. Tech. Prague 4-I*, 319). Included in a film-forming cosmetic composition were a homogeneous dispersion of anhydrous lanolin, a vegetable oil and a straight-chain fatty alcohol lactic acid ester (Kreps, U.S. 3,098,795).

EMULSIFIERS

The dynamic mechanical behavior of suspensions of fat particles in oil was studied at 50 C.P.S. by measuring bending vibrations and the damping of a torsional balance (Nederveen, *J. Colloid Sci.* 13, 276). Parameters of stability of oil-in-water emulsions were studied by an ultracentrifugal method (Vold and Groot, *J. Soc. Cosmetics Chemists* 14, 233). Polyoxethylene derivatives of monoglycerides were shown to have as good surface activity as Tween and to be superior to Tween in interfacial tension, emulsifying power and permeability (Miyagawa et al., *Yukagaku* 12, 295). Stable oil/water suspensions of cottonseed stearine, tristearin, tripalmitin, trimyristin, methyl stearate and palmitic acid in concn up to 10% were prepared and their properties studied (White and Singleton, *JAOCs* 40, 186). Monoglycerides of higher fatty acids were patented as foam reducing agents in instant coffee and tea preparations (Breivik and Johnston, U.S. 3,100,151). Blends of glycerol monostearate and 1,2-propanediol monostearate were prepared and studied as food emulsifiers (Kuhrt et al., *JAOCs* 40, 725). Uses were described for an emulsifier containing mixed crystals of glycerol monostearate in the alpha-crystalline form and 1,2-propanediol monostearate (Kuhrt and Broxholm, *JAOCs* 40, 730). A variety of emulsifiers were prepared from linseed oil and its fatty acids and alcohols and evaluated in the formation of stable linseed oil emulsion paints (Kubie et al., *JAOCs* 40, 105). Nonionic emulsifying agents were prepared by reacting glycoside polyethers with saturated or unsaturated long chain fatty acids and linseed oil (Otey et al., *JAOCs* 40, 76). A homogeneous mixture of surface active agents for emulsifying water insoluble substances was described as containing an alkali metal alkyl sulfate surfactant, the water-soluble condensation product of a mono-higher fatty acid ester of hexitol anhydride with 10-30 moles of alkylene oxide and water

(Surgant, U.S. 3,095,353). Sulfated products were prepared from minor seed oils and evaluated as wetting and emulsifying agents. Mixtures of castor oil with either coconut, tobacco seed, niger seed or sesame oils when sulfated gave better wetting and emulsifying products than when these oils were individually sulfated (Kasisviswanadham and Murti, *Indian Oil Soap J.* 28 (4), 115). An aliphatic diester of the condensate of glycerol with ethylene oxide was included as a nonionic component and alkylaryl sulphonates were included as anionic components of an emulsifier mixture for use in emulsifying organic solvent solutions of water-insoluble toxicants (Altseher and Groll, U.S. 3,071,550). A vegetable oil-soluble nonionic alkylated phenoxy compound was patented as a component of an aqueous dispersible lecithin composition (Cogswell, U.S. 3,069,361). The synthesis and surface active properties of certain amphoteric compounds were reviewed (Linfield et al., *JAOCs* 40, 114). Recent advances in fatty amine oxides and their role as emulsifiers were reviewed (Lake and Hoh, *JAOCs* 40, 628); and the formulation of fatty amine oxides and their use principally as foam stabilizers in detergent formulations were discussed (Matson, *JAOCs* 40, 640).

ESTERS, ACIDS, ALCOHOLS AND OTHER FAT DERIVATIVES

The most favorable conditions for production of monoglycerides were investigated by controlling the ratio of glycerine and oil, the temp and the degree of alcoholysis (Yukhnoshii and Volosyuk, *Lakokras. Mat.* 4, 16). Maximum yields of monoglycerides were obtained from castor oil using a 2:1 ratio of 98% glycerol and refined castor oil carrying out the reaction at 250°C under 200 psig of carbon dioxide (Kochhar et al., *Indian Oil Seeds J.* 6, 20). The high yield of castor oil monoglyceride was attributed to the superatmospheric pressure being sufficient to keep water normally present in the glycerol in effective contact with the reactants (Kochhar et al., *Ibid.* 6, 144). Optimum yields of monoglycerides from castor oil were obtained when there was present an amount of water equal to 4-5% of the wt of the anhydrous glycerol and the ratio of glycerol to oil was high (Dey et al., *Ibid.* 6, 215). When oils other than castor oil were converted to monoglycerides under the same conditions of temp and pressure, it was found that those with a predominance of unsaturated fatty acids were glycerised most readily and higher yields of monoglyceride were obtained when lower mol wt fatty acids were present (Kochhar et al., *Ibid.* 7, 46). A patented process for preparation of monoglycerides specified use of an amt of glycerine in excess of the amt required both to form the monoester and to dissolve completely the glyceryl monoester (Alsop and Krems, U.S. 3,083,216). In another process, monoglycerides were prepared by recycling reactants after neutralizing the alkaline catalyst and stripping (Birnbaum and Lederer, U.S. 3,102,129). To produce monoglycerides in a continuous process, a homogenized mixture of a glyceride and glycerol was passed through a reaction zone countercurrent to additional glycerol in the presence of an alkaline catalyst (Change and Wiedermann, U.S. 3,079,412). High yields of monoglycerides were obtained by reacting natural fats with glycerine in pyridine solution in the presence of an alkaline catalyst such as sodium methoxide, sodium ethoxide or sodium carbonate (Taufel et al., *Fette Seifen Anstrichmittel* 64, 513). Pure monoglycerides of unsaturated fatty acids were prepared by reacting methyl esters with glycerol in pyridine solution in the presence of sodium methoxide, followed by recrystallization from hexane and ethyl ether (Bertoni et al., *Revista Argentina de Grasas y Aceites* 5, 3). Glyceryl-1-monoleostearate prepared by this method was obtained in 95-98% purity after recrystallization from hexane (Crespo et al., *Revista Argentina de Grasas y Aceites* 3, 76).

Acid catalyzed conversion of glycidyl stearate to monostearin resulted in formation of distearin by-product unless conditions were chosen to avoid ester hydrolysis (Maerker et al., *JAOCs* 40, 193). Continuous azeotropic removal of water was found to suppress interesterification during formation of glycerides by esterification in the presence of *p*-toluenesulfonic acid catalyst (Feuge et al., *JAOCs* 40, 260). In a review of the mechanism of acyl migration in partially acylated glycerides, seven possible mechanisms were outlined (Buchnea, *Fette Seifen Anstrichmittel* 64, 887). Acyl migration in glyceride synthesis via tritylglycerol intermediates was minimized or eliminated by detriylation in the absence of polar contaminants (Jackson and Lundberg, *JAOCs* 40, 502). To minimize contaminants in intermediates used in the synthesis of glycerides the preparation of monotritylglycerol was improved and a method was developed for debromination of tetrabromostearic acid with minimum formation of *trans* bonds (Jackson and Lundberg, *JAOCs* 40, 276). A kinetic study of the esterification of diglycerol with stearic acid showed the max yield of monoesters was obtained when the ratio of fatty acid to diglycerol was lowest and de-

pended upon the reaction temp (Mares and Pokorny, *Papers of the Inst. of Chem. Tech. Prague 4-I*, 275). Continuous deglycerination of monoglycerides was used to obtain a glycerol content of 0.30% or less, thus meeting the smoke point requirement for superglycerinated shortenings (Monick, *JAACS* 40, 606). A study of the miscibility of glycerol with fatty acids and glycerides showed 1-monolaurin is completely miscible with glycerol at 180C (Hartman, *JAACS* 40, 142). Dipole moment measurements and number average mol wt showed some association of α -monoglycerides takes place in nonaqueous solvents, and clustering increases with decreasing cohesive energy density of the solvents (Debye and Coll, *J. Coll. Sci.* 17, 220). Solubilities of trilaurin, trimyristin, tripalmitin and tristearin in 90–100% ethanol were determined at 40 and 90C, and plots of the mole fraction dissolved vs. the reciprocal of the temp were found to be straight lines which did not coincide with ideal solubility curves (Arnold et al., *JAACS* 40, 33).

Highly unsaturated alkyl esters of straight and branched chain alcohols having 1–6 carbon atoms were prepared in nearly quantitative yields by alcoholysis of menhaden oil (Gauglitz and Lehman, *JAACS* 40, 197). A product containing at least 60% of monoesters polyunsaturated fatty acids was produced by submitting a mixture of lower alkyl monoesters and monoglycerides of substantially unconjugated fatty acids to molecular distillation conditions at temperatures below 100C (Sutherland, *U.S.* 3,082,228). A mixture of short chain methyl esters and hydrocarbons was formed by reacting unsubstituted methyl esters of higher fatty acids in the vapor phase (Moulton et al., *U.S.* 3,079,413). The esterification of erucic acid with cetyl, stearyl and oleyl alcohols was studied and rate constants, activation energy, and effect of type and amt of catalyst and the molar ratio of reactants were reported (Zajic and Buresova, *Papers of the Inst. of Chem. Tech. Prague 4-II*, 275). A method for preparing esters by heating a mixture of carboxylic acid, alkyl halide and tertiary aliphatic amine was described. Best results were obtained with primary alkyl iodides, and poorest results were obtained using tertiary halides and chlorides (Mills et al., *Chem. Ind. (London)* 1962, 2144). Light-colored fatty acid esters were obtained by including hydrophosphorus acid in catalytic amt in the esterification mixture (Mohan and Christian, *U.S.* 3,071,604). A fatty alcohol ester of citric acid was reacted with a di-fatty acid ester of pentaerythritol to form a mixed ester of citric acid di-fatty alcohol ester and pentaerythrite di-fatty acid ester (Hennig et al., *U.S.* 3,102,128). A mixture of jpanic acid, the di-basic acid portion of japan wax, and palmitic acid was reacted with glycerol to form 1,3-japanin-2-palmitin and 1,2-japanin-3-palmitin (Nagano and Tanaka, *Yukagaku* 11, 209). When 2 moles glycerol was esterified with 1 mole jpanic acid, the jpanic acid formed a bridge between two molecules of glycerine, and this bimolar glyceride was further esterified with palmitic acid to form a tetrapalmitate (Nagano and Tanaka, *Ibid.* 11, 211). A patent described an organic polycarboxy acid ester of oxyethylated castor oil (Kirkpatrick et al., *U.S.* 3,061,620). Fatty acid esters of propylene glycol and glycerol, a solubilizer such as glyceryl triacetate, triethyl citrate or triethyl phosphate and ungelatinized, water-insoluble starch were included in a molding starch composition to be used in the manufacture of confections (McGowan and Marotta, *U.S.* 3,074,803). Olefinic acid esters were produced by passing vaporized alcohol through hot unsaturated fatty acids in the presence of 5–15% by wt of potassium bisulfate while continuously removing water and unreacted alcohol under vacuum (Feichtinger and Noeske, *U.S.* 3,095,432).

α -sulfo fatty acids were reacted with a slight excess of an olefin in the presence of iron pentacarbonyl as catalyst to form dialkyl esters of the alpha-sulfo acids (McBride and Miller, *U.S.* 3,090,794). In a study of all types of olefins to determine the influence of structure on the ease of ester formation it was established that best conversions are obtained using α -olefins or symmetrical olefins and primary alkyl acid esters of dibasic acids reacting in the presence of catalysts which are strong proton generators, such as perchloric acid (Raether et al., *I & EC Product Res. Div.* 2, 133).

The reaction of vinyl acetate with carboxylic acids in the presence of H_2SO_4 catalyst was reported to give a mixture of acylals, in contrast to the ester interchange reaction and anhydride formation previously reported for a similar reaction involving the homologous isopropenyl acetate (Rothman et al., *J. Am. Chem. Soc.* 84, 3123). Cholesterol esters of dihydroxy acids were prepared by reacting cholesterol with the isopropylidene derivative of the hydroxy acid using *p*-toluenesulfonic acid as catalyst (Carloff and Deicke, *Fette Seifen Anstrichmittel* 64, 1037). In the preparation of *o*-cresyl oleate by direct esterification under azeotropic conditions, titanium tetrabutoxide was used as catalyst (Jaruzelski and Sheppard, *U.S.* 3,106,570). Oxyalkylated lecithin was prepared by reacting lecithin with glycidol (Chang, *U.S.* 3,085,100). Monolayers of diacetyl esters

of the first six members of the homologous series of dicarboxylic acids were studied and data reported for measurements of surface pressure vs. area and surface potential vs. area (Shereshefsky et al., *J. Phys. Chem.* 66, 1846). Addition of 10% fatty acid was reported to increase the rate of amidation of methyl esters of monobasic or dibasic acids (Nitanai et al., *Yukagaku* 11, 637).

Synthesis of mono- and diesters of mannitol by reaction of D,L-mannitol with *n*-alkyl isocyanates of chain length C-8, C-10 and C-12 was described (Ulsperger and Jacobi, *Fette Seifen Anstrichmittel* 64, 1093). Surface properties of the nonionic surfactants derived from esterification of sucrose with fatty acids were reviewed (Passedouet, *Riv. Ital. Sostanze Grasse* 9, 464). A pilot plant process was described for production of sucrose esters of linoleic acid by transesterification between the methyl esters of the fatty acid and sucrose in dimethylformamide solvent (Bobalek et al., *I & EC Prod. Res. Dev.* 2, 9). Analytical methods used on sucrose esters were reviewed (Roussos, *Riv. Ital. Sostanze Grasse* 9, 451); and another review discussed possible uses, toxicological properties and methods of manufacturing of sucrose esters (Nobile, *Riv. Ital. Sostanze Grasse* 9, 439). A polyoxyethylene adduct of a sucrose fatty acid ester was patented (Komori and Okahara, *U.S.* 3,102,114). It was reported that starch heated with a polyol in the presence of an acid catalyst undergoes transglycosidation and forms a mixture of polyol glycosides which can be further polyetherified and then esterified with fatty acids (Otey et al., *JAACS* 40, 76). A triester of a hexitan and a fatty acid and a polyoxyethylene derivative of a partial ester of a hexitan and a fatty acid were patented as additives for hydrocarbon fuels to improve burning characteristics and reduce smoke and soot (McGuire, *U.S.* 3,066,018). A series of patents covered a method for separating insoluble fatty material from glyceride oil by treating the oil with fatty acid esters of carbohydrates. These carbohydrate esters included dextrin esterified with saturated long chain fatty acids and short chain fatty acids (Bauer, *U.S.* 3,059,008); sucrose esters of long chain saturated and unsaturated fatty acids (Schmid and Bauer, *U.S.* 3,059,009); sucrose esters of long chain and short chain saturated fatty acids (Schmid and Bauer, *U.S.* 3,059,010); and esters of saturated long chain fatty acids and glucose, gluconic acid or glucono delta lactone (Bauer, *U.S.* 3,059,011).

Fatty acids of improved color were obtained by distillation in the presence of esters of boric acid (Henkel and Cie., *Ger.* 1,131,835). Nuclear magnetic resonance and IR absorption spectra observed at temp near the melting points of the even numbered long chain fatty acids indicated a breakdown of crystalline character and onset of liquid-like motion at scattered points in the solid structure several degrees below the melting point, the breakdown increasing in extent as the melting point is approached (Barr et al., *Can. J. Chem.* 41, 1188). Reviews discussed the chemistry of fatty acids (Cusinberche, *Rev. Franc. Corps Gras* 9, 671), electron diffraction studies of fatty acid monolayers (Bannerjee et al., *Nature* 193, 873), the history of tall oil fatty acid production (Anon., *Paint Tech.* 26 (5), 26) and the preparation and properties of synthetic fatty acids obtained by the oxidation of paraffins (Solomon, *Rev. Franc. Corps Gras* 9, 626). The chemistry, manufacture and uses of dimerized fatty acids were reviewed (Byrne, *Off. Dig.* 34 (445), 229). Other reviews discussed the Diels-Alder reaction in the field of fats (Kaufman, *Fette Seifen Anstrichmittel* 64, 1115), and the determination of polymers in fats and oils (Firestone, *JAACS* 40, 247). Soybean stand oil was fractionated on a cellulose column into five fractions and these fractions were characterized (Capella et al., *Chim. e l'Ind.* 43, 1004). Thermally polymerized vegetable oils were also examined by cellulose column chromatography and it was concluded that the initial polymers are formed exclusively by dimerization (Fedeli et al., *Fette Seifen Anstrichmittel* 65, 402). Polymeric fatty acids produced by heat polymerization in the presence of a Friedel-Crafts catalyst were further treated with water in the presence of a clay mineral to increase the acid number (Barrett and Goebel, *U.S.* 3,097,220). In another modification of the process for polymerizing in the presence of clays, a small amt of nitrogenous compound was included to react with some of the fatty acids forming ammonia soaps (Goebel and Barrett, *U.S.* 3,076,003). A process for producing polymers of linolenic acid included thermal polymerization in the presence of steam at pressures above 40 psi followed by a catalytic polymerization treatment in the presence of water and a crystalline clay mineral (Goebel, *U.S.* 3,100,784). Glyceryl-1-monostearate was polymerized by heating in sealed tubes at 200–270C for 1–6 hr and the products analyzed (Kueck et al., *Rev. Argentina Grasas y Aceites* 4, 3).

GLC was used to determine cyclic fatty acids in the monomer fraction from heat polymerization of fatty acids (Block and Eisenhauer, *JAACS* 40, 272). Using a combination of urea

inclusion compound fractionation, GLC and molecular distillation, methyl esters from heat bodied linseed oil were analyzed and the distillate of the non-adducting fraction was shown to be composed largely of cyclic or branched esters (Gast et al., *Ibid.* 40, 287). By varying reaction conditions yields of 20-42 g cyclic fatty acids fluid at -50°C were obtained /100 g linseed oil (Eisenhauer et al., *Ibid.* 40, 129). High solvent ratios at lower temp gave the best yields and diethylene glycol was found to be the best solvent. In another set of experiments yields of cyclic acids from linseed oil were increased by removing the water from the starting materials and using the monosodium derivative of ethylene glycol as catalyst (Friedrich et al., *Ibid.* 40, 584). The relation between the fatty acid composition of hardened fats and their properties was investigated, and it was shown that determination of refractive index or I.V. as indices of dilution is valid only if selectivity and rate of formation of isooleic acid are constant (Pokorny, *Papers of the Inst. of Chem. Tech. Prague* 3, 347). During the hydrogenation of unsaturated fatty acids with hydrazine it was shown that isolated double bonds react with equal speed and the rate of hydrogenation of *cis* and *trans* bonds is virtually the same (Chilling, *Fette Seifen Anstrichmittel* 65, 395). Reduction of linolenic acid with hydrazine was shown to yield an equimolecular mixture of 9-, 12- and 15-octadecenoic acids by a mechanism involving a diimide and requiring the presence of oxygen (Dutton et al., *JAACS* 40, 175). Fourteen samples of hydrogenated rapeseed oil were analyzed by GLC and the hydrogenation process was found to be highly selective for linolenic and linoleic acids (Jakubowski et al., *Rev. Franc. Corps Gras* 9, 678).

Analysis of the products of thermal polymerization of four kinds of isomers of methyl linoleate showed the same kind of dimer was obtained from each isomer and the yield of conjugated *trans-trans* isomer was highest (Nagano and Tanaka, *Yukagaku* 11, 119). Heating the methyl esters of cuttle fish oil at 200-250°C caused formation first of *cis-cis-trans* and then *trans-cis-trans* triene compounds (Miyakawa and Nomizu, *Fette Seifen Anstrichmittel* 64, 593). *Cis-trans* isomerization of oleic acid and its derivatives was carried out by heating less than two hours at temp in excess of 180°C in the presence of an acid clay (Brown and Swidler, *U.S.* 3,065,248). Comparing isomerization processes it was found that 9-*trans*, 12-*trans*-octadecadienoic acid prepared by nitrous acid isomerization could be purified by passage through a silicic acid column, whereas purification of selenium isomerized materials was virtually impossible (Harlow et al., *JAACS* 40, 505). Analysis of the equilibrium composition of *cis* and *trans* isomers using gas chromatography and IR spectroscopy showed the oleic/elaeidic equilibrium mixture contains 75-80% elaidic instead of the generally accepted 66% value. Similar values were found for *trans* bonds formed in linoleic and linolenic acids (Litchfield et al., *Ibid.* 40, 553).

Five branched chain fatty acids were synthesized from myristic acid (Haque and Saha, *J. Indian Chem. Soc.* 39 (7), 485). Three new oilseeds rich in *cis*-11-eicosenoic acid were identified (Mikolajczak, *JAACS* 40, 294). Coriander seed oil and parsley seed oil were shown to be good sources of petroselenic acid (Privett et al., *Ibid.* 40, 28). Sources, isolation and properties of petroselenic acid were reviewed (Placek, *Ibid.* 40, 319). Docosahexanoic acid was prepared in 90% purity on a large scale by molecular distillation of menhaden oil acids followed by urea fractionation (Stout, *Ibid.* 40, 40). Preparation and properties of fatty acids, fatty alcohols, wax esters and methyl esters from the seed oils of *Crambe abyssinica* and *Lunaria annua* were described (Miwa and Wolff, *Ibid.* 40, 742). Potential products and uses of the oil of *Crambe abyssinica* were evaluated (Bruun and Matchett, *Ibid.* 40, 1). Erucic acid in 95% purity was obtained by low temp crystallization of rapeseed oil fatty acids or methyl esters from acetone solution (Taufel et al., *Fette Seifen Anstrichmittel* 64, 1023). It was shown that linoleic acid of 97% purity can be obtained from safflower oil by liquid-liquid extraction on a plant scale (Sohns et al., *JAACS* 40, 169). Positional isomers of linoleic acid were synthesized by coupling 1-bromo-2-alkynes with the Grignard derivative of appropriate chloroalkylacetylenes in the presence of cuprous chloride and converting the resulting 1-chloro-*cis,cis*-heptadecadienes into 18-carbon acids by carbonating the Grignard reagents formed from them (Grensler and Bruno, *J. Org. Chem.* 28, 1254). A process was patented for enzymatic omega carboxylation of fatty acids using animal visceral organ tissue homogenates (Robbins, *U.S.* 3,080,296). A hitherto unknown *cis*-8-*trans*-10-*cis*-12-octadecatrienoic acid was found as a major component in the seed oil of *Jacaranda mimosifolia* D. Don (Chisholm and Hopkins, *J. Am. Chem. Soc.* 84, 3137).

Large samples of methyl epoxyoleate of 93.6% purity were prepared in 92% yield by a single crystallization of methyl esters of *Veronica anthelmintica* seed oil from petroleum ether

at -60°C (Barford et al., *JAACS* 40, 136). Epoxidation of oleoyl and linoleoyl esters of tetrahydrophthalyl alcohol and dioleoyl and dilinoleoyl tetrahydrophthalate was described (Scholnick et al., *Ibid.* 40, 229). A process was described for epoxidation of unsaturated fatty compounds by treatment with percarboxylic acids in the presence of oxides of aluminum (Henkel and Cie, *Brit.* 865, 271). Aliphatic compounds were converted to epoxy acids by treatment with hydrogen peroxide in the presence of an alkanesulfonic acid (Silbert and Swern, *U.S.* 3,079,411). The thermal degradation of epoxy fatty acids was studied (Suhara, *Yukagaku* 11, 473). An epoxidized vegetable oil was reacted with a 3-halocyclopentene in the presence of a Friedel-Crafts catalyst to produce a novel cyclopentenyl ether (Marcus and Fitzpatrick, *U.S.* 3,068,255). Another patent described the products obtained by reacting together polyols and epoxidized fatty compounds at 65-170°C (Groote and Cheng, *U.S.* 3,066,159). Esters of oxirane containing fatty acids were produced by alcoholysis in the presence of an alkaline interesterification catalyst at temp below 125°C (Kuester and Ohlson, *U.S.* 3,070,608). Pure hydroxy stearic acid in 50% yield was prepared from red oil by acetoxylation, deacetylation, distillation, saponification, acidification and crystallization from hexane (Munns et al., *JAACS* 40, 22). Hydroxy derivatives of undecylenic acid from castor oil were prepared and evaluated for use in ester and alkyd formulations (Rao and Achaya, *J. Sci. Ind. Res.* 21D (12), 446). A process was patented for preparing 10-hydroxydecanoic acid from ricinoleic acid (Fray et al., *U.S.* 3,084,178). The preparation of hydroxy methyl linoleate by selective reduction of the hydroperoxide with sodium sulfite and the results of treating methyl linoleate with *N*-bromosuccinimide were reported (Dulog et al., *Fette Seifen Anstrichmittel* 64, 553). Addition of polar substituents to unsaturated fatty acids or their methyl esters was found to increase their absorption affinity sufficiently to permit separation of bromo and hydroxy stearic acid derivatives and *cis* and *trans*-hydroxy isomers on silica gel columns (Sgoutas and Kummerow, *JAACS* 40, 138). The addition of hydrogen halides to cyclopropenoid fatty acids was investigated (Bailey et al., *Ibid.* 40, 69), and a procedure was described for quantitative determination of cyclopropenoid fatty acids by addition of a molecule of HCl at the cyclopropene ring (Magne et al., *Ibid.* 40, 716).

The chemistry of ozonolysis of unsaturated fatty acids and their derivatives was reviewed (Maggiolo, *Ibid.* 40, 161). Methyl azelaldehyde was prepared in 99.8% yield with 82.5% recovery by ozonolysis of commercial methyl oleate, separation of the aldehyde as the sodium bisulfite addition compound, regeneration with 10% sodium hydroxide and distillation (Miller et al., *Ibid.* 40, 720). Aldehyde oils containing an average of one or two aldehyde groups/glyceride molecule were prepared by partial ozonization of soybean oil in ethyl acetate-methanol solvent, followed by catalytic reduction with palladium on charcoal in the presence of pyridine (Pryde et al., *Ibid.* 40, 497). The presence of pyridine in the methanol solvent during hydrogenation of methyl oleate ozonolysis products in the presence of palladium on charcoal was found to reduce the amt of dimethyl azelate by-product formed and to poison the catalyst for hydrogenation of olefinic unsaturation (Pryde et al., *J. Am. Chem. Soc.* 84, 3055).

Butadiene was dimerized with sodium dispersion in tetrahydrofuran in the presence of a catalytic amount of *o*-diphenylbenzene and the dimer treated with carbon dioxide to form carboxylic acids (Hiraoka et al., *Yukagaku* 12, 335). A double decomposition soap process was patented in which the starting material was a calcium soap of a fatty acid dispersed in water (Olson, *U.S.* 3,078,288). Alkali metal carboxylic acid salts of long chain fatty acids and of α -sulfo fatty acids were determined by titration with HBr in glacial acetic acid using crystal violet as indicator (Haerberer and Maerker, *JAACS* 40, 274). The thermal behaviour of tri-soaps, isopropoxide soaps and chloride soaps of aluminum was studied using a thermogravimetric balance (Rai and Mehrota, *J. Indian Chem. Soc.* 40, (5), 359).

Alcohols having potential industrial value were prepared by selective sodium reduction of purified neem oil (Skellon et al., *J. Sci. Food Agr.* 13, 639). Diols were synthesized by the addition of ethylene oxide and propylene oxide to disodium octadiene (Hiraoka et al., *Yukagaku* 12, 343). The acid catalyzed addition of ethylene oxide to isomeric butyl alcohols was studied (Stockburger and Brandner, *JAACS* 40, 590). Lauryl alcohol and 6-hydroxycaproic acid were prepared from ozonolysis products of petroselenic acid and its ethyl ester by reduction with sodium borohydride (Fore et al., *Ibid.* 40, 30). The production and chemistry of Alfol alcohols was reviewed (Atwood, *JAACS* 40, 64). The construction and application of a multistage apparatus for zone refining of synthetic primary, normal alcohols were described (Schildnecht et al., *Fette Seifen Anstrich-*

mittel 64, 493). A study of spreading and collapse phenomena in monolayers of pure fatty alcohols showed the existence of hydrates of the alcohols (Brooks and Alexander, *J. Phys. Chem.* 66, 1851). Experiments on wave attenuation by fatty alcohols were reported and discussed in terms of theory (Goodrich, *Ibid.* 66, 1858). Unsaturated glyceryl ethers isolated from the unsaponifiable fraction of cod liver oil by a chromatographic method were shown to have high bacteriostatic activity (Emmerie and Engel, *Fette Seifen Anstrichmittel* 64, 813).

New reactions involving the double bonds of unsaturated fats and oils were reviewed (Harwood, *JAACS* 40, 204). Benzoic acid, phenols and cyclohexene were shown to add to oleic acid in the presence of methanesulfonic acid as catalyst-solvent (Eisner, *Ibid.* 40, 594). Surface active clay minerals also were described as effective catalysts for phenolating fatty acids (Barrett and Goebel, *U.S. 3,074,983*). Addition of formaldehyde to oleic acid in acetic acid as solvent, using periodic acid as catalyst, led to formation of an ester of 3-octyl-4-hydroxy-5-carboxyhexyltetrahydropyran (or 3-heptyl-4-hydroxy-5-carboxyheptyl-tetrahydropyran) and a mixture of 9- and 10-hydroxy-stearic acid (Hirai et al., *Yukagaku* 12, 201). Condensation of 1-octadecene with formaldehyde in acetic acid in the presence of periodic acid, followed by saponification, gave 1,3-nonadecadiol, 3-pentadecatetrahydropyran-4-ol and a mixture of octadecan-2-ol and octadecan-3-ol. No reaction occurred when water was present or in the absence of acetic acid (Hirai et al., *Ibid.* 12, 205). Methyl oleate was nitrated quantitatively at the double bond, using acetyl nitrate as nitrating agent, to form isomeric nitro, acetoxynitro and nitro-nitrate derivatives. These compounds were then reduced to form methyl amino stearate (Malins and Houle, *JAACS* 40, 43). Olefinic fatty acid derivatives were phosphorylated with a phosphorus trichloride-aluminum chloride complex to form phosphinic acid derivatives by addition of PO(OH) to a double bond (Jungermann et al., *Ibid.* 40, 41). Oils sulfurized with S₂Cl₂ were fractionated by absorption chromatography and extraction and their physical and chemical properties examined (Schiemann et al., *VI FATIPEC Congress, 1962*, 214). Petroleum ether extracts of alkylbenzenesulfonates were found to contain a hydrophobic fraction in the unsulfonated oil portion (Shoji and Majima, *JAACS* 40, 170).

Amides of ricinoleic acid and related hydroxylated compounds were synthesized and characterized (Appelwhite et al., *Ibid.* 40, 101). Gas chromatographic analysis of fatty acid amides was accomplished by converting them to nitriles directly on the column (Metcalf et al., *J. Gas Chromatog.* 1, (5), 32). Amides were prepared by adding an ester of a higher fatty acid to a secondary dihydroxyalkyl amine at a temp of 200–280F under nonvacuum conditions in the presence of a relatively high level of an alkali metal catalyst (Lamberti and McCrimlisk, *U.S. 3,107,258*). *N*-monooleoyl derivatives of fatty acid amides were described as minor components of a plastic composition (Clark and Hill, *U.S. 3,104,232*). Mixtures of aliphatic nitriles prepared from palmitic, oleic, stearic and coconut fatty acids were analyzed by vapor phase chromatography (Pokorny and Zeman, *Papers of the Inst. of Chem. Tech. Prague 4-II*, 255). *Bis*-cyanoethylation of fatty amines was found to take place readily in polar solvents, but in the absence of solvent or in the presence of nonpolar solvents the reaction was slow or only the monocyanoethylation product formed. Reactions investigated included the synthesis of *bis*-cyanoethyl cetylamine (Nitanai and Saito, *Yukagaku* 12, 154) and *bis*-cyanoethyl hexylamine (Nitanai and Kawamura, *Ibid.* 12, 210). The use of fatty acid derivatives in urethane polymers was reviewed (Goldblatt and Lyon, *JAACS* 40, 157). A method was described for determination of primary, secondary and tertiary amines by spectrophotometric measurement of the yellow complex these amines form with methyl orange (Silverstein, *Anal. Chem.* 35, 154). A study of the preparation of *t*-amine oxides showed that max yields are obtained by hydrogen peroxide oxidation in water (Hoh et al., *JAACS* 40, 268). In the reaction of tertiary amines with epichlorohydrin to form quaternary ammonium compounds, oxirane rings were formed only when the initial reaction products were further treated with sodium hydroxide (Nitanai et al., *Yukagaku* 12, 29). Quaternary ammonium compounds were subjected to gas chromatographic analysis on strongly alkaline columns without obtaining any evidence for the expected Hoffman degradation (Matcalfe et al., *JAACS* 40, 25).

Magnesium oxide deposited on an inert carrier was used as catalyst for the thermal decarboxylation of fatty acids to form ketones (Hammerberg and Chesrown, *U.S. 3,075,016*). The adduct formed by reaction of an anhydride of a polybasic aromatic acid with a hydroxyl group of a fatty acid ester containing at least two OH groups was patented (Matt, *U.S. 3,098,051*). Chlorides of linolenic acid, the eleostearic acids and parinaric acid were prepared using phosgene and pyridine with appropriate solvents (Kaufmann and Gulinsky, *Fette*

Seifen Anstrichmittel 64, 599). Aliphatic and some aromatic acid chlorides were treated with ethyl aluminum-sesquichloride in aliphatic hydrocarbons as solvent to form the ethyl ketones in yields of 80–85% (Bertsch and Reinheckel, *Fette Seifen Anstrichmittel* 64, 881). The halogenation of fats and oils to form fluorinated derivatives, reactive intermediates and products which can be dehydrohalogenated to produce more highly unsaturated fats was reviewed (Sountag, *JAACS* 40, 199).

FATTY MATERIALS USED IN TEXTILE AND PAPER TREATMENT, WATER-PROOFERS, CORROSION INHIBITORS, WAXES, DEFOAMERS, WELL-DRILLING FLUIDS, INCENDIARY PREPARATIONS, AGRICULTURAL AND MISCELLANEOUS

Sulfonated oils used in the textile and tanning industries were reviewed (Farran, *Lipidos* 22, (Jabones), 2). Quaternary ammonium salts containing various anions were obtained by reacting the corresponding amine salt with ethylene oxide and their properties of surface tension, wettability, antistatic effect and their adsorption by various kinds of textile material were tested (Yamamoto et al., *Yukagaku* 11, 646). Alkylated polyvinyl alcohols obtained by solution polymerization of vinyl acetate with C-8, C-12, C-16 and C-18 alcohols were shown to have excellent restraining effect for vat color and the migration of sulfide color (Konishi et al., *Yukagaku* 12, 37).

A hard ester wax was prepared by esterifying an oxyalkylated polyhydric alcohol with an aliphatic long chain carboxylic acid (Kaupp and Thalhofer, *U.S. 3,062,671*). Esters of trimesic acid, trimellitic acid and related compounds, succinic anhydride and a monoglyceride of a fatty acid were patented as smear resistant waxes (Broadhead, *U.S. 3,106,538*). The production of wool grease, a wax composed of ester of higher fatty acids with higher fatty alcohols, was reviewed (Goode, *JAACS* 40 (2), 4A).

Vat residues from soap making were suggested as raw materials for preparation of potash soaps (Gromakovskii, *Maslob. Zhir. Prom.*, 29 (1), 38). Reviews discussed the problems of the Italian olive oil industry (Coppa-Zuccari, *Grasas y Aceites (Seville, Spain)* 13, 253); the olive tree and olive oil as major factors in the economy of Spanish agriculture (Morales, *Ibid.* 14, 16); and the place of oilseeds in Indian economy (Patel and Ramakrishna Rao, *Indian Oilseeds J.* 6, 67). Location of uranium deposits by analyzing the waste liquids from olive oil mills was suggested (Martinez et al., *Grasas y Aceites (Seville, Spain)* 13, 165). In a preliminary note on measurement of the rheological properties of ground olive pastes it was noted that addition of coconut fatty acid diethanol amides increases the consistency of the pastes (Brabender et al., *Ibid.* 13, 197).

Rice bran oils obtained by expression and by solvent extraction were compared (Takeshita and Shoji, *Yukagaku* 11, 101), selective extraction of adsorbed components by a methanol-acid decolor was described (Takeshita and Shoji, *Ibid.* 11, 113) and decolorization methods were evaluated (Takeshita and Shoji, *Ibid.* 11, 162). Reviews of the production, composition and uses of specific oils included: Palm oil (Loncin and Jacobsberg, *JAACS* 40 (6), 18A); menhaden fish oil (Lane and Krieger, *Ibid.* 40 (1), 5A); peanut oil (Lambou et al., *Ibid.* 40 (12), 4A); cottonseed oil (Decossas et al., *Ibid.* 40 (4), 4A); rubber seed oil (Azzimodini and Thirumala, *Rubber Board Bulletin* 6, (2), 1); tallow (Moulin, *Rev. Franc. Corps Gras* 9, 601).

The preparation and properties of vinyl monomers containing saturated or unsaturated fatty radicals were reviewed Teeter, *JAACS* 40, 143). Dipentene was found to be an effective chain transfer agent in the styrenation of fatty vinyl ether polymers of unsaturated fatty alcohols (Gast et al., *Ibid.* 40, 88). A programmed temperature gas chromatography procedure for separating 1-olefins ranging in chain length from C-8 to C-18 was described (Poe and Kaelble, *Ibid.* 40, 347). A method was patented for fat liquoring skins and leather with an aqueous composition including the reaction product of epoxidized esters of higher fatty acids and alcohols with polybasic inorganic acids (Plapper and Dieckelmann, *U.S. 3,101,238*). Vegetable oil and a water-dispersible polyuronide were listed as active components of a patented oil emulsion composition which could be extruded into a precipitating bath to form filaments, ribbons or sheets (Schram, *U.S. 3,085,015*).

A process for encapsulation of finely divided lipophilic material comprised preparing a dispersion of fatty material in an aqueous solution of a styrene maleic anhydride copolymer, adding an insolubilizing salt until clouding occurred, adjusting the pH of the mixture to obtain an opacity in the mantle and separating the resulting capsules from the aqueous liquid (Jensen and Wagner, *U.S. 3,069,370*). Small amt of fatty acids (or fats or oils) and an oleophilic petroleum sulfonate were included in a patented formulation of a hydraulic cement (Harris,

U.S. 3,097,955). A method was described for sweetening fatty acid soil contaminated dry cleaners' solvents by preferentially adsorbing fatty acid from the medium with particulate hydrated calcium silicate (Riede, U.S. 3,099,626).

FATTY MATERIAL IN LUBRICATION, METALWORKING AND TEXTILE OILING

Patents were issued for preparing a calcium salt-calcium soap grease by a shearing process (Roach and Crookshank, U.S. 3,068,175); for a grease composition composed of calcium salts of fatty acid having 1-3 carbon atoms, calcium soaps of fatty acids and hydroxy fatty fatty acids having 12-18 carbon atoms and small amt of an estolide of an hydroxy fatty acid having 10-24 carbon atoms (Pelton and Odel, U.S. 3,068,174); and for an extreme pressure calcium base grease thickened with 17-30% by wt of a calcium soap-calcium salt complex containing esters and calcium acid salts of a low mol wt fatty acid and of a high mol wt fatty acid (Roach and Jordan, U.S. 3,068,173). Another lubricant composition was described as containing alkaline earth metal salts of acetic acid and alkaline earth metal soaps of C-14 to C-30 fatty acids (Morway, U.S. 3,077,450). To prevent age hardening, a small amt of an acetoxy substituted fatty acid, ester or triglyceride was included in a lime soap lubricant grease composition (Swenson and Zajac, U.S. 3,100,193). A soap-salt thickener for a lubricating oil composition comprised alkaline earth metal salts of C-2 to C-4 fatty acids and elaidic acid (Morway, U.S. 3,098,822). In a second formulation an alkaline earth metal soap of tall oil was used in place of the soap of elaidic acid (Morway, U.S. 3,098,823). Improved wear characteristics of a lubricant were obtained by irradiating the mixture for a time sufficient for the absorption of 24 megareps radiation (Ambrose and Trautman, U.S. 3,100,185). Up to 3% of a hindered phenol was included in a lubricant composition (Morway, U.S. 3,107,220). Applications of lanolin, wool grease alcohols and ethoxylated lanolin in rust preventive compositions, strippable coatings, putty, printing inks and paints were reviewed (Clark and Kitchen, *Paint Manuf.* 32 (No. 1), 9; (No. 2), 55).

PRODUCTS (EXCEPTING DETERGENTS)

DRYING OILS, PAINTS, RESINS AND PLASTICIZERS

Specific Oils: Source, Composition, Properties

Data on the linoleic and linolenic acid contents of a number of different vegetable oils were collected (Blatná and Manouskora, *Nahrung* 1962, 332). A review discussed the composition and principal applications of soybean oil (Ramos, *Grases y Aceites* 14, 122). A process for extracting oil from vegetable seeds such as soybeans, rape seeds and cotton seeds involved treating the crushed seeds with a substance such as boric acid, potassium carbonate, sodium hydroxide, potassium hydroxide or calcium hydroxide capable of gelatinizing the proteins in the seeds (Nanatan, *Jap.* 10,163/62). Studies on sunflower oil included the development of a rapid extraction method for determining the oil content of seeds (Costanzo and Sameh, *Rev. Agr. Grases y Aceites* 3, 57), demonstration of a poor correlation between oil content and percentage of kernel in the seed (Costanzo and Maymo, *Ibid.*, 109), and determination of differences in the analytical values and compositions of oils from different regions of Bulgaria (Rankov et al., *Izv. Inst. Obsta. i Neorg. Khimiya i Org. Khimiya, BAB* 8, 193). Smooth rolls were preferable to Bauer-type disc dehullers for dehulling of safflower seeds. Dehulling was more satisfactory at 6% moisture than at higher and lower moisture levels (Ahmed et al., *Indian Oil Seeds J.* 15 (5), 6). Changes in the lipid classes in Raja flax and Indian safflower seeds as the plants matured were followed. Triglycerides increased and phospholipids decreased with increasing maturity (McKillean and Sims, *JAOCs* 40, 108). The physical and chemical properties of a linseed oil from the seed of a linen flax were similar to those of an oil from flax seed grown for its oil content (Alexa and Caraculacu, *Studii Cerc. et Sti. Chim., Iassy* 12, 137). Side reactions taking place on the vacuum distillation of linseed acids were studied. Refluxing of the acids apparently caused formation of acid anhydrides (Yoshitomi et al., *Yukagaku* 12, 399). Occurrence, isolation, composition and properties of isano oil were summarized (Poulquien, *Peint. Pig. Vernis* 38 (2), 69; (3), 129). A review of current research on tung oil in the U.S. and Argentina discussed thermopolymerization of elaeostearic esters, production of a water-soluble oil by reaction with fumaric acid, catalytic air blowing to improve film properties, copolymerization of the air-blown oil with styrene and epoxidation (Austin, *Paint Ind. Mag.* 77 (9), 23). Reviews covered the production of tall oil and its fatty acid and rosin components (*Paint Tech.* 26 (5), 26; *Asche, Farbe u. Lack* 68 (7), 448;

(8), 518). The following derivatives of castor oil were prepared in order to study their use in alkyd resins; undecylenic alcohol, dihydroxyundecane, trihydroxyundecane and the monoglyceride of undecylenic acid (Subbaroa and Achaya, *J. Sci. Ind. Res.* 21D (12), 446). The seed oil of hops was extracted and analyzed. It contained a total of 80% of linoleic, linolenic and 6,9,12-octadecatrienoic acids. Hemp seed oil contained 73% of the first two of these acids but only a trace of the third (Roberts, *Chem. Ind. (London)* 1963, 608). The properties of the oil of katalpa, a Russian plant, were compared with those of linseed and tung oils. Use of katalpa oil in alkyd resins was suggested (Vodnya et al., *Lakokras. Mat.* 1962 (5), 78).

The seeds of *Astragalus sinicus* contained 5.9% of an oil whose iodine value (I.V.) was 129.6 and which contained 73.7% of unsaturated acids (oleic, linoleic and linolenic) (Ueno and Hamada, *Yukagaku* 12, 358). The seeds of purple passion fruit (*Possiflora edulis*, Sims) contained 23.8% of a semi-drying oil (Pruthi, *Indian Oil Soap J.* 28 (3), 55). The fatty acids from chloroplasts of *Spinacia oleracea* contained over 70% of polyenoic acids, a high proportion of which were hexadecatrienoic (Debuch, *Experientia* 18, 61). α -eleostearic acid was found in the oil of Valerianaceae, in certain species of Rosaceae and in *Momordica charantia*. The oil of *Momordica balsamina* was a convenient source of punicic acid. Other members of this family contained no conjugated acids. A new isomer of α -eleostearic acid was the major acid in the oil of *Catalpa ovata* (Hopkins and Chisholm, *Review of the National Research Council, Canada* No. 6816, 102). This acid was *trans-9,trans-11,cis-13*-octadecatrienoic acid. It was also present to the extent of 18% in the seed oil of *Chilopsis linearis* along with 5-10% of 10,12-octadecadienoic acid (Hopkins and Chisholm, *Chem. Ind. (London)* 1962, 2064). The seed oil of *Jacaranda mimosifolia* D. Don contained *cis-8,trans-10,cis-12*-octadecatrienoic acid (Chisholm and Hopkins, *J. Org. Chem.* 27, 3137). The major acid (43 and 57%, respectively) in the seed oils of *Comandra pallida* A. DC. and *Ostrya alba* L. was an acetylenic acid, probably *trans-11*-octadecen-9-yonic (ximenynic) (Mikolajczak et al., *JAOCs* 40, 342). A new hydroxy fatty acid, 12-hydroxy-*cis-9,cis-15*-octadecadienoic acid, was found as a major constituent of the seed oil of *Lesquerella densipila* and was named densipolic acid (Smith et al., *J. Org. Chem.* 27, 3112). A study of the fatty acids in maturing *Vernonia anthelmintica* (L.) Willd. showed a high concn of (+) *threo-12,13*-dihydroxy-*cis-9*-octadecenoic acid, a probable precursor of epoxyoleic (vernolic) acid, at an intermediate stage (Miwa et al., *JAOCs* 40, 225). The seeds contained enzymes which became active only after the seed was ground. If the enzymes were deactivated, an oil rich in trivernolin was obtained. If the enzymes were not deactivated, the oil underwent changes which were due, at least in part, to the formation of dihydroxyoleic acid (Scott et al., *Ibid.*, 587). A number of *Vernonia* seeds were found to have oil contents ranging from 1.6-26.9%, concn of oxygenated acids (mainly epoxyoleic) in the oils ranging from 8-90% (Badami and Gunstone, *J. Sci. Food Agr.* 14, 481).

The manufacture of fish oil and fish meal was reviewed (Brenner, *Rev. Arg. Grases y Aceites* 5, 13). Nuclear magnetic resonance studies indicated that the double bonds of highly unsaturated fish methyl esters had the divinylmethane arrangement rather than divinylethane and that the double bond farthest from the ester group was in the 2,3-position from the end of the carbon chain (Hashimoto et al., *JAOCs* 40, 124). A review covered the source, production methods, composition and use of menhaden oil (Lane and Krieger, *Ibid.* (1), supp. 4). A method for obtaining docosahexaenoic acid from menhaden acids involved fractional molecular distillation of the methyl ester followed by urea adduct formation (Stout, *Ibid.* 40, 40). The compositions of the oils from skipper (Ito and Fukuzumi, *Yukagaku* 12, 272), sardine, cuttlefish, oil-flatfish (*Cynopsetta dubia*), goby, tunny, swordfish, cod-liver and shark-liver were determined. Although the relative percentages of the various acids varied depending upon the source of the oil, the same acids were found in all cases. No acids characteristic of a specific kind of fish were found (*Ibid.*, 278). The oils of half-beak, *Pagrosomus major*, *Harengula zunasi* and *Saurida argeyrophane* had I.V. of 160.4, 164.4, 168.1 and 195.4, respectively (Ueno and Hamada, *Ibid.* 11, 526, 630). Isolation and degradation of the highly unsaturated fatty acids of kelp bass, *Paralabrax clathratus*, following injection of methyl linolenate-1-C¹⁴ led to the deduction of a probable route for the conversion of linolenic acid into the highly unsaturated acids (Kayama et al., *JAOCs* 40, 499).

The Drying Process; Autoxidation

A review covered the theories of autoxidation of monounsaturated fatty acids and esters (Skellon and Wharry, *Chem. Ind. (London)* 1962, 929). The role of metallic driers in both

the drying and aging of films was studied (Myers, *Off. Dig.* 34 (449), 575).

The induction period in the oxidation at 100C of linseed and soybean oils was decreased by the removal of phosphatides and tocopherols and completely eliminated by small additions of the ordinary lead, manganese or cobalt driers (*Tech. Notes* (British Oil and Cake Mills) 45, 1 p.). The drying of linseed oil was accelerated by subjecting the oil to a previous partial oxidation to destroy antioxidants and to form peroxides. The greatest decrease in drying time corresponded to the oxidation stage at which the peroxide content reached a maximum. The drying rate was dependent not only upon the peroxide content, but also upon the rate of oxygen introduced during the oxidation stage (Pokorný, *Papers of the Inst. of Chem. Tech., Prague 4-II*, 223). The autoxidation of blown linseed oils proceeded as a first order reaction. Their peroxide content was so high that there was not a sufficient amt of oxidizable fatty acids present to utilize the ability of hydroperoxides to start a chain reaction. If the blown oils were heated to decompose peroxides, their autoxidation then started at a low rate and proceeded by an autocatalytic second order reaction, reverting again to first order after a sufficient amt of peroxides had been formed (*Ibid.* 3, 261). Color changes of linseed oil during autoxidation were studied. The optical density at 450 m μ first increased, then fell at the end of the induction period to a value below that of the original oil, then increased on further oxidation (*Ibid.* 4-I, 205). The drying of raw dimorphothea oil (*Dimorphothea aurantiaca*), which was highly inhibited, was accelerated if the oil were heat processed (Rheineck and Sobol, *Paint Tech.* 27 (5), 18).

The carbonyl compounds in autoxidized salmon oil included C₇-C₁₂ alkanals, C₇-C₁₂ alk-2-enals and C₆-C₁₀ alka-2,4-dienals (Wyatt and Day, *J. Food Sci.* 28, 305). Studies were made on the geometric configuration of the double bonds and on the content of conjugated double bonds, hydroperoxides and dihydroperoxides, and carbonyl compounds in peroxide cone from the autoxidation of methyl esters of highly unsaturated acids derived from cuttlefish oil. The reactions included the autoxidation of methyl eicosapentaenoate (Fukuzumi et al., *Yukagaku* 12, 89) and methyl docosapolyenoate (*Ibid.*, 348) at 0-2C in the dark, methyl docosahexaenoate (*Ibid.*, 351) at 33-35C in the dark and methyl esters of mixed highly unsaturated acids (*Ibid.*, 392, 396) by blowing at 35C in sunlight.

Products Formed Via Double Bond Changes

A symposium paper on the chemical modification of oils discussed the addition of maleic anhydride to unsaturated acids, the Diels-Alder reaction of conjugated polyunsaturated acids, the dimerization of dienolic acids and increasing the unsaturation of oils by elimination reactions (Harwood, *JAOCs* 40, 204). The production of fractions with increased unsaturation from linseed, safflower and rice bran oils by urea adduct formation was studied. A linoleic acid of 86% purity was obtained from safflower acids (Yoshitomi, *Yukagaku* 11, 641).

ISOMERIZATION. By nitrous acid isomerization of a linoleic acid cone from safflower acids 9-*trans*,12-*trans*-octa-decadienoic acid was obtained (Harlow et al., *JAOCs* 40, 505). Studies of the selenium or nitrous acid isomerization products of oleic, linoleic and linolenic acids indicated that the equilibrium mixtures contained 75-80% of *trans* double bonds (Litchfield et al., *Ibid.*, 553). When cuttlefish methyl esters were heated at 200-250C, *cis-cis-trans* and then *trans-cis-trans* triene compounds were formed, which then underwent inter- and intramolecular cyclization (Miyakawa and Nomizu, *Fette Seifen Anstrichmittel* 64, 593). The alkali fusion of unsaturated fatty acids was reviewed (Vasquez, *Grasas y Aceites* 14, 66). Lipid C₁₈ saturated monobasic acids containing a ring structure (cyclic acids) are formed by heating linseed oil in ethylene glycol in the presence of sodium hydroxide, followed by distillation and hydrogenation of the resulting fatty acid monomers. A study of reaction conditions showed that yields were improved by using higher solvent ratios, higher percentages of sodium hydroxide catalyst and using diethylene glycol as the solvent (Eisenhauer, *JAOCs* 40, 129). Yields were also improved by using water-free starting materials and using the monosodium derivative of ethylene glycol as the catalyst (Friedrich et al., *Ibid.*, 584).

DEHYDRATION AND DEHYDROHALOGENATION. Dehydrated dimorphothea oil, prepared similarly to dehydrated castor oil, dried rapidly (Rheineck and Sobol, *Paint Tech.* 27 (5), 18). A review on halogenation in fat technology referred to drying oils prepared by the polychlorination of fatty acids followed by dehydrochlorination to produce highly unsaturated acids (Sonntag, *JAOCs* 40, 199).

POLYMERIZATION. The manufacture and uses of dimerized fatty acids were reviewed (Byrne, *Off. Dig.* 34 (445), 229;

Paint Tech. 26 (3), 28; Van Veersen, Riv. Ital. Sostanze Grasse, 10, 517). Thermodimerization of the geometric isomers of methyl linoleate was studied. It was concluded that the dimer had a six membered ring formed by the Diels-Alder reaction of the conjugated *trans-trans* isomer with the nonconjugated *trans* isomer (Nagano and Tanaka, *Yukagaku* 11, 119). Heating glyceryl-1-monoleostearate at 200-270C produced mostly dimer (deKuck et al., *Rev. Arg. Grasas y Aceites* 4, 3). Using various methods of fractionation and analysis the compositions of thermally polymerized vegetable oils (Fedeli et al., *Fette Seifen Anstrichmittel* 65, 402), including a soybean stand oil (Capella et al., *Chim. e Ind.* 43, 1004) and two heat-bodied linseed oils (Gast et al., *JAOCs* 40, 287), were studied.

Difficulties in the use of isano oil in the varnish industry were discussed. Because of the high reactivity of the oil it had to be heat processed below 200C. The heat processing of 4:1 linseed oil-isano oil mixtures at 250C was studied (Priester, *Farbe u. Lack* 68 (12), 879). Polymerized tall oil was prepared by heating the oil at 50-200C in the presence of H₂SO₄ and clay (Zenkoku Noson Kogyo Nogyo Coop. Union, *Jap.* 10,165/62). Unsaturated fatty acids were polymerized by heating in the presence of a surface-active crystalline clay mineral, water and a small amt of a nitrogen compound capable of forming an ammonium soap (Myers et al., *U.S.* 3,076,003). Another process consisted of polymerization at 260-340C at steam pressures above 40 psi, then continued polymerization at 180-200C in the presence of water and a crystalline clay mineral (Goebel, *U.S.* 3,100,784). In a similar process the first stage of polymerization was carried out in the presence of a Friedel-Crafts catalyst, and the second stage, during which the acid number of the polymer increased, was carried out at 180-260C (Barrett and Goebel, *U.S.* 3,097,220). A good surface coating material was obtained from tobacco seed acids by heating at 240-29.C in the presence of 2% of boric acid using tetralin as an azeotropic solvent (*Annual Report* (Hyderabad Reg. Res. Lab.) 1960-61, 15). A review covered the preparation, properties and uses of fatty α -olefins capable of polymerization by vinyl-type mechanisms (Teeter, *JAOCs* 40, 143).

DIELS-ALDER REACTIONS. The use of the Diels-Alder reaction for analysis, structure research and preparative work in the field of fats was reviewed (Kaufmann, *Fette Seifen Anstrichmittel* 64, 1115). Addition of ethylene, propylene, butylene and acetylene to the conjugated systems in fatty methyl esters and triglyceride oils were carried out at high temp and pressure. The adducts were dehydrogenated to yield aromatic compounds (Kaufmann and Buscher, *Ibid.* 65, 105; *Farbe u. Lack* 68 (12), 880). The film-forming properties of sunflower oil and of sunflower oil alcoholized with pentaerythritol were improved by treating the oils with maleic anhydride vapor present in the contact gasses obtained during the manufacture of the anhydride (Moskaleva, *USSR* 141,239; *Russian Patent Abs.* 30 A/B, Gp. 1, p. 2). Film forming materials were made from tall oil by copolymerization with cyclopentadiene (Subbotin, *Lakokras. Mat.* 1962 (5), 27).

OXIDATION; SULFURIZATION. Unsaturated aldehyde oils containing 1 or 2 aldehyde groups/glyceride molecule were obtained by partial ozonization of soybean oil, followed by hydrogenation (Pryde et al., *JAOCs* 40, 497). The reaction of S₂Cl₂ with oils was studied. Phenolic resin-oil varnishes were prepared using fractions of the sulfurized oils (Schiemann et al., *VI FATIPEC Congress* 1962, 214).

Products Formed Via Carboxyl Reactions

ESTERS WITH POLYHYDRIC ALCOHOLS; ALKYD RESINS. A study of the glycerolysis of linseed oil at 235C showed that equilibrium was reached in about 1 hr (Rybicka, *Chem. Ind. (London)* 1962, 1947). The alcoholysis of linseed oil with pentaerythritol at 200C was investigated and the products were compared to those obtained by alcoholysis at 220-250C (Thuriaux, *VI FATIPEC Congress* 1962, 59). Reviews covered the preparation and properties of oleoresinous and alkyd enamels (Long, *Irish Painter & Decorator* 1 (4), 9, 21) and the use of linoleic acid in alkyd resins (Mestre, *Lipidos* 22, 38, 69). A manufacturer's brochure discussed the use of fatty acids, including dehydrated castor acids and dimeric acids, in alkyds (*Tech. Bull.* (Wolf Ltd.) 1962 (2) (2nd ed.), 25 pp.). Combinations of starting materials described in patented compositions included triethylene glycol, trimethylolpropane or trimethylolpropane and a mixture of dimer and trimer acids (LeBras and Park, *U.S.* 3,068,254); trimellitic or hemimellitic acid or anhydride, a polyalkylene glycol monoalkyl ether, a polyunsaturated fatty alcohol, a drying oil, a polyhydric alcohol and phthalic acid or anhydride (Broadhead, *U.S.* 3,066,108); a polyester of rosin, a glycol and fumaric or maleic acid and a material from the group consisting of tung oil, tung acids, tung methyl esters, blown tung methyl esters and allyl oleostearate (Root, *U.S.* 3,092,596). Non-drying alkyds suitable

for baked finishes were prepared using the glycidyl esters of synthetic saturated fatty acids (Goppel et al., *Farbe u. Lack* 69, 181). A waxy solid resin was prepared from trimesic, trimellitic or hemimellitic acid or anhydride, a saturated fatty mono-glyceride and succinic anhydride (Broadhead, *U.S.* 3,106,538).

ESTERS WITH UNSATURATED ALCOHOLS. A review covered the preparation, properties and uses of vinyl and allyl esters of saturated or unsaturated fatty acids, which are capable of polymerization or copolymerization (Teeter, *JAACS* 40, 143). The emulsion polymerization of vinyl stearate was studied and the quantitative theory of emulsion polymerization was critically examined (Parts and Morse, *J. Oil Color Chemists' Assoc.* 45 (9), 648).

Products Formed Via Epoxide Reactions

Products obtained from the reaction of epoxidized fatty oils, fatty acids or their derivatives with oxyalkylated polyols were described (DeGroot and Cheng, *U.S.* 3,066,159). Epoxidized vegetable oils reacted with a 3-halocyclopentene in the presence of a Friedel Crafts catalyst (Marcus and Fitzpatrick, *U.S.* 3,068,225). Free carboxyl groups in liquid coating compositions were eliminated by heating the material at 170–240C with an epoxidized fatty oil (Chatfield, *U.S.* 3,086,949). Resins obtained by the phthalic anhydride cure of epoxidized tetrahydrophthalyl dioleate and dilinoleate and of epoxidized dioleoyl and dilinoleoyl tetrahydrophthalate were compared with the resins obtained by the phthalic anhydride cure of the corresponding hexahydrophthalyl and hexahydrophthalate derivatives. The tetrahydro resins had higher heat distortion temp than did the hexahydro resins (Scholnick et al., *JAACS* 40, 229). The changes undergone by epoxy fatty acids and their derivatives when heated in nitrogen at temp up to 150C were studied. Solid epoxy compounds became liquid upon losing ca. 20% of their oxirane oxygen. The loss of 70% of oxirane oxygen caused gelation (Suhara, *Yukagaku* 11, 473).

Products Formed Via Hydroxyl Reactions

ESTERS AND ETHERS. Drying oils having secondary hydroxyl groups on unsaturated fatty chains were improved by reaction with beta-propiolactone (Bortneck and Vona, *U.S.* 3,059,002). Fatty esters containing two hydroxyl groups, at least one of which was on the fatty chain, were esterified with the anhydride of an aromatic polybasic (at least tribasic) acid (Matt, *U.S.* 3,098,051). Oxyethylated castor oil (15–45 moles of ethylene oxide) was esterified with a polycarboxylic acid (Kirkpatrick et al., *U.S.* 3,061,620). A review covered the preparation, properties and uses of vinyl ethers, allyl ethers, and acrylic esters of fatty alcohols, which were capable of polymerization or copolymerization (Teeter, *JAACS* 40, 143). Copolymers and terpolymers of vinyl ethers of linseed conjugated alcohols were evaluated as various types of protective coatings. They showed promise as baking finishes (Dent et al., *JAACS* 40, 713). Fatty vinyl ethers were treated with styrene in dipentene. The products, evaluated as baking finishes, were more alkali-resistant than those prepared in aromatic solvents (Gast et al., *Ibid.*, 88).

URETHANES. A review covered the chemistry of polyurethanes and of the use of fats and fat derivatives in these products (Goldblatt and Lyon, *Ibid.*, 157). Another review described the properties of urethane oils, for which the term "uralkyds" was proposed (Wells and Hixenbaugh, *Am. Paint J.* 46 (47), 88). Castor oil was treated with an organic polyisocyanate in the presence of an organotin catalyst (Hostettler and Cox, *U.S.* 3,084,177). A cellular product was prepared by the reaction of an alkyd resin, a polyhydric alcohol and an aromatic polyisocyanate, the resin and the alcohol containing small amt of water (Simon and Thomas, *U.S.* 3,106,537).

Drying Oil-Resin Combinations

A number of products were described which consisted of mixtures or reaction products of drying oil derivatives with other resins. These products included the reaction product of a polycyclopentadiene with an oil-modified alkyd resin (Dissen, *U.S.* 3,088,927); varnishes prepared from phenolic resins and dimorphothea oil (which were equivalent to tung oil varnishes) (Rheineck and Sobol, *Paint Tech.* 27 (5), 18); a heat-curable alkyd-amino resin combination catalyzed by a monoester of oxalic acid (Moffett and Walus, *U.S.* 3,102,866); a mixture of a fatty glycidyl ester and a cellulose ester (Clark, *U.S.* 3,066,033); and the product of the reaction of drying oils or acids with formaldehyde-treated rosin (*Annual Report* (Hyderabad Reg. Res. Lab.) 1960–61, 17). Epoxy resin-drying oil combinations included the reaction product of dehydrated castor or tall oil acids, tung acids or methyl esters and an epoxy resin (Goldblatt and Hopper, *U.S.* 3,079,354); a tin coating composition composed dehydrated castor and soy fatty acids,

styrene and epoxy resin (Tsurumi and Matsi, *J. Jap. Soc. Col. Mat.* 35 (1), 13); a corrosion inhibiting metal coating formed by adding an epoxy resin to a rice oil-polyfunctional amine reaction product (Meigs, *U.S.* 3,099,634); and a solventless varnish consisting of an oil-modified alkyd resin and an epoxy compound dissolved in a vinyl or allyl monomer (Meidensha Electric Mfg. Co., *Jap.* 2976/62).

Water-Dispersible Resins

A liquid water-dispersible composition consisted of the reaction product of a drying oil acid-polyhydric alcohol ester and a polyoxyethylene polyol (Schroeder and Pawlak, *U.S.* 3,100,157). A surface coating consisted of an aqueous emulsion of a fatty ester of an unsaturated alcohol-styrene copolymer and etherified amino resin, and a fatty ammonium salt as an emulsifier (Carney and Hahn, *U.S.* 3,069,368). Linseed monoglycerides, linseed sorbitan esters, linseed esters of polyoxyethylene ethers of sorbitan and polyoxyethylene ethers of linseed alcohol were investigated as emulsifiers in linseed oil emulsion paints (Kubie et al., *JAACS* 40, 105).

Non-Drying Oil-Based Resins

Polyesters prepared from tetrahydrophthalic anhydride, fumaric acid, diethylene glycol and styrene were suitable for furniture, automobile and appliance finishing (*Chem. Week* 90 (2), 41). A paint was manufactured by preparing a polyester from propylene glycol, a trihydric alcohol and a terephthalic ester and then mixing the polyester with polycarbonate ester and a small amt of a titanic acid ester or titanium chelate compound (Tokyo Tokushu Electric Wire Paint Co., *Jap.* 17,358/62). A bibliography on the prevention of air inhibition of polyesters included patents on the use of polyisocyanates, allyl compounds and long chain fatty esters and on an improved method for using paraffin wax (Whale, *Continental Paints & Resins* 1962 (66), 4).

The formulation, application and properties of urethane coatings were discussed and their resistance to 95 different chemicals was tabulated (National Assn. of Corrosion Engineers (USA), *Materials Protection* 1 (6), 105). Coatings formed on a surface by a chemical reaction between components of the vehicle, e.g., between an isocyanate and a polyether or alkyd, were referred to as "reaction lacquers." They showed a number of desirable properties (Foulon, *Wochbl. Papierfabrik* 1962 (90), 248, 250).

Properties, application and uses of baked phenolic coatings were described, with emphasis on their chemical resistance (*Materials Protection* 1 (8), 87). Crude cashew oil was freed of saturated alkyl and mono-olefinic components by low temp crystallization. The remaining oil was heated at 200C in an inert gas and then condensed with a methylol phenol to yield a paint vehicle (Nagata, *Jap.* 16,424/62) or the fractionated oil was methylolated with formaldehyde and then condensed with a monoglycidyl ether of a catechol derivative to yield a paint vehicle (Saito, *Jap.* 16,425/62).

The toxicity of uncured epoxy resins and of the amine catalysts used in them was reviewed (Tepper, *New England J. Med.* 267, 821). Abietic acid or tall oil rosin was hydroxymethylated by treatment with formaldehyde in the presence of acetic acid or a higher fatty acid (Hirai et al., *Yukagaku* 12, 149). Lacquers resistant to acids and alkalis were formed by the reaction of polyhalocyclopentadienes with polymers of conjugated dienes (Bayer Farbenfabriken, *Ger.* 1,131,345; *Ger. Patent Abs.* 1962, 2 (28), Gp. 1, p. 1). Mixtures of nitrocellulose, an amino resin and an epoxy plasticizer or epoxy resin, in the presence of an acid catalyst, gave hard, solvent-resistant coatings (Kraus, *Farbe u. Lack* 69, 171).

Analytical Methods

The Industrial Oils and Derivatives Committee of the AOCs recommended changes in the method for "Gardner color and viscosity by bubble time" and recommended that a number of analytical methods in use for other fatty derivatives be adopted as official methods for the analysis of polymerized fatty acids also (*JAACS* 40, 605). A nuclear magnetic resonance method for the determination of the oil content of seeds was applied successfully to the seeds from 18 plant species containing 1.5–53% oil (Conway, *Ibid.*, 265). A colorimetric method for the determination of small amt of C₉–C₁₅ saturated acids and palmitoleic, oleic, linoleic and linolenic acids was developed (Duncombe, *Biochem. J.* 88, 7). A gas-liquid chromatographic (GLC) method using both normal and organosilicone polyester columns was developed for the identification of the unsaturated C₁₆ acids of marine oils (Ackman and Jangaard, *JAACS* 40, 744). Tritium-labeled fatty esters could be prepared by exposing the esters to tritium gas. The tritium added to the unsaturated bonds of methyl oleate, methyl linolenate and methyl stearolate (Dutton et al., *J. Org. Chem.* 27,

2648). The use of the diene value (maleic anhydride addition) in determining the conjugation and geometric isomerism of double bonds in fatty compounds was discussed (Von Mikusch, *Double Liaison* 1962 (87), 75). Partial oxidation with peracids was studied as a method for determining the position of double bonds in unsaturated fatty acids (Gunstone and Sykes, *Riv. Ital. Sostanze Grasse* 11, 561). A colorimetric analysis using titanium chloride was found to be a sensitive method for determining peroxides in fats (Janíček and Pokorný, *Papers of the Inst. of Chem. Tech., Prague* 3, 233). The changes in concn of mono-, di- and triglycerides during the glycerolysis of linseed oil were followed by thin layer chromatography with silicic acid as the adsorbent (Rybicka, *Chem. Ind. (London)* 1962, 1947). A GLC method for determining the cyclic monomers formed by heating linseed oil in ethylene glycol in the presence of sodium hydroxide was described (Black and Eisenhauer, *JAACS* 40, 272). A discussion of the analytical methods for polymerized oils referred to acetone number, I.V., mol wt, dielectric constant, viscosity, refractive index, molecular distillation, urea fractionation and chromatographic techniques (Firestone, *Ibid.*, 247). The German DGF official methods for the analysis of polymerized fats were of practical value only for heat-treated oils (Rost, *Fette Seifen Anstrichmittel* 65, 463). The qualitative and spot tests which were found to be most useful and reliable for the analysis of various types of polymers and resins were reported (Lucchesi and Tessari, *Off. Dig. 34* (447), Pt. 1, 387). Mixtures of mono-, di- and tri-pentaerythritol were analyzed by acetylation, followed by GLC separation of the acetates (Wiersma et al., *Anal. Chem.* 34, 1533). X-ray and electron microscopic methods were used to study the physical structure of blown linseed oil gels (Kronstein, *Paint, Var. Prod.* 52 (3), 26, 72).

The Protective Coating Industry and Paint Technology

ECONOMICS. An analysis of the world market for drying and semi-drying oils discussed the effects of technological and market changes in the protective coating, printing ink, and linoleum industries on the demand for various oils (Horne, *Tropical Sci.* 5 (1), 39). Papers on economic aspects of the paint industry covered profit histories of British paint and printing ink companies and British production and imports of raw materials (*Fisk's Paint Year Book 1962*, 181), availability and economics of raw materials (Arnold, *Ibid.*, 85), 1962 production of coating materials in West Germany (up 7% from 1961) and the recruiting of personnel (Durholt, *Farbe u. Lack* 69, 159), and the effect of the Common Market on the Scandinavian paint industry (Hill-Madsen, *Paint J.* 14 (110), 475). Trends in the administration of the industry, including combining of manufacturers into large groups, absorption of paint-makers by the chemical industry and closer control of paint companies over sale and use of their products were discussed (Gay, *Fisk's Paint Year Book 1962*, 61).

GENERAL TECHNOLOGY. The development of paint technology was reviewed (Sunderland, *Ibid.*, 95) and its scientific foundations explained (Marwedel, *Ind.-Lack-Betrieb* 30, 370). The properties and uses of modern paints were reviewed (Abelsnes, *Norges Ind.* 43 (18), 354) as were those properties of the various chemical types of film-forming materials which were likely to cause problems in paint manufacture and application (Petit, *Peint Pig. Vernis* 38 (11), 622). The selection of the proper type of paint for specific purposes and exposures was discussed (Marshall, *Surveyor* 120 (3619), 1239).

The present status and future prospects of the use of drying oils in protective coatings were summarized (Weaver, *JAACS* 40 (5), supp. 4). Reviews covered the use of tomato seed oil (Balbi, *Lipidos* 22, 66) and pine seed oil (Balbi, *Ibid.* 23, 4) in paints and varnishes. The use in paints of limed oils (the reaction products of stand oils and calcium hydroxide) was described (Montorsi, *Pittura e Vernici* 38, 77). Differences between the drying reactions and adhesion of linseed oil paints and the new synthetic resin paints were not yet fully understood by painters (Gemberling, *Am. Paint J.* 46 (29), 82). Information on quality control and testing of paints included reviews of testing methods (*Tijd. Opperolaktetechn.* 5, 211) and of the regulations of the East German government (Taschow, *Plaste u. Kautschuk* 9, 156) and a course outline used at the University of New South Wales (Hall, *Austral. Paint J.* 6, 13). Improved color fastness and control of surface characteristics of paints were predicted (Gay, *Fisk's Paint Year Book 1962*, 61).

Bubble formation, vapor permeability and water absorption of films from zinc oxide-pigmented linseed oil and from linseed oil emulsions were compared (Wiff et al., *Fette Seifen Anstrichmittel* 65, 117). The uses of radiation in paint technology, particularly in promoting cross-linking and polymerization, were discussed. It was proposed that paints could be applied as pigment dispersions in monomers, which would then

be cured by radiation from a radioisotope added just previous to application (Blom, *Chem. Rundschau (Solothurn)* 13, 93). Outdoor exposure tests on a number of clear wood finishes showed that those based on relatively newly developed resins were no more durable than the more conventional alkyd and phenolic varnishes. All of the clear finishes were inferior to good 3-coat paint systems. Priming with linseed oil prior to clear finishing was beneficial (Bussell and Goldstraw, *Dept. of Supply, Austral. Defence Sci. Service Defence Standards Laboratories 1961*, Rept. No. 251, 14 pp.). Electron microscopy was used to study the mechanism of degradation of baked acrylic enamels on accelerated weathering. The first stage of degradation was shrinking caused by depolymerization of the vehicle under the influence of UV radiation (Nye and Mackie, *Off. Dig. 34* (450), 716). Although fungi will grow on paint films, cases in which film breakdown could be definitely attributed to fungal attack were rare (Shapiro, *Ibid.* (449), 622).

PIGMENTS. Modern paint formulation was described as being based upon the concepts of pigment volume concn (PVC), critical pigment volume concn (CPVC) and solid content by volume (SC) (Korinsky, *Plaste u. Kautschuk* 9, 311). European and American work on CPVC (Flamm, *Peint, Pig. Vernis* 38 (6), 320) and the qualitative correlation of PVC with paint performance were reviewed. Quantitative studies showed that the effective PVC within a paint changed with time and that variations also occurred between paints of identical formulation and manufacture (Newton, *J. Oil Col. Chem. Assoc.* 45, 180). The relation between CPVC and the amt of material adsorbed on the pigment was studied with titanium dioxide in linseed oil. The two quantities were not directly proportional. Addition of fatty acids, fatty amines and other surface-active agents eliminated the dependence of CPVC on the initial PVC (Svoboda, *Plaste u. Kautschuk* 9, 105). A dielectrographic study of the wetting of pigments indicated the occurrence of two different types wetting (österle, *VI FATIPEC Congress 1962*, 341). The adsorption of binder on pigments and the electric charge on the pigments was studied. These factors influenced pigment agglomeration, dispersion stability and sedimentation volume (Hamann, *Ibid.*, 76). In a study of adsorption of the binder on pigments and agglomeration of the pigment, aging of pigment-linseed oil dispersions was explained on the basis of an equilibrium between these two effects (Svoboda, *Chem. Průmysl* 12/37 (1), 48). Electrokinetic charge transport in pigmented alkyd resins was studied. Titanium dioxide was found to selectively adsorb the most polar constituents of an alkyd (Sjollema and Radielovic, *VI FATIPEC Congress 1962*, 356). Electrophoretic studies were made of the electrokinetics of titanium dioxide in alkyd resins and in melamine resins. The zeta-potential of titanium dioxide was positive in alkyd resin-xylene systems, negative in melamine resin-xylene systems (Oyabu et al., *J. Jap. Soc. Col. Mat.* 35 (3), 98). The properties of alkyd flat paints containing calcined clays were improved by using clays which had been surfactant-coated (Naylor, *Off. Dig. 34* (444), 51). Interaction between zinc oxide and titanium dioxide in water was increased by conventional dispersing agents but was reduced by ethylene glycol and eliminated by inorganic phosphates (Princen and DeVena, *JAACS* 40, 131).

ADDITIVES. The chemistry and applications of driers, anti-skinning agents, bodying agents and fungicides were summarized (Stewart, *Double Liaison* 38, 77). The gelation of vinyltoluene-modified oil varnishes was inhibited by the addition of a small amt of a compound selected from a group of amines (Lowe, *U.S. 3,075,933*). The use of silicone oils in unsaturated polyester finishes for curtain coating and in automotive repair finishes was discussed (Krauss, *VI FATIPEC Congress 1962*, 332), as was the use of lanolin and its derivatives in various types of surface coatings (Clark and Kitchen, *Paint Manuf.* 32 (1), 9; (2), 55).

FORMULATIONS FOR SPECIFIC PURPOSES. Reviews covered the formulation of paints for specific purposes (e.g., anti-corrosive paints, cement paints) (*Munic. J., Lond.* 69 (3590), 3891), including the needs of naval aviation (Pfeiffer et al., *Armed Forces Chem. J.* 15 (6), 18). The British Whiting Federation developed a flat paint formula containing titanium dioxide 22%, whiting 43, bodied alkyd resin 9.5, mineral spirits 25.2 and drying fatty acids 0.3 (Hammond, *Paint, Oil Col. J.* 141 (3311), 799). The improved application properties obtained by using thixotropic alkyd resins in paints and the instrumental methods used in formulating such paints were described (Berry, *Paint Manuf.* 32 (12), 431). The formulation of paints and the selection of the gas for spray paints was discussed. The gas was usually a mixture of a fluorinated hydrocarbon and a hydrocarbon (Kossmann, *Ind.-Lack-Betrieb* 30 (1), 8).

The major classes of metal finishing materials were reviewed (Grover, *Applied Plastics* 5, 25). The adhesion of polyamide coatings to metals was improved when a trivalent salt

of chromium or aluminum was present in the polyamide (Pavlov et al., *USSR 143,949*). The different types of anticorrosive primers and their properties were discussed (*Irish Painter & Decorator 1* (2), 6). Exposure results were reported on a number of anti-corrosive paints based upon modified Argentine linseed and tung oils (Rascio, *Peint. Pig. Vernis 38* (5), 254). The preparation of zinc dust pigment and the formulation and properties of paint containing it were described (Van Oeteren, *Deutsche Farben-Z. 16* (3), 99). The advantages of zinc-rich primers for the protection of iron were enumerated (*Corrosion et Anticorrosion 10* (4), 148). Pigments for corrosion-inhibiting primers included zinc dust, zinc chrome-iron oxide and zinc chrome-zinc tetroxychromate (Mack, *National Builder 42*, 1226). A ten-year evaluation program on zinc paints as priming and finish coats and aluminum paints as finish coats on rusty galvanized metal roofing was completed. The best system was aluminum over red lead or gray metallic zinc primer (MZF), which lasted longer than ten years. The best 1-paint system was two coats of gray MZF-soybean oil, which lasted ten years (Muehling and Curtis, *Illinois Agric. Experiment Station, Bull. No. 676*, 27 pp.). The behavior of Hungarian bauxite red in priming paints and alkyd resins was investigated. A thixotropic rust-preventive paint containing this pigment was developed (Huisz, *Plaste u. Kautschuk 9*, 311).

Paints for special effect finishes such as wrinkle, ice, metalized, crackle, multicolor, marble and web were discussed. Hammer finishes, the most common type, could be obtained with cellulose, cellulose-alkyd, polyurethane or epoxy resins (Bruhn, *Galvanotechnik. u. Oberflächenschutz 3*, 87). Reviews covered multicolored (Paint Manufacturers' Executive Council, *Chem. Trade J. 150* (3915), 1202), phosphorescent, fluorescent and radioactive paints (*Trav. Pent. 17* (2), 42).

A fire- and chemical-resistant paint contained epoxy, silicone and urea resins and a heat-resistant pigment such as titanium dioxide (Chugoku Paint Co., *Jap. 2975/62*). A discussion of heat-resistant paints stated that those based on silicone resins and butyl titanate with mineral pigments were most successful. Fluorinated polymers and polymers containing boron or phosphorus offered promise (Rabaté and Rabaté, *Peint. Pig. Vernis 39* (1), 11). Air-drying heat-resistant coatings for metals based upon dimethyl hydrogen phosphite (alone or with ethyl acid phosphate), zinc oxide and colloidal silica were studied extensively. Other organic phosphates and phosphites and other metal compounds were included in the study (Mileski and Raeber, *Southern Research Inst., Birmingham, Ala., Rept. No. 6151-1264-IV*, 13 pp.; Liggett, *Ibid.*, *Bimonthly Progress Rpt. 1962* (3), 17 pp.). A coating resistant to temp up to 2000C contained a polyester resin, exfoliated vermiculite, colloidal silica, zirconium oxide, titanium dioxide, white cement and active carbon (Oda, *Brit. 889,866*).

UV radiation caused a change in the optical properties of most reflective organic coatings which were studied as a means of achieving temperature control in space vehicles. Zinc sulfide and leafing aluminum were the reflective pigments which were most stable to this radiation (Field et al., *U.S. Naval Res. Lab., Washington, Interim Rept. No. 5737, 1962*, 28 pp.; AD-273,716). IR-reflecting marine paints were discussed (*Tijd. Oppervlaktetechn. 5*, 188). A hydroxyl- or methyl-containing naphthalene derivative, such as β -naphthol or methylnaphthalene, was used in paint for repelling animals (Yonesawa, *Jap. 4611/62*). Pesticidal paints contained a chlorinated hydrocarbon such as γ -hexachlorocyclohexane as the active ingredient and naphthalene as a sublimation agent (Yamamoto, *Jap. 10,350/62*). Fungus damage to coatings and its prevention by suitable coating compositions and by the addition of fungicides and bactericides was discussed (Hirshfeld, *Farbe u. Lack 69*, 174). An anti-blemish paint composed of polyisoprene, a filler and a fatty acid or fatty acid soap in a petroleum hydrocarbon solvent was applied to the sidewalls of tires prior to molding and curing (Cuthbertson and Dodge, *U.S. 3,106,443*). The properties of electrically conducting paints were discussed (*Chem. Rundschau (Solothurn) 14*, 466). A paint for detecting radiation contained a yellow azo dye in polyvinyl chloride. Upon irradiation, hydrogen chloride released from the polyvinyl chloride caused the dye to turn red (*New Scientist 16* (314), 441). Encapsulation of fats or waxes was achieved by dispersing the fat or wax in an aqueous solution of a styrene-maleic anhydride copolymer (the anhydride groups of which were at least 50% hydrolyzed), adding an insolubilizing salt, adjusting the pH and separating the resulting capsules (Jensen and Wagner, *U.S. 3,069,370*). A coating composition which was a water-in-oil emulsion consisted of water, low-boiling petroleum hydrocarbons, petroleum wax, a sorbitan mono-fatty acid ester and a mahogany sulfonate soap in a high-boiling petroleum hydrocarbon. A similar composition contained boiled linseed oil (Sheldahl and Entwistle, *U.S. 3,086,870-1*).

Plasticizers

The status of epoxidized soybean oil as a plasticizer for polyvinyl chloride was summarized (Kalinska, *Polimery 7* (7-8), 245). The reaction of olefins with alkyl acid *o*-phthalates produced neutral *o*-phthalate esters which were evaluated as plasticizers for polyvinyl chloride (Raether et al., *I & EC Product Res. Dev. 2*, 133). Methyl pentachlorostearate in combination with epoxidized soybean oil or the butyl ester of epoxidized soybean acids showed promise as a polyvinyl chloride plasticizer (Murata, *Yukagaku 11*, 513). A mixture of morpholides of selectively hydrogenated cottonseed acids was used as a vinyl plasticizer. Most of the polyunsaturation in the fatty chains had been hydrogenated to monounsaturations (Magne et al., *U.S. 3,066,111*). A review on petroselinic acid and its derivatives mentioned the morpholide of parsley seed acids as a good vinyl plasticizer (Placek, *JAOCs 40*, 319). *N,N*-bis(2-acyloxyethyl)-amides in which one of the three acyl groups was a fatty group were tested as vinyl plasticizers. Some of them were also suitable as nitrile rubber softeners and cellulose acetate plasticizers (Magne et al., *Ibid.*, 541). An *N*-oleyl fatty amide was used to the extent of 0.01-1% as an additive in polyethylene (Clark and Hill, *U.S. 3,104,232*).

PRODUCTION PROCESSES EXTRACTION

Several new processes for extraction include a process in which macerated fatty tissues are heated by frictional energy, followed by centrifugation to separate fat from residue (Downing, *U.S. 3,078,287*). Less solvent and heat than that of conventional extraction methods are needed when solvent vapor is used in a closed system to extract fat or oil from animal and vegetable products (Bruera, *U.S. 3,064,018*). The moisture content of oilseeds is adjusted to 10-40% before extraction in a Schall extractor (Peter, *Ger. 1,139,597*). Direct extraction of oil from the seed in a Blaw-Knox rotary extractor is described (Zharskii, *Maslob-Zhir. Prom. 12*, 37 (1962)). Extraction of ricebran at low temp in a few steps yields a light-colored oil with less wax content than oil obtained by pressing (Takeshita et al., *Yukagaku, 11*, 101 (1962)). A method of non-isothermal multistage countercurrent extraction is discussed (Neshchadim, *Maslob-Zhir. Prom. 12*, 9 (1962)). The practical aspects of the data obtained for the optimum degree of oil extraction from prepressed cottonseed meats are discussed (Kats et al., *Maslob-Zhir. Prom. 29*, 6 (1963)).

Mixtures of ligroine with benzene, dichloroethane or acetone are studied as solvents for extraction. Ligroine-acetone is found to be the best solvent system for efficient extraction of oil and gossypol from cottonseed (Markman et al., *Dokl. Akad. Nauk. Cz. SSR. 19*, 23 (1962)). The color of the oil obtained from cottonseed by two-step method using 75-5% aqueous acetone at 40C is better than the oil obtained by usual commercial processes. (Sabirow et al., *Otd. Geol.-Khim. Nauk. 133* (1961)).

Removal of mechanical impurities from sunflower oil miscella is achieved by employing hydracyclones with a diam of 100 mm. (Maslikov et al., *Maslob-Zhir. Prom. 29*, 27 (1963)). The temp-solvent stripping performance of sunflower oil-pet. naphtha miscellas as influenced by the load, vacuum and steam pressure is reported for a climbing-film DC-70 evaporator (Beloborodov, *Maslob-Zhir. Prom. 29*, 5 (1963)). Important industrial factors like the amt of steam, the thickness of the bubbling layer of oil in the column for an effective distillation of miscella by the pulverization method are discussed (Beloborodov, *Ibid.*, 29, 9 (1963)). The thermal requirements of a double effect evaporator incorporating heat recovery through compression of solvent vapors following miscella distillation are investigated (Vernois, *Rev. Franc. Corps Gras. 10*, 279 (1963)). Empirical formulae pertaining to the relationship between bp of miscella and its concn at a given pressure have been derived (Kovalenko, *Maslob-Zhir. Prom. 29*, 7 (1963)).

Mechanical extraction of cottonseed oil (Bestraten, *Lipidos, 22*, 34 (1962)) and extraction of olive oil by "Extroil" method (Arino, *Ibid.*, 22, 31 (1962)) are reviewed.

REFINING

Methods for degumming include a process for sunflower oil in which the oil is agitated for 30 min at 80C with 5% solution of trisodium phosphate or tripolyphosphate (Guillaumin et al., *Rev. Franc. Corp Gras 10*, 557 (1963)). Degumming of peanut oil with 5% HNO₃ offers no advantage over degumming with water (Guillaumin et al., *Ibid.*, 10, 207 (1963)). The effects of HNO₃ concn, temp, agitation and contact time in rapeseed oil degumming are discussed (Defromont et al., *Rev. Franc. Corps Gras 9*, 486 (1962)). The theory of formation of a double monomolecular layer during hydration of soybean phosphatides is valid only when the min amt of water necessary for the

process is used (Jakubowski, *Ital. Sostanze Grasse* 10, 512 (1962). Centrifugation is better than heating and settling process for removal of impurities from crude ricebran oil (Takeshita et al., *Kukagaku*, 11, 165 (1962).

New equipments include a unit for refining of fats in an inert atmosphere (Chubinidze, *Maslob-Zhir. Prom.* 29, 35 (1963) and podbielniak-duozon countercurrent, liquid-liquid extractor for continuous refining with caustic solution (Sourelis, *Dechema Monograph* 46, 201 (1963). The installation and operation of the DeLaval Short-mix process in which the oil is treated with caustic solution in a centrifuge at 70–80C for 30–40 sec and then washed and vacuum-dried after removal of the slime, are discussed (Neumann, *Ibid.* 46, 211 (1963). In a modification of the Short-mix process the oil is mixed with a solution of alkali and heated quickly to 90C to break the emulsion formed, washed with 10–15% water at 80–90C and dried under vacuum (Sedlaczek, *Tluszcze i Srodki Piorace* 5, 216 (1961).

Several new processes have been patented. Refining losses of ca. 70% of the official cup loss are obtained when a mixture of crude soybean oil, solution of sodium carbonate and sodium hydroxide is subjected to shearing forces equivalent to turbine tip speeds in excess of 850 ft/min for at least 15 sec followed by centrifugation (Schmitt, *U.S.* 3,102,898). Improved yield of oil is obtained when the oil at 40–80C is first centrifuged, then cooled in an intermediate cobler and finally refined in continuous separators (Akopyan *USSR* 148, 870). Centrifugal refining of olive and soybean oils gives a lower refining loss than conventional methods (Ramos, *Grasas y Aceites* (Seville, Spain) 13, 193 (1962). Continuous refining of fats and oils is achieved by passing uniform sized drops of oil through a bed of alkali maintained at a constant concn (Bergman, *Ger.* 1,120,623). 40–50% reduction in refining loss is obtained by addition of 0.3% urea in concn aqueous solution, to the glyceride before refining. (Repapis, *U.S.* 3,065,249). The addition of NaOH during degumming of soybean oil with Ac_2O improved the yield and color of refined oil (Fiala, *U.S.* 3,093,667). Dilution with H_2O of a mixture of alkali and oil before the "break" occurs gives a higher yield of neutral oil (Desai, *Brit.* 935,500). Monoethanolamine (2%) as an additive can replace the excess of alkali used in refining of crude cottonseed oil (Rao et al., *Indian Oilseeds J.* 6, 43 (1962). The yield and color of refined oil can be improved by the use of hydrogen peroxide during alkali refining (Rao, *Ibid.* 6, 130 (1962). The dry method of alkali refining is found to be more advantageous than the wet method for cottonseed oil. Addition of salicylic acid and tetrasodium pyrophosphate in small quantities during alkali refining reduces refining loss significantly (Krishnamurthy et al., *Ibid.* 6, 14 (1962).

A reduction in refining loss results for oils refined with gaseous ammonia. However the oil color is substantially higher (Zeitoun et al., *JAOCs* 40, 279 (1963). Fats and oils refined under agitation with ammonia gives a higher yield of neutral oil than obtained by conventional refining (Hatzopoulos, *Fr.* 1,295,595). High quality edible oil is obtained by the addition of 7% NH_4OH to cottonseed oil miscella in acetone (Markman, et al., *Maslob-Zhir. Prom.* 29, 9 (1963). Glycerides of cottonseed oil are separated from other components by liquid-liquid fractionation with ligroine-ethyl alcohol-water mixture (Rzheklim et al., *Maslob-Zhir. Prom.* 29, 3 (1963). An improved soybean oil is obtained when crude degummed oil is extracted with methanol at 40–140F (White et al., *U.S.* 3,069,449). Low grade olive and chestnut oils containing 8–40% free fatty acids are refined by dissolving in a hexane-acetone mixture followed by neutralization with 20–30% KOH solution (Foresti et al., *Boll. Inform. Ind. Olearia Saponiera*, 8, 3 (1962). In the deacidification of oils containing more than 10% free fatty acids, best results are obtained by partial neutralization with 5% Na_2CO_3 followed by treatment with 30% excess of 3N Na_2CO_3 (Niewiadomski et al., *Tluszcze i Srodki Piorace* 5, 227 (1961). Esterification of the free fatty acids in rice oil with glycerol followed by molecular distillation produces an edible oil (Sakurai, *Trans. Natl. Vacuum Symp.* 8, 647 (1962). Solid fats are refined by passing through the molten fat at 30–100C drops of NaOH solution with a diam of 0.2–5 mm, followed by centrifugation to remove the soap granules (Eger et al., *U.S.* 3,085,101). The emulsion formed during alkali refining can be broken by adding a water solution of protein like casein (Bloem, *Netherlands*, 102,036). Anion exchangers are suited for deacidification of rice bran oil (Inoue et al., *Yukagaku*, 11, 109 (1962). The effect of refining on alteration in color of the oil is followed by spectrophotometry (Giordano et al., *Olearia* 5–6, 168 (1962).

BLEACHING

Alumina treated with sulfurous acid is effective in decreasing the amt of oil-soluble color pigments in cottonseed oil and gives

a sulfur free bleached oil with negative Halphen test (Pons et al., *U.S.* 3,087,946). Oil of light yellow color is obtained by treating rice bran oil pretreated with 5% oxalic acid, with 5% acid clay at 110C for 20 min. (Chung-Sung Wu et al., *Chemistry*, (Taipei) 181 (1961). Both pigments and fatty acids are removed from castor oil by treatment at 90C for 10 min with active earth from volga region (Timofeeva, *Matem. Saratov*, 82 (1961). Acid activated earths are found to increase rather than decrease the color of the sesame oil due to conversion of sesamoline to sesamol (de Castro, *Grasas y Aceites* 14, 1 (1963). Rice oil is decolorized by passing a hexane solution at 45C of oil pretreated with 0.5% concn H_2SO_4 for 15 min at 30C, through a column containing Amberlite IRA 401 (Inoue and Noguchi, *Japan* 10,161 (1963). A preliminary cost study of bleaching off-colored cottonseed oils with activated alumina indicated that costs could be lowered by reducing oil losses and losses of alumina during regeneration and by increasing filtration rates (Decossas et al., *JAOCs* 40, 218). Regeneration of spent earth is achieved by boiling, with an aqueous solution of H_2SO_4 and potassium permanganate, the spent earth which has been previously washed with detergent to remove the adsorbed oil (Thompoulas et al., *Rev. Franc. Corps Gras* 9, 611 (1962).

DEODORIZATION, WINTERIZATION AND FRACTIONATION

A laboratory deodorizer with a capacity of 50–2500 g oil has high degree of reproducibility and operation convenience (Heide-Jensen, *JAOCs* 40, 223). In the steam deodorization of oils, crossflow of oil and stripping steam in a column with helical or radial internal guide vanes is more economical than counterflow with usual plates (Kehse et al., *Chem. Process Eng.* 44, 431). Odorless oil is obtained by filtering through activated clay, rice oil which has been pretreated with small amt of acetic acid and yeast culture filtrate (Nao Tominaga, *Japan* 9581, (1961).

Separation of stearin from cottonseed oil is achieved by cooling the oil with brine to 7.22C, followed by centrifugation at 6250 rpm (Little, *Belg.* 622,549). Saturated glycerides are separated from directed rearranged soybean oil by precipitating with a dextrin fatty acid ester followed by filtration (Thomas Headly and Co., *Brit.* 904,048). The crystallinity of solid fat from soybean oil or cottonseed oil is improved by the addition of 0.005–0.1% sucrose ester of a fatty acid (Schmid et al., *U.S.* 3,059,009). Cooling of a solution of glyceride oils containing 0.001–1.0% by wt of oil of fatty acid ester of glucose or its derivative results in fast filtering glyceride crystals (Bauer, *U.S.* 3,059,011 and *U.S.* 3,059,008). An equipment for the continuous solvent crystallization of glyceride fractions from fats and oils is described (Austin, *Ind. Chemist*, 39, 401). A process for fractionation of vegetable and animal fats and oils is patented (Y. Toyama et al., *U.S.* 3,105,844). Linoleic acid of 85.9% purity can be obtained from safflower fatty acids by urea adduct formation (Yoshitomi et al., *Yukagaku* 11, 641). The application of various methods of fractionation to fish oil products is discussed (Gruger Jr., *Proc. Gulf Caribbean Fisheries Inst.* 14, 53 (1961).

HARDENING

An apparatus for selective hardening of unsaturated vegetable and animal oils and fats comprises an autoclave with partitioning walls for dividing the autoclave into a plurality of adjacent chambers (Gfeller, *U.S.* 3,089,755). Both organic and inorganic sulfur compounds are removed from gaseous hydrogen used for hydrogenation by the use of absorbent, GIAP-10 (Chubinidze et al., *Maslob-Zhir. Prom.* 12, 24 (1962). The catalytic activities of supported metal hydrogenation catalysts are increased by high energy irradiation (Graham, *J. Phys. Chem.* 66, 510 (1962). A copper containing catalyst for selective hydrogenation of fats and oils can be produced by reaction of an aqueous acid solution of Cu with alkaline solution of Cr, Al or Zn (Asahi Electro-Chemical Co., *Brit.* 932,991).

Several kinetic studies are reported. The rate of hydrogenation of linolenate depended upon both temp and catalyst concn. However transformation is essentially a function of temp while selectivity is little influenced by either parameter (Johnston et al., *JAOCs* 40, 285). Effects of temp, pressure, catalyst concn and degree of agitation used in commercial practice on the extent of isomerization are discussed (Cousins, *Ibid.* 40, 206). Kinetics of linolenate hydrogenation have been reviewed (Dutton, *Ibid.* 40, 35). Mechanism of formation of trans-isomers of oleic acid radicals has been discussed (Tyutyunnikov et al., *Maslob-Zhir. Prom.* 29, 13 (1963).

Greater selectivity is observed with Pd catalyst than with Pt catalyst. However, the degree of selectivity decreases with both catalysts as their concn is increased. But the rate of

hydrogenation increases with the increase in the amt of catalyst and temp (Rozhkova et al., *Otd. Geol. Khim. Nauk.*, 154 (1961)). Cottonseed oil is softer when hydrogenated with pd catalyst than with pd + pt catalyst (Sokol'skii et al., *Tr. Inst. Khim. Nauk. Akad. Nauk. Turkm. SSR* 8, 100 (1962)). Continuous hydrogenation of cottonseed oil is carried out by passing a solution of cottonseed oil in naphtha or toluene over a fixed bed Ni-Al catalyst (Sokol'skii et al., *Ibid.* 8, 128 (1962)). Preheating of the Cu-Ni oxide catalyst to 300C facilitates the hydrogenation of ricebran oil of high acid number. The presence of 1% trichloroethylene in the oil is found beneficial (Takeshita et al., *Yukagaku* 11, 168 (1962)).

The slow hydrogenation of rapeseed oil is attributed to the inhibiting influence of erucic acid on the hydrogenation of linoleic and oleic acid (Tyutyunnikov et al., *Maslob-Zhir. Prom.* 29, 14 (1963)). The conjugated hydrogenation (H₂ supplied by a donor compound) of peanut oil has been studied using primary and secondary alcohols. Selectivity is greater with primary alcohol than with secondary alcohol (Basu et al., *J. Sci. Ind. Res. (India)* 21 D, 467 (1962)). The optimum conditions, for hydrogenation, from the stand-point of the stability of the hydroxyl group and of the formation of 12-hydroxystearic acid, are 160C and 0.5% Ni catalyst (Hladik et al., *Papers of the Inst. of Chem. Tech. Prague* 4-11, 241 (1960)). In the presence of alcohol as solvent the hydrogenation of castor oil is rapid with little dehydroxylation (Kane et al., *Fette Seifen Anstrichmittel*, 64, 1026 (1962)). Hydrogenated castor oil of high hydroxyl number and high mp is obtained by hydrogenation with 2% Raney Ni catalyst, for 5 hr at 150C at 9-11 kg/sq cm pressure (Rao et al., *Res. Ind. (New Delhi)* 8, 125 (1963)). Hydrogenation of acid oils and oils recovered from spent bleaching earth is achieved more quickly and with lower catalyst consumption by applying increased hydrogen pressure (Wessebaeh, *Fette Seifen, Anstrichmittel* 64, 967 (1962)).

Ni and fat are recovered by treating the spent catalyst with a mixture of pet ether and formic acid in a closed vessel at 70-5C for 2 hr. Recovery of Ni and fat is 98.3 and 97.7%, respectively, of the original (Rebello et al., *Indian* 73, 787). Various aspects of selective hydrogenation have been reviewed (Forch, *Lipidos* 22, 11 (1962)).

INTERESTERIFICATION

The fat or oil is subjected to interesterification conditions in an inert atmosphere in the presence of granular alkali metal hydroxide catalyst supported on a carrier (Nippon Oils and Fat Co., *Japan* 16, 968). Best results for transesterification of tall-rapeed oil mixtures are obtained by a multistage transesterification in which the mixture is heated for 6 hr, with 0.5% MeONa being introduced every 2 hr (Kaczanowski et al., *Pluszcze i Srodki Piorace* 6, 1 (1962)). Esterification of glycerides without interesterification is carried out using *p*-toluenesulfonic acid catalyst (Feuge et al., *JAACS* 40, 260).

PARTIAL ESTERS AND FAT SPLITTING

Several new processes include a method for continuous manufacture of monoglycerides in which a mixture of a glyceride and a first portion of glycerol is passed countercurrently to a flow of glycerol, into a reaction zone maintained at a temp of 200-350C in the presence of an alkaline alcoholysis catalyst. The reaction mixture is continuously withdrawn from the reaction zone and the catalyst immediately inactivated (Chang et al., *U.S.* 3,079,412). A process for making monoglycerides from polyglycerides consists of continuously feeding a glyceride, a polyhydric alcohol, an interesterification catalyst and an inert gas into and through a reaction zone at 200-275C and immediately through a cooling zone (Giddings et al., *U.S.* 3,095,431). A method for the manufacture of monoglycerides in which the residue after the separation of monoglycerides is recycled, is patented (Birnbaum et al., *U.S.* 3,102,129). The catalytic treatment of natural fats with glycerine in pyridine solution in the presence of sodium methylate, ethylate or carbonate gives a high yield of monoglycerides (Taufel et al., *Fette Seifen Anstrichmittel* 64, 513). Monoglycerides from castor oil are prepared by heating a 2:1 mixture of 98% glycerol and refined castor oil in an autoclave to 250 under 200 psig carbon dioxide for 2 hr (Kochhar et al., *Indian Oilseeds J.* 6, 20 (1962)).

The preparation of monoglycerides of long chain hydroxy acids is carried out by hydroxylation of allyl esters of hydroxy fatty acids (Kaufmann and Baltes *Ger.* 1,148,224). Higher fatty acid monoglycerides are prepared by treating acylating agents which contain C₁₆-C₁₈ fatty acid groups with excess glycerol at 270C (Alsop et al., *U.S.* 3,083,216). Monoglyceride conen of high purity are obtained by molecular distillation of glycerolysis products of partially hydrogenated whale oil (Mori et al., *Nippon Suison Chuo Kenkyusho Hokoku*, 9, 1 (1961)). Patents for the production of monoesters of polyunsaturated

fatty acids (Sutherland, *U.S.* 3,082,228) and for the preparation of mixed esters (Hennig et al., *U.S.* 3,102,128) have been issued.

The influence of time, temp and the amt of catalyst on the yield of monoglycerides obtained from the catalytic glycerolysis of natural fats in pyridine has been studied (Franke et al., *Fette Seifen Anstrichmittel* 65, 275). 50-200 psig pressures that retain the water normally present in the commercially pure glycerol are highly conducive to the high monoglyceride conen at equilibrium (Kochhar et al., *Indian Oilseeds J.* 6, 144 (1962)). During glycerolysis of oils the ratio of glycerol to oil present at anytime in the reaction mixture determines the composition of the final product (Dey et al., *Ibid.* 215 (1962)). When transesterifying triglycerides with conventional amt of glycerol, the theoretical content of monoglycerides in the mixture does not exceed 54-5% (Yukhnovskii et al., *Lakokrasochnye Materialy i Ikh Primenenie*, No. 4, 16 (1962)). The change in the dielectric constant is used to detect the equilibrium point in the alcoholysis of linseed oil with glycerol (Hippe et al., *Przemysl Chem.* 42, 236 (1963)). A continuous process for removing glycerol from commercial monoglycerides using a thin-film evaporator operating at 340F under an absolute pressure of 6 mm has been discussed (Moniek, *JAACS* 40, 606). Higher degree of splitting is obtained when the fat is first treated with spent glycerol solution from a preceding run followed by treatment with fresh glycerol solution (Klozar, *Czech.* 104, 662). The rate of hydrolysis of fats is independent of the oil-to-water ratio, but the degree of final splitting increases with increase in the proportion of water present (Sarma, et al., *Indian Oilseeds J.* 6, 270). Operating data have been developed for the autoclave splitting of linseed and cottonseed oils and for the production of glycerol and fatty acids in a commercial plant (Narasimha et al., *Indian Oilseeds J.* 7, 39). Hydrolysis of ricebran oil by natural decomposition in bran is not suitable as the raw material for obtaining fatty acid by distillation (Takeshita, *Yukagaku* 11, 105 (1962)).

VEGETABLE AND ANIMAL FATS AND OILS

Commercial feasibility of producing edible oil in Columbia from rice polishings is investigated (Hernando, *Rev. Inst. Invest. Technol.* (Bogota) 3, 15 (1961)). Diethylenetriamine, borax, urea and sodium silicate are found to arrest the color fixation that occurs during storage of crude cottonseed oil (Paulose, et al., *Indian Oilseeds J.* 6, 171). Cashewnut germs contain 19-24% of nondrying oil (Barve et al., *Indian Oil Soap J.* 28, 34 (1962)). Single pair, smooth rolls and Bauer type 18-in. disc dehullers have been successfully used for dehulling of safflower seed (Ahmed, et al., *Indian Oil Seeds J.* 6, 6). Reviews have been published on modern technology of fats and fatty products (Kaufmann et al., *Fette, Seifen, Anstrichmittel* 64, 857); economic and technical aspects of production of tall oil in Finland (Kahila, *Suomen Kem. A* 35, 73 (1962)); the production, composition and fractionation of tall oil (Asehe, *Farbe u Lack* 68, 448 (1962)); the source, the production and distribution of tallow in the world (Moulin, *Rev. Franc. Corps Gras.* 9, 601 (1962)); and manufacture of fish oil and fish meal (Brenner, *Revista Argentina de Grasas y Aceites* 5, 13 (1962)).

BY-PRODUCTS

Optimum conditions to bleach soya lecithin by using hydrogen peroxide as bleaching agent and ammonium hydroxide as assistant are investigated (Yoshitomi, et al., *Yukagaku* 11, 123 (1962)). Granular lecithin is produced by extruding the powdered soya lecithin and cutting the extruded particles (Yoshitomi, et al., *Ibid.* 11, 344). Pure soy lecithin is obtained by treating the raw lecithin with a ternary solvent composed of hydrocarbons, acetone and water (Pardun, *Fette Seifen, Anstrichmittel* 64, 536 (1962)). Olive trees growing in uranium-containing soils are found to contain up to 123 ppm uranium in their olives (Martinez et al., *Grasas y Aceites* 13, 165 (1962)). Vegetable oil distillates forming part of deodorization vapors are recovered by scrubbing with water to form an oil-in-water emulsion which is then heated and centrifuged to separate the organic and the aqueous phases (Fiala, *U.S.* 3,061,622). Ground cottonseeds are treated with sodium carbonate to transform the oil soluble impurities like gossypol into water-soluble non-poisonous residues (Cavanagh, *Ger.* 1,153,848). A method for treating oleaginous seeds to remove toxic effect of gossypol from the seed meat consists of heating the meat with aqueous NaOH at 160-190F followed by treatment with hydrogen peroxide (Johnson et al., *U.S.* 3,084,046). A process for preparing hard ester waxes is described (Kaupp et al., *U.S.* 3,062,671). Treatment of tall oil fatty acids with a crystalline clay mineral prior to purification by distillation gives a product of improved color, odor and heat stability (Hampton, *U.S.* 3,052,701).