

volatile compounds or other compounds which were completely lost in the first passage through the extraction plant, the solvent loss would be only 1.25% as compared to the 1.0% loss assumed for the first solvent. Thus, the absurdity of blaming the extraction naphtha, when something in the plant operations suddenly results in a great increase of solvent loss, becomes apparent. This is especially true if the naphtha in the unusually high solvent loss period is the same as that used in the lower normal loss periods or at least is of the same type to such an extent that the most advanced and painstaking laboratory analytical technique is necessary to show the difference, if any, in chemical composition of the naphtha fraction in question.

Because of their ready chemical activity as compared to chemically inert paraffins and naphthenes, the olefins and other unsaturates are undesirable as constituents of extraction naphthas. As judged by the bromine number data in Table IV, which was determined by the A.S.T.M. D.875-46T method, each of the commercial hexane type naphthas is free from all except traces of olefins or unsaturates; in fact, the bromine number for each is in the range of the experimental error of the test procedure. By way of comparison with some other petroleum products, it might be mentioned that the bromide number of a

good grade of cracked motor gasoline may be as high as 26.0 for an olefins or unsaturates content of about 14.3%; the highest of the bromine numbers in Table IV is 0.34 for an olefins or unsaturates content of only 0.18% by volume. It is considered that satisfactory operations can be obtained with an extraction naphtha which has a bromine number of 1.0 for an olefins or unsaturates content as high as 0.52% by volume, although lower values of course are desirable.

In conclusion, it might be mentioned that each of the commercially available naphthas of the hexane type possesses a mild-sweet odor, a very desirable feature from a safety standpoint since the presence of solvent liquid and vapor manifests itself through the workman's sense of smell.

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## Annual Review of Literature on Fats, Oils, and Soaps. Part 1

### Report of the Literature Review Committee \*

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#### Introduction

In the broad field of fats, oils, and soaps, progress seemed steady with many papers of general interest, but it has been difficult to choose something for special emphasis. However, important disclosures attracted interest in the form of discussions, confirmations, and applications, thus reflecting the importance of the items.

**STATISTICS AND OUTLOOK.** Statistics and outlook on production, use, demand, and price were issued periodically by the Bureau of Agricultural Economics, U. S. Department of Agriculture (*Fats and Oil Situation Nos. 123-9*), and Office of Domestic Commerce, U. S. Department of Commerce (*Ind. Rept.—Fats and Oils, January 1949*). These seemed identical rather than supplementary along the lines of information that follow.

On the basis of statistics available, the yearly production of fats and oils from domestic materials beginning with crop year 1941-42, through estimates for 1948-49, were 9,625, 10,557, 10,989, 9,599, 8,827, 9,652, 9,838, and 10,515 million pounds, respectively. During 1948, the net imports were 300 million pounds less than in 1947 because of decreased receipts of Philippine copra, due to storm damage.

Domestic disappearance of fats and oils rose to 10.6 billion pounds as against 10.3 billion in 1947. This was exceeded once in our history when the all-time consumption record of 10.8 billion pounds was established in 1941.

The decline in the fats and oils market has brought most prices to the lowest levels since OPA ceilings.

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\*Literature Review Committee

W. H. GOSS  
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Greater prospective supplies for the 1948-49 season, the possibility of continuing large production in the 1949-50 crop year, and lower demand have been factors in the downward trend. The Department of Agriculture price index of 27 fats and oils stood at 223 in December (1935-39 average equals 100), as compared with 300 in January 1948.

The feeling in industry was that 1948 was a year of transition. During 1949 improvement in world supplies will continue, oilseed planting will be high, a 10% increase in pigs will materialize, and copra trade should be re-established. These factors were reflected in cautious buying of primary fats and vigorous selling policies, which should continue until an outlook of stability materializes.

Other economic treatises on fats and oils were prepared by Lund (*Foreign Com. Weekly* 32, No. 3, 3), Burtis (*Ind. & Eng. Chem.* 40, 998), Philippart (*Oleagineux* 3, 590), Kretzschmar (*Ibid.* 518, 597), Faure (*Ibid.* 453), Heyworth (*Ibid.* 2, 553), and anonymous (*Food Manuf.* 23, 356). The American statistics on production, consumption, and stocks were tabulated for the years 1943-1947, inclusive (*Dept. Com. Bureau Census, M-17-7-07*, 46 pp.). It was interesting to note in one economic report that the French sardine industry was 11% of normal, and will increase to capacity only when oil supplies become available (de Torquat—*Oleagineux* 3, 523).

Some general articles treated the oil industries of specific geographic locations. The texts of these were oil culture and production in Africa (Bourlet—*Oleagineux* 3, 363; Varon—*Ibid.* 373; Vivoli—*Olearia* 2, 135; Ferrara—*Olearia* 1947, 342), in French colonies (La Rochebrochard—*Oleagineux* 3, 613), in Malay Archipelago (Ferrara—*Olearia* 2, 157), in Germany (Engels—*Allgem. Oel- u. Fett-Ztg.* 38, 351), in Lombardia (Consolini—*Olearia* 2, 412), in Sicily (Zanini—*Ibid.* 1, 234), in tropical America (Ciferri—*Ibid.* 339) and in the tropics (Ehart—*Oleagineux* 3, 1). The general treatises on specific oils dealt with a new variety of castor bean (Cortesi—*Olearia* 2, 79), castor seed oils (Saboor—*Indian Soap J.* 13, 281), cacao butter (Brouhns—*Olearia* 1948, 309), drying oil of the French industry (Lebon—*Oleagineux* 3, 78), the fish oil industry of North America (Lovern—*Food Manuf.* 23, 323, 359), fish, shark, and whale oil (Tondou—*Cahiers Coloniaux, Inst. colonial Marseille* 1948, 174; Bassi—*Olearia* 2, 845), gourd oil (Salomone—*Olearia* 1948, 91), grape seed oil (Nobori and Akabane—*J. Soc. Chem. Ind. Japan* 47, 146), flax oil plant (Desgrange—*Oleagineux* 3, 80), oiticica oil (Hermann—*Centraal Inst. Materiaal Onderzoek Afdel. Verf. Circ. No. 42*, 7 pp.), olive oil culture (Morettini—*Olearia* 2, 658, 668; Kaloyereas—*J. Am. Oil Chem. Soc.* 25, 22), palm oil (Ferrand—*Oleagineux* 2, 617), Pourghere oil (Larochas—*Ibid.* 3, 321), peanut oil (Prevot—*Ibid.* 4, 1; Devuyst—*Ibid.* 3, 513; Faure—*Ibid.* 87; Anon.—*Olearia* 2, 678), use of soybean oil (Kenyon *et al.*—*Ind. Eng. Chem.* 40, 1162; Daubert—*Soybean Digest* 7, No. 1, 24), soybean culture (Guerrini—*Oleagineux* 2, 539), use of safflower oil (MacMillan—*Peintures, pigments, vernis* 24, 110), sunflower culture (Crocioni—*Olearia* 1, 217), whale oil production (Skeen—*Soap Sanit. Chemicals* 24, No. 6, 49) and wool fat (Lederer & Velluz—*Ind. Parfum.* 2, 282; Lower—*Ibid.* 319; Levy—*Chim. peintures* 10, 271). The publication dealing with substitutes for drying

oils treated synthetic drying (Razzano—*Am. Paint J.* 32, No. 29, 70) oils suitable for floor-covering industry (O'Hare—*J. Am. Oil Chem. Soc.* 25, 105), and some new or little known oils, which could be made available (Hilditch—*J. Oil and Colour Chem. Assoc.* 31, 1).

Among the above, the reports on peanut oil had information on the so-called British-African ground nut project. Most information on this appeared in newspapers. This is an enormous project intended to supply much oil in the future, but still in the formation stages.

The literature communications on synthetic fats from coal were reviews (Thomas & Weitzel—*Deut. Med. Wochenschr.* 71, 18; *Suddeutschen Apotheker Ztg.* 87, 255; Wachs & Reitstötter—*Angew. Chem.* 20B, 61; Schiller—*Z. Lebensm.-Untersuch. u. Forsch.* 88, 174; Krautwald—*Deut. Gesundheitsw.* 3, 354). In regard to biosynthesis of fats, Popova & Puchkova (*Mikrobiologiya* 16, 51), obtained most economical results by the action of *Oidium lactis* on whey; White & Werkman (*Arch. Biochem.* 17, 475) produced fat from acetates with *Saccharomyces cerevisiae*, and Fiore (*Ibid.* 16, 161) reported the production of fats by the action of *Fusarium lini*, *F. lycopersici*, and *F. solani*, on xylose to hexoses. A review of microbe methods of preparing fats was compiled by Verona (*Olearia* 1947, 141).

NEW COMPREHENSIVE LITERATURE. Two new books, one on "Fatty Acids and Their Derivatives" (Ralston—*Published by John Wiley & Sons, Inc.* 986 pp.) and one on "Cottonseed and Cottonseed Products" (Bailey—*Interscience Publishers, Inc.*, 936 pp.), were valuable additions to the book literature because they brought together and classified the information under these specialized titles. A book on "Allergy to Cottonseed and Other Oilseeds" (*National Cottonseed Products Assoc.* 275 pp.) contained a compilation of excerpts from testimony of six experts, witnesses on allergy of oilseeds with emphasis on cottonseed.

Oil and fat reviews treated the history of oilseed processing (Goss—*Oil Mill Gaz.* 53, No. 3, 16), recent technology progress (McBride—*Food Inds.* 20, 1015), research accomplishments at the Northern Regional Research Laboratory in 1946-47 (Hilbert—*Soybean Digest* 7, No. 1, 42), and an annual review of the chemistry of fats (Folch-Pi & Sperry—*Ann. Rev. Biochem.* 17, 147).

### Production

ANIMAL FAT. This year, Maillet (*Oleagineux* 3, 131) again described the modern rendering equipment, with special emphasis on Titan rendering process. New rendering equipment patented by Schroeder (*U. S. 2,443,274*) passed the charge through a battery of tank renderers containing special means for stirring, draining, and transferring incompletely rendered residue into the succeeding tank of the series. Bailey (*Nat'l Provisioner* 119, No. 18, 10) described continuous operation in a single tank, in which successive measured charges were dropped from each of a series of trays which were heated at progressively higher temperatures. Rendering was done under vacuum and the tank was supplied with the necessary fat and residue discharging devices.

The addition of alkali (Deatherage—*U. S. 2,456,684*) and hydrated silica (Libby & Henderson—*U. S. 2,455,374*) during rendering was considered desirable, because it allowed use of lower rendering tempera-

tures and yielded products having improved stability and less color. "Schmalzkonserven," a German partially rendered canned lard product was described by Grau (*Z. Lebensm.-Untersuch. u. Forsch.* 88, 245), giving method of manufacture and detailed analysis of laboratory-made and commercial samples.

A new fat recovery skimmer for industrial waste water (Grum—*U. S.* 2,453,219) comprised a chamber designed to allow recovery of light fatty material from factory waste into a top separation compartment.

Microscopic aspects of butter manufacture were studied. Accordingly, Mulder (*Chem. Weekblad* 33, 414) found that butter formation was not a complete reversal of phases, as generally assumed, but that it consisted of two continuous fat and water phases interwoven by bridges between the butter globules and canals between the water droplets. His researches (*Netherlands Milk & Dairy J.* 1, 57, 232, 235) also involved the use of the microscope for studying the factors influencing the butter manufacturing process and the finished butter. Summer butter of good consistency was made by culturing cream just above the crystallization temperature of the fat and churning it at 10°C. Thin creams required long churning and gave butters of smooth "closed" surface; while rich creams favored formation of flakes consisting of small granules. The butter of thin creams was more difficult to work and retained more buttermilk. Buttermilk was found to retain some of the smallest fat particles even on vigorous centrifuging. With similar technic, King (*Ibid.* 19, 114) demonstrated microscopic differences between the fat globules of butter produced in ordinary churns and that produced in the Fritz continuous process. The globules of the latter process were appreciably deformed because of strong agitation. Two other publications on butter-making suggested, respectively, general means for producing butter with a good aroma (Pette—*Ibid.* 2, 12) and methods for controlling the consistency of winter butter (Adriani & Tamsma—*Verlag. Landbouwk. Onderzoek* 1946, No. 52G, 1).

**VEGETABLE FATS.** Papers of general interest on the processing of vegetable oils were a history of oilseed milling (Goss—*Oil Mill Gaz.* 53, No. 3, 16), a review of current technical problems (Braun—*Pharmazie* 2, 10), a description of Skipine seed treatment (Anon.—*Oleagineux* 3, 384), and a description of a new sunflower oil mill built at Altona, Canada (Anon.—*Food Manuf.* 23, 57).

Seed quality investigations were related to analysis of storage condition and care for production of high quality oils. Krober and Collins (*J. Am. Oil Chem. Soc.* 25, 296) in a report on weather-damaged seeds found the acid number of oils from these seeds ranged from 1.5 to 47.9% as against 2.9 maximum for sound seed. In another investigation, Hoffpauir *et al.* (*Ibid.* 127) found that most of the viable seeds contained less than 1% free fatty acids while dead seeds showed 1-30% free fatty acids in the extracted oil. Pons *et al.* (*Ibid.* 308) in compiling deterioration changes in stored cottonseed confirmed increases in free acids and the development of red gossypol as recorded by Podolskaya. A new criterion developed for cottonseed deterioration was a measure of the increase in the absorption of the extracted oil in the region of diene conjugation. This criterion was also applicable to other oil seeds.

Hygroscopic equilibrium at between 11 and 93% relative humidity and analyses were recorded for cottonseeds and cottonseed products (Karon & Adams—*Ibid.* 21). In addition these data are useful for designing storage procedures and for calculation of the moisture content of the seed components. Thus a seed of 12% moisture will yield linters, delinted seed, kernels, and lint-free hulls having 9.4, 12.7, 10.8, and 15.4% moisture, respectively.

The preservation of seed quality during storage by preheating has been experimentally demonstrated. In Whitten's (*Oil Mill Gaz.* 53, No. 3, 13) tests the cottonseeds flash heated at 450°F. were stored six months without appreciable change in free fatty acid content. In similar work Lyman *et al.* (*J. Am. Oil Chem. Soc.* 25, 246) flash heated dielectrically and observed that moisture was reduced, the enzymes responsible for free fatty acid liberation were destroyed, and treated seeds even with 20% moisture accumulated free fatty acid only very slowly during storage. The heat treatments destroyed germination. Other reports on storage of seeds recorded that rape seed, as judged from the extracted oil, does not deteriorate in two years' storage if dry and well ventilated (Alam & Ahmad—*Indian J. Agr. Sci.* 16, 279); and that shelled sunflower seeds should be kept at humidities below 60%.

The standard double, single, and universal hulling and seed preparation processes for cottonseed milling were briefly described by Wamble (*Oil Mill Gaz.* 53, No. 1, 36). Olcott (*J. Am. Oil Chem. Soc.* 25, 125) evaluated the conditions under which the toxic factor in cottonseed can be nullified by oxidation and combination with soluble iron salts, and destroyed by steam autoclaving. The purpose was to develop basic information for planning processing conditions that were not as deleterious to the proteins as present cooking procedures. Vilboux (*Olearia* 1948, 225) cautioned processors of palm oils against drying the kernels at temperatures above 113°C., for such temperatures reduce the stability of the oil. A new continuous oilseed mill patented by Pavesi (*Ital.* 412,562) was designed to accomplish crushing, grinding, warming, and pressing in a single apparatus.

The review and discussion communications on extraction of vegetable oils included an economic analysis of pressing and solvent methods (Paleni—*Olearia* 1948, 14), a few general discussions on solvent methods (Greaves—*Oil Colour Trades J.* 114, 496; Paleni—*Olearia* 2, 647), advice on pretreatment of cottonseeds before extraction (Wamble—*Oil Mill Gaz.* 53, No. 3, 31), a hexane continuous system (Seymour—*Food* 16, 351), experience at the Southern Regional Laboratory on continuous extraction (Gastrock & D'Aquin—*Ibid.* No. 4, 13), a description of the Allis-Chalmers equipment (Bilbe—*Ibid.* No. 1, 39) and Central Soya Plant (Kenyon—*Ind. Eng. Chem.* 40, 186), effects of method of extraction on the nutritive values of the residues (Antoniani—*Olearia* 1947, 26), equipment used for extraction of vegetable oils in French Equatorial Africa (Gautier—*Coton fibres trop.* 2, No. 3, 90), various methods used for extraction of olive oil (Rousseau—*Oleagineux* 2, 405; Sericano—*Olearia* 1947, 320; Buzi—*Ibid.* 2, 408; *Olivicoltura* 1, No. 5, 7) and diagram methods for approximating oil milling yields (Cuvier—*Oleagineux* 3, 199).

Many laboratory tests on solvent behavior with oleaginous material provided data applicable for

process development. Spadero *et al.* (*J. Am. Oil Chem. Soc.* 25, 345) showed that liquid sheer by high speed impellers could disintegrate cottonseed flakes in solvent slurry; that bone dried flakes had no advantage over normally dried flakes (2.5-4% moisture); that the presence of hulls aided disintegration; and that pigment glands were very resistant to mechanical rupture. The investigations of Ayers & Dooley (*J. Am. Oil Chem. Soc.* 25, 372) on the suitability of petroleum solvents for cottonseed oil extraction showed a superiority for methylpentanes and the less branched isohexane. In order of decreasing solvent efficiency the following ranked below the above mentioned solvents: paraffins, highly branched isohexanes, cycloparaffins, and aromatics. Diffusion coefficient data of "Skellysolve F" and "Skellysolve B" in the solvent extraction of peanut oil were recorded (Fan *et al.*—*Ind. Eng. Chem.* 40, 195). A diagram of the solubility in a system of oleic acid-olive oil-carbon disulfide-methanol was prepared in a study on olive oil extraction (Moreno & Gonzalez—*Anales real soc. españ. fis y quim ser. B* 44, 391). It was suggested that conditions in the systems of solutions of oil in carbon disulfide could be adjusted so that the free acids could be washed out with methanol. Factory tests by Duncan (*J. Am. Oil Chem. Soc.* 25, 277) on production of soybean oil by means of trichloroethylene extraction showed 0.005-0.01% residual solvent in oil and 0.03-0.06% in the meal, and an oil produced of low color and with an average refining loss of 6.9%. Igarashi (*J. Soc. Chem. Ind. Japan* 49, 67, 135) published his experience on developing solvent extraction procedures for the Japanese soybean oil industry. He favored the use of commercial benzene containing a small amount of water and developed data on optimum conditions of temperature, solvent-bean ratio, cooking, rolling, extraction time, etc., for use of this solvent and also for ethanol. Presumably the above solvents were most available to the industries of that location. The grayfish liver oil extracted with petroleum was one per cent more potent in vitamin A than that obtained by cooking in water (Miyauchi & Sanford—*Com. Fisheries Rev.* 9, No. 9, 19). Richet *et al.* (*ITERG Bull.* 1947, No. 4, 24) tried 15 solvents for extraction of rapeseed under identical conditions, and the amount extracted, quality, and characteristics of the oils were recorded.

Beckel *et al.* (*U. S.* 2,445,931, *J. Am. Oil Chem. Soc.* 25, 7, 10) patented a method of extracting oil-seeds with alcohol in which the extracted oil was separated from the solvent by cooling. Details comprising comparative efficiencies of the lower alcohols and their effects on the physical and chemical properties of the oil, meal, and protein showed that ethanol gave the best results and also debittered the soybean meal. One new patent on extraction dealt with the mechanical aspects of counter-current contacting, heating, and straining (Dinley—*U. S.* 2,447,845). Two other improvements of such apparatus were a separator which combined flotation and settling to separate residue from miscella (Langhurst—*U. S.* 2,441,200), and new means of sealing the machine and parts to inhibit solvent loss (Ford—*U. S.* 2,451,081). A discussion on prevention of solvent loss in oil extraction dealt chiefly with prevention of leakage and improvement of efficiency of solvent separators (Pardun—*Seifenseider-Ztg.* 73, 121, 141).

Safety advice was the main text of three communications. Data pertaining to fire and health hazards of various solvents were compiled by MacGee (*Oil Mill Gaz.* 53, No. 2, 13). Advice on preventing explosions when repairing flammable liquid containers was issued by Schwarz (*Allgem. Oel u. Fett-Ztg.* 38, 327). Long term observations in the olive oil production industry indicated that toxicity to carbon disulfide becomes evident at concentrations of 0.006-0.012 mg. per liter in air (Graziani & Pecora—*Folia Med. Naples* 31, 129).

TALL OIL. A newly patented process (Huff—*U. S.* 2,434,699) for refining tall oil, comprised heating the oil with a combination of sulfuric and phosphoric acids, removing the sludge formed, and treating the oil with clay. Gordon & Ragot (*Bull. mens. ITERG* 1948, No. 4, 32) advised that the oil could be rendered suitable for soap manufacture by hydrogenation at 30 pressures of atmospheres. Under this condition it was decolorized and only the fatty acids were hydrogenated.

Other processes of creating useful material from this by-product of the paper pulp industry involved fractionation to recover the fatty acids. Kalman (*U. S.* 2,441,197) and Babayan (*U. S.* 2,441,198) heated the oil with acids, oxides, or oxychlorides of phosphorus and distilled it under conditions that decarboxylated the rosin acids, thus allowing collection of separate distillates of fatty acids and rosin hydrocarbons. Olson (*Swedish* 119,359) selectively saponified the fatty acids with zinc oxide and distilled off the unsaponified material. Houpt (*U. S.* 2,437,643), dissolved the tall oil in secondary amyl alcohol, neutralized the fatty acids with lye and separated the fatty acid soaps from the solvent solution of rosin acids by dehydrating the mixture. Bliss & Sussky's (*U. S.* 2,451,377) process was based on the characteristic that when dioxane solutions of tall oil were hydrogenated and cooled they separated into two phases, a fatty and a resin liquid phase. Cummings & Vogel (*U. S.* 2,444,730) selectively esterified the fatty acids with lower alcohols, extracted the resultant mixture with a mixture of lower nitroalkane and petroleum solvents which yielded a solution that separates into two phases from which fatty acids and rosin acids were recovered separately.

The reviews on tall oil were quite comprehensive, for they treated production, composition, refining, fractionation, and applications (Harmann—*Centraal Inst. Material Onderzoek, Afdel. Verf. Circ.* 44, 8 pp.; 45, 3 pp.; Frydlander—*Rev. prod. chim.* 50, 6; Wheeler—*Central Mfg. District Mag.* 32, No. 9, 33).

HARDENING OF OILS. Zajcev (*Seifen, Öle, Fette, Wachs Schrift* 74, 4, 27) proposed the use of melting interval, difference between melting and solidification points, and dilation as suitable characteristics to evaluate the selectivity of hydrogenation and as a basis for selection of oils for margarine manufacture. Oil hardened with poor selectivity had a low dilation, a large difference between melting and solidification points, and a large melting interval as compared to more desirable selectively hardened oils. This type of data was tabulated on 20 samples together with consistency and chewability.

Smith (*J. Am. Oil Chem. Soc.* 25, 328) improved linseed oil for making non-yellowing alkyds by partial hydrogenation. Batch methods were more successful than continuous methods, possibly because there

was more selective hydrogenation of the linolenate radical to linoleate. Hydrogenation of castor oil without dehydroxylation permitted the production of a solid wax-like product melting at 85-88°C. (Paquot & Richet—*Oleagineux* 3, 26). The most favorable conditions for this were a pressure of 100-150 kgs. and temperature of 100-110°C. Several investigators fostered the use of polycatalyst, i.e., mixtures of several metals and metal oxides, for hydrogenation (Paterson—*U. S.* 2,437,705-6; Casaus—*Combustibles* 7, 151; Paquot—*Bull. soc. chim. France* 1948, 520). These were said to produce a decolorization simultaneously with hydrogenation; and they permitted hydrogenation at temperatures lower than commonly used, thus yielding fats more stable against incidence of rancidity. Akhmedli (*J. Applied Chem. U.S.S.R.* 21, 164) issued instruction for hydrogenating seal oil with nickel-alumina catalyst and recorded data on the course of decrease of iodine value with the time of hydrogenation. Factory data on using dissociated ammonia as a source of hydrogen for hardening were recorded (van De Eerve *et al.*—*J. Am. Oil Chem. Soc.* 25, 60). The hydrogen consumed was comparable to that of hydrogen from other sources. The advantage seemed to be the simplicity of the equipment.

Two communications were on hardening fats by isomerization. Oils of high oleic acid content were converted to solid fats by Eipper (*U. S.* 2,456,691) by isomerization while in organic solvent solution and with the use of nitrous acid as the catalyst. Rankov's (*Annuaire univ. Sofia, Faculte phys. math.* 38, 133) work on the subject indicated that selenium, and its oxides and acids were active catalysts; and that contrary to some patents and literature, tellurium and tellurium compounds were inactive.

**REFINING AND DEODORIZATION.** The publications on refining varied in text from complete method to recommendation for specific oils and advice for limited steps in the process.

Gupta (*J. Proc. Inst. Chem. India* 20, 41) suggested that crude castor oil be stored for a while to allow a deposit to settle to the bottom, and that this residue be processed to recover a phosphatide which may be useful as a lecithin substitute. Newly described methods of removing "break" constituents from oils comprised special heat treatment over a critical temperature (Sullivan—*U. S.* 2,441,923), washing with an aqueous solution of halogenated lower aliphatic acids (Jakobsen—*U. S.* 2,448,434), and a procedure including the addition of water and centrifuging at 80°C. Helme & Desnuelle—*Oleagineux* 3, 121). The latter method was specifically for extracted peanut oil and designed to recover lecithin.

The designing of treating process for shea butter was complicated by the presence of a large amount of unsaponifiable containing latex-like material and resinous alcohols. Efforts by liquid-liquid extraction indicated that some groups were resistant to solvent segregation (Andre & Pradain—*Oleagineux* 3, 72). A suggested refining procedure for this fat comprised caustic neutralization, alcohol or acetone washes to remove resin alcohols and reduce emulsification, and deodorization.

Optimum conditions for refining erucic acid oils were determined by two laboratories. For rape oil, Gordon & Ragot (*Bull. mens. ITERG* 1947, No. 8, 32; No. 9, 28) recommended 1% excess of 30° Bé caustic,

a temperature of 60-80°C. and the use of centrifuges to remove foots. For either rape or mustard seed oils, Grace *et al.* (*Can. J. Res.* 26F, 349) suggested refining with 10° Bé caustic, bleaching 20 minutes at 212°F. with 2-4% superfiltrol, and deodorization at 464°F. for one hour.

Samuel *et al.* (*Indian J. Vet. Sci.* 16, 11) suggested to the Indian industry that high-acid ghee be neutralized with lime because of its availability and low cost.

The Sharples Corp. continuous alkali refining process was described by Tyler (*Food Ind.* 20, 1456, 1618). Both the caustic and a newer soda ash process were discussed. Mattikow's (*J. Am. Oil Chem. Soc.* 25, 200) communication on the same subject supported the use of refining with soda ash followed by a caustic treatment because there was better removal of phosphatides and lower refining losses. Clayton (*U. S.* 2,437,075) obtained better separation and softer foots in the continuous method by centrifuging in the presence of abietic and naphthenic acids. Desnuelle *et al.* (*Bull. mens. ITERG* 1947, No. 7, 28) cautioned refiners to remove all residual soap in oils for it catalyzes hydrolysis of oils.

The literature on refining oil with solvents was reviewed by Martinenghi & Cardillo (*Olearia* 2, 295; 459). They also presented data showing that olive and grapeseed oils can be refined by washing with acetone or furfural. In a review on use of furfural in conjunction with naphtha for liquid-liquid fractionation, Gloyer (*Ind. Eng. Chem.* 40, 228) showed the utility of the process for deacidification, concentrating vitamin A from liver oils, segregating constituents of tall oil, and fractionating free fatty acids. The other reports on liquid-liquid refining dealt with the use of alcohols to remove the free fatty acids. Rius & Moreno (*Chem. Products* 11, 63) developed curves and diagrams experimentally for various oleic acid-olive oil-methanol systems to show the behavior of the system and serve as a basis for designing liquid-liquid extraction processes for deacidifying olive oil. Moreno (*Olii minerali grassi e saponi colori e vernici* 25, 45) also described a continuous plant based on methanol removal of the acids. Experiments on removal of allyl isothiocyanate from mustard seed oil with ethanol by Ukil & Goswami (*Indian Soap J.* 12, 258) indicated that the process was more expensive than passing steam through the oil followed by a bleaching earth treatment.

Two new patents on decolorizing oils were based on the use of water soluble chlorite and persulfate compounds (Hampel—*U. S.* 2,433,662) and a mixture of ferric salts and silicates (Greentree—*U. S.* 2,450,549) respectively. Lin and Wu (*Res. Bull. Fukien Acad.* No. 2C, 4) recorded the efficiencies of some Chinese clays for the purpose.

Results of attempts to deodorize hazelnut oil to an edible product were recorded by Nizi (*Olearia* 1947, 176). The hazelnut odor could be removed by steam or acidified potassium dichromate solution but a strong rancid odor and flavor took its place. Mixing with olive oil made it satisfactory for eating purposes when the mixtures contained less than 50% of the hazelnut oil.

A new closed-in drum-type fat cooler was designed specifically to give continuous operation, protecting the fat from the deteriorating effect of air and metallic contamination (Murray—*U. S.* 2,433,475).

**SPLITTING AND FRACTIONATION.** General discussion on fatty acid processing giving composition, manufacture, and utility were published by Stingley (*Inst. Spokesman* 11, No. 10, 6) and Brown (*Soap Sanit. Chemicals* 24, No. 2, 55).

Autoclave splitting of fats was described by Hetzer (*Seifensieder-Ztg.* 73, 4) and Barnebey (*J. Am. Oil Chem. Soc.* 25, 95). The latter listed the advantages of this process over the Twitchell process as higher rates of operation and splitting, production of products of lighter color and better grade, and lower over-all cost of splitting. In an investigation on batch autoclave splitting of copra and palm oils, Paquot and Richet (*Compt. rend.*, 226, 925) recorded that at 271°C. equilibrium was reached in 150 minutes giving 61.3% free fatty acids. According to a patent assigned to Emery Industries Inc. (*Brit.* 594,141) counter-current autoclave splitting took place at 180° in water. Combined splitting and hydrogenation of sardine oil as suggested by Yonese (*J. Soc. Chem. Ind. Japan* 49, 133) were carried out under similar conditions except that hydrogen was added at 20-50 pressures of atmospheres. An improvement for counter-current equipment comprised introducing oil into the autoclave by means of steam at pressure higher than that in the autoclave.

In two series of investigations of contact catalysts for splitting of fats, a decided preference was shown for sulfuric acid (Ondovilla—*Anales fis. y quim.* 42, 97); Nishizawa *et al.*—*J. Soc. Chem. Ind. Japan* 46, 1237; 47, 18, 233, 329, 482; 49, 133, 190, 191). Data on about 15 catalysts were presented. Hetzer (*Seifen-Öle-Fette-Wachse* 74, 172) preferred zinc oxide as a catalyst for splitting palm kernel oil because it caused only a slight darkening of color. Newly patented catalysts were the sulfonic acids of high boiling polyalkylated benzenes (Griesinger—*U. S.* 2,442,925).

Mueller and Holt (*J. Am. Oil Chem. Soc.* 25, 305) followed the course of the Twitchell splitting reaction by analyses taken from a 15,000-pound batch of crude coconut oil during a three boil splitting operation. These analyses confirmed the earlier theories that the reaction proceeds stepwise. The split fatty acids should be washed with water to prevent re-esterification during distillation.

Good quality fatty acids were derived from cottonseed foots by completely saponifying them, treating with potassium persulfate and sodium oxychloride, and releasing the fatty acids with an inorganic acid (McClain—*U. S.* 2,435,456).

In the field of fatty acid distillation a comprehensive paper (Fawcett—*Chemistry & Industry Suppl.* 1948, 27) appeared on the subject in a symposium on high vacuum technic. The object of one still invention was to obtain a better fraction by distilling a part of the fatty acids with steam and to complete the process under vacuum (Potts—*U. S.* 2,450,611-12). Another still, using low pressure and steam, was designed to produce fractions of unsaturated, polymerized and saturated fractions (Abbey—*Brit.* 593,569). Buxton (*U. S.* 2,434,789) added antioxidants to distillation charges to protect the products from oxidative deterioration.

Other fractionation literature dealt with solvent segregation of the acids. A study of the ternary systems oleic acid-stearic acid-hexane and similar system with acetone indicated that oleic acid of high purity can be obtained by application of a segregat-

ing process to the mixed free acids derived from fats (Singleton—*J. Am. Oil Chem. Soc.* 25, 15). In these the solubility of stearic acid was less in the system containing acetone than that with hexane. Alpar (*Rev. faculte sci. univ. Istanbul* 13A, 30) issued instructions on separating saturated and unsaturated acids by crystallization from 80% alcohol at -10° to -15°C. A similar patented process comprised fractionation by distillation and segregating the unsaturated from the saturated acids by crystallization from solvents (Colt—*U. S.* 2,443,181). An apparatus for crystallization from solvents contained devices for continuously filtering the crystals formed (Gee—*U. S.* 2,450,235).

Solvent segregation was also applied to oils. Tests on using methanol and 2-furaldehyde on cameline oil of iodine value 142.4 gave unsaturated fractions of iodine value 155 and 159, respectively (LeComte & Paquot—*Bull. mens. ITERG* 1948, No. 5, 26 pp.). However, the elimination of 2-furaldehyde from the oil was difficult with vacuum and had to be carried out with steam. Gordon (*Ibid.* No. 2, 31) obtained drying-oils from rape oil by fractionating with hot methanol or furfural. Detailed descriptions of commercial plants for segregating soybean oil into a drying-oil and an edible-oil fraction by liquid-liquid extraction in naphtha with furfural were presented by Kenyon *et al.* (*Ind. Eng. Chem.* 40, 1160). Paquot & Najand (*Bull. soc. chim. France* 1948, 483) tested the liquid extraction process with selective solvents such as ethanol, methanol, mixtures of ethanol-acetone, ethanol-ether, naphtha-ether, acetone-water, and furfural. Fractions of considerably higher iodine value were produced from cameline and soybean oils but not from cottonseed oil. In one respect poppyseed oil was opposite to the above oils in that the fraction soluble in the extraction solvent had an iodine value lower than that of the original oil.

Basic data for useful application to produce better drying oils from linseed and mustard oil by solvent extraction were developed by Pal & Mukherji (*Indian Soap J.* 13, 291). They mixed various oil-solvent ratios, allowed separation to layers and analyzed both layers; thus conditions for producing specific results can be interpreted from the data obtained. Equipment was designed to separate fats into three fractions by crystallization from propane (Dickinson & Morfit—*U. S.* 2,454,638).

**INTERESTERIFICATION AND ESTERIFICATION.** During the past several years interesterifying glycerides with lower alcohols was reported as a step in a new soap making process wherein glycerol was efficiently recovered after alcoholysis and the methyl alcohol used was recovered during the saponification. Another application of the interesterification procedure was to vitamin containing oils, in which the alcoholized oils were distilled to yield fatty esters distillate and a vitamin concentrate residue. This latter process suggested to Karnovsky *et al.* (*J. Am. Oil Chem. Soc.* 25, 36) the possibility of preferential transesterification of vitamin A esters in liver oils and chromatographic concentration of the vitamin A derivatives. The results showed that preferential esterification of vitamin A was not feasible. One foreign patent (Lever Brothers & Unilever N. V.—*Dutch* 60,567) on interesterifying fats with alcohol was comparable to patents issued here in recent years, in which alkali was used as a catalyst. In two new communications



on the process, sulfuric acid (King & King—*U. S. 2,447,186*) and a mixture of sulfuric acid and aluminum sulfate (Mikumo—*J. Soc. Chem. Ind. Japan 46, 985*) were used as catalyst.

A new application of interesterification comprised rearranging the fatty radicals in fats so that the totally saturated glycerides were increased and could be separated (Eckey—*U. S. 2,442,531-6; 2,442,539; Ind. Eng. Chem. 40, 1183; Abbott—U. S. 2,442,538; Lever Brothers & Unilever Ltd.—Brit. 590,951*). When fats and oils were heated with alkali as a catalyst, rearrangement occurred in which a maximum trisaturated glyceride content appeared at an equilibrium which coincided with the arrival of random distribution of fatty acids among the glycerides. When the process was carried out with stepwise lowering of the temperature, trisaturated glycerides were removed from the system by crystallization and the rearranging continued to yield more trisaturation while the unsaturated radicals were concentrated in the liquid glyceride fraction. Suggested practical applications for the process were: an oil like cottonseed oil could be converted to a semi-solid type shortening without hydrogenation; tallow also could be converted into satisfactory fat material for shortening. The graining-out process of segregating fish and other oils into fractions having superior drying properties for varnish and harder fats for soap, would be improved; and with mono- and di-glycerides prepared from a natural fat, the product could be separated into fractions, one predominantly solid and the other liquid. Observations on the transesterification rearrangement of glycerides were also recorded by some French investigators. Naudet *et al.*'s (*Oleagineux 3, 57*) work was for the purpose of demonstrating that harder fats of better texture and consistency could be made from mixing solid fats (coconut oil) with fluid fats (peanut oil) if the mixture was subjected to interesterification conditions. Reutenauer & Sisley (*Oleagineux 3, 305; Bull. mens. ITERG 1947, No. 11, 32*) transesterified linseed oil with rapeseed, sunflower seed, and physic-nut oils and obtained products that dry in somewhat less time than the linseed oil. Their purpose was to economize on the use of linseed oil.

The kinetics of esterification of various fatty acids and glycerol in the presence of fluoride catalyst were recorded by Wocasek & Koch (*J. Am. Oil Chem. Soc. 25, 335*). Of 15 fluorides studied all afforded some catalysis but only antimony trifluoride and fluorides of zinc and cobalt were outstanding. Esterification of  $C_{18}$  fatty acids to the triglycerides was more efficient as the unsaturation increased. With each acid, and with zinc fluoride as the catalyst, the monoglyceride was formed at four times the rate of the uncatalyzed reaction and the diglyceride at a six-fold rate; while the triglyceride was formed at a rate which did not diminish as rapidly as that of the uncatalyzed reaction. Attempts to prepare fatty diesters of pentaerythritol from fatty acid soaps and dibromohydrin of pentaerythritol by Savary (*Oleagineux 3, 65*) were unsuccessful, because they transformed into more complete esters by interesterification.

#### Products (Except Detergents)

**EDIBLE PRODUCTS.** In the literature on shortening, one review treated the improvements in the taste,

odor, appearance, and stability of modern lard (Vibrans—*Food Inds. 20, 855*). Gudheim (*U. S. 2,455,363*) super-cooled liquified fat to 15°C. before crystallization started in order to obtain a solid shortening of improved texture. Hydrogenated vegetable oils of iodine value 65-85, when submitted to interesterification to rearrange the fatty acids among the glycerides became more suitable as a shortening for puff pastry (Eckey—*U. S. 2,442,537*). An all-climate shortening having desirable plastic characteristics over a wide temperature range was a blend of edible fatty oil with a hard fat of glycerides of palmitic and stearic acids, 15-30% being palmitic acid (Ziels & Schmidt—*U. S. 2,430,596*). Lecithin for shortening was mixed with Irish moss gel to yield a dry product, which mixed more conveniently with dry flour (*Allingham—U. S. 2,417,726*). A dry lecithin-sugar combination was for the same purpose (Bigelow—*U. S. 2,430,553*).

Some experimental cookery investigations involved the behavior of fats during the cooking processes. In potato chip manufacture, low ash content, long storage, low moisture, hot brine treatment, and use of unhydrogenated vegetable oils as the frying fat tended to decrease the oil uptake of the chips (Stutz & Burris—*Food Inds. 20, 1146*). The unextracted oil left in soybean flour acted as a shortening when the flour was used to make pastry wafers (Frantz & Simpson—*Food Res. 12, 461*). Twenty-three methods of mixing cake ingredients were used to study factors affecting the quality of cakes made with oil (Ohlrogge & Sunderlin—*J. Am. Diet. Assoc. 24, 213*). The best cakes came from stirring the oil in a "sponge" or meringue made of stiffly beaten whole egg or egg white and adding one-fourth of the sugar late in the mixing process. The batter structures were oil-in-water emulsions. In work on leavening cake with air, water vapor, and carbon dioxide, variations occurred with the type of fat used (Hood & Lowe—*Cereal Chem. 25, 244*). Leavening with water vapor in the presence of air was greatest with oil, intermediate with butter, and least with hydrogenated lard. Conversely the effectiveness of carbon dioxide was greatest with hydrogenated lard and least in the oil cake.

The winterizing of salad oils, i.e., improvement of resistance to freezing, was enhanced by the presence of lecithin during the process (Gooding & Rich—*U. S. 2,435,626*). Accordingly, the crystals of the high melting constituents were modified so that they were more conveniently and efficiently removed.

Butyl stearate was compared with cellulose acetate as a coating for enteric tablets (Bauer & Masucci—*J. Am. Pharm. Assoc. Sci. Ed. 37, 124*). The coatings were put on barium sulfate tablets, and *in vivo* tests, which were followed by x-ray examination, disclosed that disintegration of the tablets occurred in the ileum and colon.

A patented oleomargarine manufacture operation comprised a standard cooling step followed by treatment in a colloid mill (Nelson—*U. S. 2,434,429*). A coloring capsule coated with sugar was patented for introduction into the block margarines retailed in mixing bags (Adler *et al.*—*U. S. 2,454,420*).

**EMULSIFIERS AND DEMULSIFIERS.** Several emulsifiers were specifically intended for use in food products. The polymerized and oxidized fats, and mixtures of mono- and diglycerides, and ethyl esters patented by

Schou (*Brit. 586,109; 586,112; Danish 65,598*) were for use in margarine and shortening. Mannitol derivatives of beef fat when used as emulsifiers in ice cream mixes, decreased the whipping time necessary for unhomogenized mixes and produced an improved whipped product, but shrinkage exceeded that of control samples (Naden—*J. Dairy Sci.* 31, 704). Propylene glycol esters of fatty acids added to eggs suppressed foaming during drying (Frey & Miller—*U. S. 2,447,063*).

Many emulsifiers were made for a variety of technical and pharmaceutical products. Patented general emulsifiers were alkylolamides of trihydroxystearic acid (Schaeffer—*U. S. 2,440,349*), such mixtures as monoricinolein and triethanolamine monoricinoleate (Meade & Lankro Chem. Ltd.—*Brit. 587,534*), and condensates of fatty acid esters of cholesterol with polyethylene glycols (Lerner—*U. S. 2,437,261*). A communication on polyethylene glycols and their derivatives contained formulas for using these emulsifiers in cosmetic creams and lotions (Anon.—*Schimmel Briefs No. 158; Soap Perfumery and Cosmetics* 21, 799); similar communications treated stearyl alcohol (Leddon—*Drug & Cosmetics Ind.* 61, 308), and stearic acid (Winter—*Soap, Perfumery & Cosmetics* 21, 42), respectively, as the emulsifier. A patented ointment base contained wool-wax alcohols as the emulsifier (Croda Ltd. & Lower—*Brit. 572,318*). The scopes of general papers on emulsifiers were evaluation of emulsifying agents (Hollenberg—*Soap, Perfumery & Cosmetics* 21, 474), methods of preparing emulsions (Leslie—*Mfg. Chemist* 18, 494), technical applications of lecithin (Hilty—*J. Am. Oil Chem. Soc.* 25, 186) and monoglycerides (Latteur—*Oleagineux* 3, 297), and a comparison of polyvinyl alcohols with several common emulsifiers (Biehn & Ernsberger—*Ind. Eng. Chem.* 40, 1449). Mail (*Chem. Inds.* 62, 238) fostered preparation of insecticide for retail in emulsified form because it made them easier to ship and safer to use.

For water-in-oil emulsions containing ethanol, compounds with hydrophilic groups on terminal carbons were ineffective as emulsifiers, whereas internal hydrophilic groups (carboxyl, sulfo, etc.) were effective (Rzymkowski & Reitstotter—*Pharmazie* 2, 509). An investigation on several emulsifiers for water-in-oil emulsions indicated that single compounds were more effective than a mixture of two or more. Several papers in the new book "Colloid Science: A Symposium" (various authors—*Chem. Publ. Co. 1947*, 208 pp.) were of interest in regard to the theoretical aspects of emulsions.

Demulsifiers, usually certain surface active fat derivatives, were most used in the petroleum industry to release petroleum from water emulsions. Natural petroleum from wells treated with inorganic acids is sometimes obtained in an emulsion from which it must be segregated by demulsification. The newly patented compounds for this purpose were principally fat derivatives (Eickmeyer—*U. S. 2,452,736*; Harlan—*U. S. 2,454,382*; Kirkpatrick & Wilson—*U. S. 2,454,808*; DeGroot et al.—*U. S. 2,442,073-7, 2,450,124, 2,450,332-3, 2,454,435*; Bond—*U. S. 2,457,634*; Savoy—*U. S. 2,457,735*). One communication on breaking emulsions of sea-water in fuel oil, based on results of war-time investigations of the British Admiralty, contained a discussion of the theoretical aspects and calculations when using synthetic deter-

gents as the demulsifiers (Lawrence—*Chemistry & Ind.* 1948, 615).

In two patents on prevention of foaming in steam boilers, the demulsifiers or defoamers were amino fat derivatives such as  $\alpha$ -palmitylamino-N-hexadecylvaleramide,  $p$ -palmitylaminophenyl-N-hexadecylacetamide (Bird—*U. S. 2,428,775-6*).

PROTECTIVE COATING, RESINS, AND PLASTICS. A review on oils for the protective coating industries by Sutheim (*Chem. Inds.* 62, 65, 241) contained brief information on processing, bodying, isomerization, dehydration of castor oil, copolymerization, alkyds, and substitutes. A summary of the scientific work on drying oils recorded in Europe during the war years, 1938-47, was compiled by Bockenoogen (*Chem. Weekblad* 43, 796). Another review on drying oils was principally on dehydration, isomerization, and theories of blowing and heat-bodying (Elm—*Paint, Oil, Chem. Rev.* 111, No. 13, 11). A comprehensive review on chemical reactions of pentaerythritol should also interest drying oil chemists because of the use of some such esters as drying oils (Marrian—*Chem. Rev.* 43, 149).

Some experiments were concerned with the mechanism of the autoxidation of drying oils. Bickford et al.'s (*J. Am. Oil Chem. Soc.* 25, 251, 254) experimental data supported the theory of free radical chain mechanism for autoxidation of fats, which was analogous to that proposed by Farmer, Kock, and Sutton. This mechanism differs from that generally accepted because the ethylene linkage was not attacked, but the addition of oxygen occurred at the adjacent methylene group. Support for their theory was based on the observation that maleic anhydride behaves like oxygen toward unsaturated compounds, and they experimentally demonstrated that maleic adducts of alkylbenzenes were attached at the  $\alpha$ -carbon atom of the alkyl group and that with methyl oleate the attachment was at a carbon atom not having a double bond. Swern et al.'s (*Ibid.* 193) review of the theories involved favored addition of oxygen at the  $\alpha$ -methylene group in mono olefins and non-conjugated olefins, but in case of conjugated compounds they believed that peroxides were formed by addition of oxygen at the double bond. Radlove & Falkenburg's (*Ibid.* 1) comparison of the bodying of conjugated and nonconjugated linseed and soybean oils indicated that during bodying complete conjugation does not take place, for conjugated oils produced superior products. He suggested that polymerization of oils involved more than one mechanism. In a comparison of bodying linseed oil by heat and by electric discharge (Vian and Yzu—*Ion.* 7, 749) better results were realized from the latter method. They believed this was due to more conjugation taking place during the electric process.

The kinetics of oxidation of oils were studied by Scheiber (*Farbe u. Lack.* 1947, 29) and Lunberg (*Biol. Antioxidants, Trans. 1st Conf.* 1946, 26). The former recorded the antioxidant effect of many antioxidants on linseed oil films; the latter's data of similar nature demonstrated that positive or negative catalysts primarily influence the speed of drying but do not alter the composition of the oxidation products.

Linseed oil containing drier did not thicken when exposed to light in glass tubes, thus indicating that oxygen was necessary for thickening of the film (Rinse & Dierdorp—*Verfkroniek* 17, 85). However,



Slansky (*J. Oil & Color Chem. Assoc.* 31, 161) dried linseed oil films under air and under carbon dioxide and since under the latter process less weight was gained, he assumed drying was by polymerization. Such films were more water resistant. In air drying, polymerization and water resistance were realized to an increasing extent as thicker films were tested. The rapid gelation of amides of maleic acid adducts of methyl esters of fatty acids was attributed to polymerization (Teeter *et al.*—*J. Am. Oil Chem. Soc.* 25, 158).

Fading of certain pigments in fatty oil paints was attributed to the oxidative action of the oil peroxides formed, for the same pigments faded in paraffin oil paints when benzoyl peroxide was added (Anderson—*Festschr. J. Arvid Hedvall 1948*, 13).

Two investigations were made in regard to applying spectrophotometry to paint studies. Hendrickson *et al.* (*J. Am. Oil Chem. Soc.* 25, 73) verified a principle previously reported that the quantity of light absorbed by an oil in the region of 320-400  $m\mu$ . was indicative of its durability in a paint film and they also designed procedures for such testing. Kolb & Hauser's (*Paint, Oil, Chem. Rev.* 110, No. 23, 104) spectrographic tests on resin-bodying reactions indicated that Raman spectra were hampered by fluorescence and that ultraviolet absorption was not useful; but infrared absorption gave indications of being useful.

Data and experiences recorded in some papers should be useful to the bodying oil industry. Rossetti (*Olii minerali grassi e saponi, colori e vernici* 25, 23) plotted the course of the viscosity during polymerization of linseed oil. Gupta & Chatterji (*Paint Manuf.* 18, 171) recommended a preliminary sulfuric acid refining before bodying oils to remove antioxidants and allow bodying to occur more readily. Bernstein (*J. Phys. and Colloid Chem.* 52, 613) recorded the development of polymers in heat-polymerized nonconjugated vegetable oils. The data were determined by a selective solvent technic of segregating various polymers. Pale and low acid bodied linseed oil of the type obtained in closed kettle bodying under carbon dioxide could be obtained in open kettles by covering the oil with an aluminum cover of slightly smaller diameter than that of the kettle at final oil level (*Köln-Farben, Lacke, Anstrichstoff* 2, 83). New patents on bodying covered the following: a new apparatus designed for efficient stirring and aeration that produced oxidized oils with a minimum of polymerization (Hazlehurst—*U. S.* 2,446,652), polymerization of oiticica oil, containing boron fluoride, to a desired point and arresting the bodying by adding water (Berger *et al.*—*U. S.* 2,440,000), partially distilling an oil, bodying the residue and again subjecting to distillation to remove unpolymerized oil (Barnitz—*U. S.* 2,437,343), and treating linseed oil with azelaic acid to displace non-drying constituents which were removed by distillation (Myers & Muckerheide—*U. S.* 2,440,667). According to Paek & Holmes (*Proc. Am. Tung Oil Assoc.* 1947, Pt. 1, 21) the conditions for gelling American tung oil were: heating by means of a steam coil at 80 lb. per sq. in. pressure for 25 hours or for 12 hours at 140 lb. per sq. in.

A considerable amount of conjugation was induced in linseed and soybean oils without appreciable polymerization by heating the oils at 260-300°C. in the

presence of anthraquinone (Falkenburg *et al.*—*J. Am. Oil Chem. Soc.* 25, 237). Over 95% of the anthraquinone separates out on standing at room temperature. Waterman *et al.* (*Research* 1, 183, 186; *Koninkl. Nederland. Akad. Wetenschap. Proc.* 50, 1181) demonstrated their process of conjugation with sulfur dioxide catalyst by describing the production of linseed oils with diene values of 13-26. They said that the products fixed phenol and bound hydrochloric acid in the same manner as tung oil. Fatty acids were conjugated by passing the vapors over fuller's earth (Brit. Paints Ltd. & Slansky—*Brit.* 590,784). Plank (*U. S.* 2,435,695) used a small amount of boron trifluoride-bodied tung oil gel as a conjugation catalyst. Stevens (*Brit.* 577,202) conjugated oils by aerating at temperatures below 70°C.; these oils had a reduced tendency toward development of color during bodying.

Castor oil is prepared for use in paint and varnish by dehydroxylation which occurs on heating in the presence of a catalyst. Two new patents on the process made use of ammonium chloride (Monroe & Ipatieff—*U. S.* 2,439,982) and a mixture of boric and phosphoric acids (Rust—*U. S.* 2,456,996), respectively, as catalyst. The process was carried out continuously on a laboratory scale by passing the oil with sulfuric acid in thin layers through a column under *vacuo* at 300-320°C. (Radlove *et al.*—*J. Am. Oil Chem. Soc.* 25, 268). Kappelmeier *et al.*'s. (*Paint Technol.* 13, 261) study of the castor oil dehydroxylation reactions showed that during the process interesterification took place in a manner that protected some hydroxyl groups against analytical determination unless the oil was saponified. This indicated that the degree of dehydroxylation cannot be measured by hydroxyl value changes. Other variations encountered in the bodying of dehydroxylated castor oil were attributed to fluctuations of the undecylenic acid formed. Wilson (*J. Oil & Colour Chem. Assoc.* 31, 41) recorded experiences in utilizing castor oil dehydrated by various procedures. In dehydrating under reduced pressure products of decomposition were removed, and the residue was less viscous, lower in acid, more dehydrated and had a higher percentage of conjugated unsaturation. Such oils gave less tacky films. When the oils were used with alkylid resins and linseed oil, increases in dehydrated castor oil increased the drying time. Dooper & Hermann (*Centraal Inst. Materiaal Onderzoek Afdel. Verf. Circ.* No. 47, 19 pp.) likewise described properties of various samples of dehydrated castor oil and then showed their behavior with various paint pigments.

The process of improving drying oils by converting them into pentaerythritol esters was most satisfactorily accomplished by double-ester exchange reaction starting with the acetate ester of pentaerythritol and methyl esters of the fatty acids (Chipault & Lundberg—*Ann. Rpt. Hormel Inst.* 1946-47, 42). Adelson & Gray (*U. S.* 2,426,913) prepared polymeric allyl alcohols which could be esterified with fatty acid to prepare improved drying oils. Frilette (*U. S.* 2,440,467) added three per cent sulfur to drying oils to improve the flexibility and the resistance to alkali and soap of the films therefrom. Sulfur reacted better with fatty oil when small amounts of dicyclohexylamine were present (Roberts—*U. S.* 2,450,384). Heating linseed oil acids with sorbic acid and glycerol was said to yield a rapid-drying and water-

resistant coating oil (Barthel—*U. S. 2,420,694*). In three patented coating oils the improvements were accomplished by addition of certain resins (Butler—*U. S. 2,452,992*; Rummelsburg—*U. S. 2,445,637*; Hewitt & Armitage—*U. S. 2,441,068*). A mixture of tall oil rosin and linseed oil (Bergström *et al.*—*U. S. 2,437,931*) and a combination of drying oil, resin, and shellac (Zoutewelle—*Dutch 61,650*), respectively, were patented as impregnating oil for hardening fibreboards. The patents on producing oils which yielded wrinkled finishes described methods by which semidrying oils or drying oils were heat treated with allyl cobalt (Williams—*U. S. 2,441,738*), lead dipropyl (Williams—*U. S. 2,441,739*), propylene glycol and polycarboxylic acids (Waldie—*U. S. 2,443,284*), gilsonite and oil-soluble resin (Waldie—*U. S. 2,443,212*), certain phenol formaldehyde resins (Waldie—*U. S. 2,455,541*), certain cellulose compounds (Beynon—*U. S. 2,456,670*) and latex (Beynon—*U. S. 2,456,671*). Another wrinkle finish product was a specially heat treated mixture of raw castor oil, dehydrated castor oil, drier, and pigment (Waldie—*U. S. 2,455,540*). Protective coating products in the form of water emulsions were also patented (Auer—*U. S. 2,433,831*; Paterek—*U. S. 2,433,783*; Iliff & Torrey—*U. S. 2,440,953*). A new flattening agent for drying oil coatings was a mixture of rosin soap and certain cellulose esters (Auer—*U. S. 2,433,833*). The soaps of cobalt, thorium, uranium, vanadium, beryllium, and molybdenum were evaluated for their catalytic influence in the autoxidation of unsaturated oils (Skellon & Spence—*J. Soc. Chem. Ind. 67, 365*). The soaps most easily dispersed were most active. The high efficiency of the linoleates was attributed to unsaturation which readily absorbed oxygen.

Each year there appear some papers treating the use of specific oils in the drying field. The subjects of some of those of the present year were argemone oil (Nanda & Mathur—*J. Sci. Ind. Res. India 6B, 93*), corn oil (Brambilla & Balbi—*Chim. peintures 9, 207*), fish oils (Schwitzer—*Paint Manuf. 18, 159*), lallemantia oil (Bergner—*Farbe u. Lack 1947, 25*), soybean oil (Terrill & Mitchell—*Western Paint Rev. 34, No. 3, 29A; No. 4, 29A*), soybean-tung oil combinations (Pittsburgh Paint & Varnish Prod. Club—*Paint, Oil, Chem. Rev. 110, No. 23, 99*), sunflower seed oil (Castorina—*Olearia 1948, 391*), Japanese vegetable oils (Nobori & Nakajima—*J. Soc. Chem. Ind. Japan 49, 13*), and tall oil (Mann—*Am. Paint J. 33, No. 3, 66*; Kemner—*Farben, Lacke, Anstrichstoffe 1, 20*; Otte—*Farve og Lak, 1944, No. 19, 10*). Bare & Stubblebine (*U. S. 2,439,377*) utilized tall oil for drying oil purposes by polymerizing it with linseed oil. For the same uses, Magnusson & Richtet (*Swed. 118,422*) converted the tall oil to glycerol and pentaerythritol esters and blew the products with air or other gases containing sulfur, selenium, or tellurium. Drying oils were prepared from marine animal oils by interesterification to rearrange the glycerides, followed by removal of the saturated constituents (Eckey—*U. S. 2,442,533*). Synthetic drying oils were made from petroleum (Block—*U. S. 2,440,459*; Johnstone—*U. S. 2,440,477*;—Rinse & Dost—*Dutch 61,516*).

The reviews in fat derived resin were on alkyd resins (Drummond—*Chemistry & Ind. 1947, 763*; Phillips—*Ibid. 1948, 3*; Cornish—*Ibid. 39*; Levesque

—*Official Digest Federation Paint & Varnish Production Clubs No. 278, 245*). Goldsmith (*Ind. Eng. Chem. 40, 1205*) reported that in the preparation of alkyd resins the primary hydroxyl of glycerol in monoglycerides reacted more readily with phthalic carboxyl than with fatty acid, whereas the reverse occurred with the hydroxyl in the second position.

Hultsch (*Kunststoffe 37, 43*) discussed the activity of phenol resins in regard to combining with fatty oils, and emphasized rendering them active by appropriate heating with resinic acids. In studies on condensing phenol and drying oils, by Doshi & Mehta (*J. Sci. Ind. Res. 6B, No. 5, 63*), sulfuric acid catalyzed the reaction at 100°C., while gaseous hydrochloric caused esterification and phosphorus pentoxide was not active below 250°C. With condensation, ethylene linkages were attacked.

Swern & Jordan (*J. Am. Chem. Soc. 70, 2334*) prepared the vinyl, 2-chloroallyl, methallyl, allyl, 3-buten-2-yl, crotyl, and furfuryl esters of several fatty acids and recorded some of their properties. Most of the products were wax-like solids, one a viscous oil. By polymerizing these alone or with other material as styrene, diallyl phthalate, etc., derivatives with a wide range of properties were attainable. Glycine esters of fatty acids when spread in layers polymerized to form insoluble films which contained polypeptide linkages (Baniel *et al.*—*J. Org. Chem. 13, 791*).

Several new patents were issued on resin products. A polymer of cyclopentadiene-maleic adduct, fatty acid, and polyhydric alcohol served as a resinous stabilizer for coating emulsions (Butler—*U. S. 2,437,293*). Heat treating ethylene glycol, tetrachlorophthalic anhydride, and stearic acid mixtures yielded fusible, flame-resistant, wax-compatible resins (Nordlander & Cass—*U. S. 2,455,873*). Adducts of fumaric acid with isoprene, butadiene, and other dienes were made as intermediates for varnish oils and in use were condensed with drying oils (Lane & Parker—*U. S. 2,444,263*). Copolymerization of drying oils and lower dienes yielded resins suitable as plasticizers and varnish constituents (Huff & Clynch—*U. S. 2,442,085*). Higher dienes such as dicyclopentadiene were also polymerized with maleic acid and fatty oils to yield resins (Gerhart & Adams—*U. S. 2,436,641*). Resins were also made by interpolymerization of styrene, natural resins, and drying oil (Arvin & Gitchel—*U. S. 2,457,768*). Other resinous substances were prepared by polymerizing fatty drying oils with polyacrylic acids (Watson—*U. S. 2,449,828*), acrylonitrile (Brunson & Niederhauser—*U. S. 2,440,140*), and ethylene diamine (Cowan *et al.*—*U. S. 2,450,940*). Rosin and tall oil were converted to resins suitable for protective coatings by condensation with organic acids (Auer—*U. S. 2,440,242*) or heating with lime (Rice—*U. S. 2,448,621*). Fatty acids (Geiges—*U. S. 2,431,800*) and mixed esters such as pentaerythritol, triacetate, and monostearate (Barth & Burrell—*U. S. 2,441,555*) and fatty acid esters of thioglycol (Pollack—*U. S. 2,454,568*) were utilized as plasticizers. Vinyl resins were stabilized against the effect of heat and light with phenoxy lead stearate (British Thompson-Houston Co.—*Brit. 587,444*).

TEXTILE WATER REPELLENTS AND SOFTENERS. Excepting detergents and spinning lubricants, the most common application of fat derivatives to textiles was

for the purpose of making them water repellent. Calcium soap products, which are the most commonly used were discussed by Oldenroth (*Melliand Textilber.* 28, 27). Beside adding water repellancy, these soaps lubricate the fabric and increase its resistance to failure on flexing. For instance, an unwashed but desized control fabric failed after 2,062 flexings; after treatment with calcium soap the flexing failure was raised to 3,000. Newly patented fat derivatives for softening and rendering fabrics water repellent were: reaction products of bis (chloromethyl) ether, fatty oil, hydrogenated fatty amide, thiourea, and sodium chloroacetate (Soc. pour l'ind. chim à Bâle—*Swiss* 216,164, 216,301, 216,302, 218,270, 219,924), dispersions of cetyl acetamide, zirconium soap and zirconium formate (Ariente & Allen—*U. S.* 2,455,886), and reaction products of sodium fatty acid-sulfosuccinamates and condensates of alkylene oxide, and mixtures of N-alkylcarbamate salts of fatty acid guanidines and amines (Vitalis & Lynn—*U. S.* 2,427,242). Fat acid esters of polymerized ethylene oxide were applied to textiles to give a seroopy feel (Soc. pour l'ind. chim. à Bâle—*Brit.* 599,280). One water-proofer for textiles comprised pigment, bodied drying oil, protein, and resin emulsion, and was evidently a composition for making oilcloth (La Piana & Bosland—*U. S.* 2,453,752).

FAT DERIVED ACIDS, ESTERS, ALCOHOLS, KETONES, AMINES, AND HYDROCARBONS. Methods of commercial production of pure fatty acids were recorded. The new procedures for stearic acids depended upon crystallization of the fatty acid mixtures from lower ketones (Adelson—*U. S.* 2,443,063), or ethanol (Rao—*J. Sci. Ind. Res., India*, 7, No. 1B, 10). Experimental separation of stearic acid and oleic acid by various chromatographic methods was done in the laboratory, but the process did not seem economically feasible for commercial scale operation (Mazumdar & Goswami—*Indian Soap J.* 12, 227). McKay (*J. Org. Chem.* 13, 86) detected the presence of 11% stearic acid in bayberry tallow; this report was important because manufacturers of myristic and palmitic acids have assumed that only a trace of stearic acid was present. In a process for preparing oleic acid, polyunsaturated acids were removed by heating the mixed soaps at 280-310°C., to cause selective partial decomposition of the polyunsaturation constituent and thus render the oleic acid more easily removable by physical means (*J. Ross—U. S.* 2,435,159).

Epoxy compounds were prepared from unsaturated fatty acids by reaction with alcohols in presence of sulfuric acid, and the physical and chemical properties were recorded (Swern *et al.*—*J. Am. Chem. Soc.* 70, 1226, 1228, 1235; *U. S.* 2,457,328-9). The possible uses suggested for these were as plasticizers or after thermal polymerization as viscous material. Curtis *et al.*'s (*J. Soc. Chem. Ind.* 66, 402) studies on ketonizing fatty acid indicated that optimum conditions were a magnesia catalyst and a temperature of 330-360°C. These products were wax-like. A patented method of ketonizing hydroxy fatty acid made use of oxidation with hexavalent chromium compounds (Price & Sprules—*U. S.* 2,416,849).

Some fatty acids were synthesized for a variety of purposes such as development of synthesis methods, establishing the structure of some native materials, developing fundamental data for analysis, and for

use in studies on fat nutrition and metabolism. These preparations were diastereoisomers of tetrahydroxystearic acid (McKay & Baker—*J. Org. Chem.* 13, 75), branched-chain fatty acids (Prout—*J. Am. Chem. Soc.* 70, 298), 3-6-diketo fatty acids (Breusch & Ulusoy—*Rev. faculte sci. univ. Istanbul* 13A, 51), 1-hydroxyl-3-keto acids of chain length C<sub>9</sub>-C<sub>15</sub>, 1-2-3-keto acids of C<sub>6</sub>-C<sub>10</sub> acids, 1-2-dihydroxy-3-keto C<sub>9</sub> and C<sub>10</sub> acids and some branched acids (Breusch & Keshin—*Arch. Biochem.* 18, 305), stearolic acid (Adkins & Burks—*Org. Syntheses* 27, 76), margaric acid (Prostenik—*Arkiv Kemi* 18, 1), several unsaturated fatty acids from alkyl acetylenes (Ahmad & Strong—*J. Am. Chem. Soc.* 70, 1699), and palmitic acid and tripalmitin labeled with C<sup>14</sup> (Dauben—*Ibid.*, 1376).

Fatty alcohols which are used in cosmetics as emulsifiers and intermediates for preparation of special detergents and other compounds were principally obtained by the reduction of fats and fatty acids. Reviews on the preparation and application of these were written by Bert (*Soap Perfumery & Cosmetics* 21, 48), and Martinenghi (*Olearia* 1947, 311). In a method for manufacture of lauric alcohol, coconut butter was hydrogenated at 200 kg. pressure and 300°C. with copper-chromium catalyst and the product was segregated from the mixture (Willemart *et al.*—*Oleagineux* 3, 68). Komori (*J. Soc. Chem. Ind. Japan* 44, 740) used similar conditions except that his catalyst of mixed metals was mostly iron, and he obtained reduction of the fatty acids to alcohols without saturating the double bonds. Moretti (*Compt. rend.* 226, 188) using Raney nickel as the catalyst demonstrated that reduction can continue through aldehyde, alcohol, and finally to hydrocarbon and carbon dioxide. A modification of the sodium process for reducing fatty acids into alcohols dealt with the introduction of ammonium chloride or carbon dioxide during the process to prevent the sodium from combining with the alcohol (Anon.—*Bull. mens. ITERG* 1947, No. 9, 3). Yields were raised to 94-8%, but 20-40% higher than theoretical amounts of sodium were required as compared to an excess of 5% in the usual process.

In regions where there is a lack of motor fuel, oleaginous material is sometimes submitted to pyrolysis for the manufacture of hydrocarbons suitable for internal combustion engines. The new publications on this described methods and yields obtained. Mandekar *et al.* (*J. Indian Chem. Soc. Ind. & News Ed.* 9, 110; 10, 1) used a pressure of 45 lb. per sq. in. and a temperature of 326-397°C. and obtained the following motor fuel yields from the oils given: coconut 46.2, sesame 41.4, cottonseed 37.1, and castor 50.0%. Working with the entire palm fruit, Francois (*Oleagineux* 2, 304; 3, 602) demonstrated that a pyrolysis process could yield: hydrocarbons (motor fuel), other combustible material, ash (fertilizer), ammonia, fuel vapors, and active carbon.

A new method for making ethyl esters of fatty acids comprised adding together ether solutions of acid chlorides and alcohol, respectively, in the presence of magnesium ribbon (Paquot & Bouquet—*Bull. soc. chim. France* 1947, 321). Yields were better than 90%, and the authors suggested that magnesium reacted in the complex by a mechanism similar to that of Grignard compounds. Beta-chloro fatty acid esters were prepared for x-ray study of their structure (Rodier—*Bull. soc. chim. France* 1948, 637). Twenty-

six aromatic compounds were compared in the synthesis of arylstearic acid and aryloleic acid by the Friedel-Craft's reaction, mainly to study this type reaction with fatty acids (Stirton *et al.*—*J. Am. Oil Chem. Soc.* 25, 365). Yields and properties were recorded. Teeter (*Ibid.* 25, 243) studied the behavior of fat in the Ziegler reaction, i.e., the hydrogen atom on a methylene group adjacent to a double bond was easily replaced by bromine by means of N-bromo-succinimide. The brominated methyl esters of soybean oil contained some dimer-like substance. Fatty acid esters of methyl glucosides were prepared by the alcoholysis reaction, and the effect of method and catalyst on yields, and the properties of the products were recorded (Wolff & Hill—*Ibid.* 258). Dihydro-hydrocarpoyl and dehydrochaulmoogroyl chlorides were reacted with nitrobenzene to give compounds which were suggested for use as antituberculosis drugs (Buu-Höi & Cagniant—*Rec. trav. chim.* 67, 53).

Reutenauer *et al.* (*Bull. mens ITCG* 1947, No. 11, 32; 1948, No. 1, 32) wrote brief accounts on experimental preparation of  $\alpha$ -chlorinated fatty acids and nitriles. The former was best prepared by passing chlorine at 100°C. in carbon tetrachloride solution of the fat containing four per cent phosphorus as a catalyst. The nitriles were best prepared in sunlight and at about 50°C. Kaplan's (*U. S.* 2,444,828) method for nitriles comprised heating fatty acids or fats with cyanuric acid at 250°C. Potts (*U. S.* 2,448,275) designed equipment to react ammonia vapor and fatty acids for the preparation of nitriles. Stearic acid substituted on the ninth and tenth carbon atoms by a hydroxyl group and a substituted for unsubstituted amino group was synthesized for use as an anesthetic and as an intermediate for organic synthesis (Swern & Findley—*U. S.* 2,445,892). In demonstrating the acylation of aliphatic amine with the corresponding amide, MacGregor & Ward (*J. Soc. Chem. Ind.* 66, 344) used some fatty acid amines in exemplifying the reaction. The dodecylamine salt of 2-mercaptobenzothiazole was useful for mothproofing and as a fungicide (Minich—*U. S.* 2,437,170).

Commercial products were prepared from fat constituents, other than glycerides. For example, Johnson (*Chem. Inds.* 62, 922) describes how cholesterol is now derived from wool fat. Some cholesterol products were converted to 7-dehydro-cholesterol to serve therapeutically as vitamin D (Callan—*U. S.* 2,436,195). Several cholesteryl quaternary salts were prepared for the purpose of learning more about the structure of these types of compounds (Dodson & Subluskey—*J. Am. Chem. Soc.* 70, 1176). Tocopherol, vitamin E material, was recovered from fat deodorization sludge (Embree & Kuhrt—*U. S.* 2,454,692). Suggestions were also made on recovering gossypol from cottonseed pigment glands (Castillon *et al.*—*J. Am. Oil Chem. Soc.* 25, 233).

INCENDIARY FUELS, RUST PROOFERS, AND WAXES. Incendiary fuels are of interest to fatty oil chemists because they are based on inflammable liquids thickened with aluminum soaps and stearic acid. Formulas for such material adapted for specific uses were issued by Cawley *et al.* (*J. Inst. Petroleum* 33, 649; 34, 90) and Rueggerberg (*J. Phys. & Colloid Chem.* 52, 1444). Methods for testing these were devised by Finkelstein (*Ibid.* 1460). The evaluation and

characterization were by means of a torsionmeter which gave a measure of the elasticity and consistency.

Rust-preventive oils are usually composed of mineral oil containing some polar molecules; the latter in many cases were fat derivatives. A treatise on the insight to the physical action of such compounds dealt principally with the ability of compounds to form oriented multimolecular film layers on the metals (Barnum *et al.*—*Corrosion* 4, 423). Two newly patented rust proofing agents were mineral oil compositions containing partial fatty acid or fatty alcohol esters (Fuller *et al.*—*U. S.* 2,443,578-9). An oil that would penetrate rusty screw threads was a mixture of acetic acid and castor oil (Vuyk—*U. S.* 2,429,735).

Synthetic waxes were prepared by esterifying special mixtures of pentaerythritol, fatty acids, and maleic acid (Burrell *et al.*—*U. S.* 2,427,255), and by condensing aromatic amines with fatty acids (Koray Ltd.—*Brit.* 577,515). The physical properties of hydrocarbon waxes were modified with metallic soaps.

LUBRICANTS. The reviews on metal soaps treated principally their use for lubricating grease manufacture (Lower—*Ind. Chem.* 23, 645; Elliott—*Inst. Spokesman Natl. Lubricating Grease Inst.* 11, No. 10, 12; Loury—*Oleagineux* 3, 136). A patented metal soap product comprised those soaps made from the final and first distillation fractions of tall oil (Bergström—*Swed.* 120,174). Metallic soap products of unsaturated fatty acids were stabilized against oxidative decomposition by small amounts of aluminum salt of  $\alpha$ -(anilino hydroxy) stearic acid.

A group of analytical procedures for grease contained standard Am. Soc. Testing Materials Methods and modifications of the same on fillers, soap, glycerol, alkali, lithium soaps, etc. (Barnett *et al.*—*A.S.T.M. Proc.* 46, 1560). A new consistency tester for grease mechanically worked the lubricating grease and measured its flow characteristics during the operation (McKee & White—*A.S.T.M. Bull.* 153, 90). Grease penetration data obtained from the A.S.T.M. grease penetrometer with cone tips of varying dimensions were recorded to serve as a basis for design of the tips (Brunstrum & Weitkamp—*Ibid.* 149, 48). The work served to establish tolerances for the standard instrument.

Metallic soaps were studied to determine their chemical, physical, and colloidal structure. Tests in which several aluminum soaps obtained by aqueous precipitation were extracted by organic solvents suggested that most of the original precipitates were aluminum di-soaps (Smith *et al.*—*J. Am. Chem. Soc.* 70, 1053). Gallay & Puddington (*Can. J. Res.* 26B, 155) with the same tests and titration tests on aluminum stearate postulated that this existed only as the mono-soap, and that additional stearic acid was only absorbed on the aluminum monostearate. Coe *et al.* (*J. Colloid Sci.* 3, 293) interpreted similar tests as follows: (a) firmly bound fatty acid, resistant to solvent, amounted to two moles per gram atom of aluminum, producing the distearate; (b) loosely bound or sorbed fatty acid amounted to 0.6 mole per gram atom of metal; and (c) free fatty acid dissolves in the soap to form solutions of concentrations up to saturated solutions. During extraction, the soap if moist tended to hydrolyze, thus giving false indication that the soap was lower in acid than the distearate. McBain *et al.* (*Trans. Faraday Soc.* 42B, 173), Mysels (*J. Colloid Sci.* 2, 375); Shreve

(*Ibid.* 3, 259), and Marsden *et al.* (*J. Am. Oil Chem. Soc.* 25, 454), supported the existence of aluminum disoap, principally with work on the laurates. Extracted aluminum dilaurate was shown by x-rays to exist in crystalline form, and the presence of free fatty acids in the unextracted precipitate was also confirmed by this technic. The presence of moisture was believed to be purely a surface attachment for it had no effect on the x-ray diffraction. Other data developed by this group of investigators characterized the colloidal systems involved in the aluminum soaps-hydrocarbon systems, their structure, mechanical properties, and thermal behavior. These were fundamentally of interest with regard to the use of the products in lubricating greases. For the same purpose Sheffer (*Can. J. Res.* 26B, 481) tabulated and graphically presented the viscosity, molecular weight, and osmotic pressure of benzene solutions of aluminum soaps of the C<sub>10</sub> to C<sub>18</sub> saturated fatty acids. He assumed the structure to be that of high polymers formed by weak bonds. Roberts & Schulman (*Nature* 162, 101) also published work of this sort on the same mixtures and made use of the coordination theory to conclude that aluminum soaps-hydrocarbon gels were large molecules loosely held by hydroxyl groups.

Calcium soap-hydrocarbon systems also received attention in regard to their physical and colloidal aspects. Lawrence (*J. Phys. & Colloid Chem.* 52, 1504) in reviewing the subject gave most attention to factors influencing peptization. In x-ray studies on various forms of anhydrous calcium stearate Vold *et al.* (*J. Colloid Sci.* 3, 339) identified transformations at 65, 86, 123, 150, and 195°C., and melting with decomposition at 350°C. with moisture, a monohydrate occurred that decomposed at 110°C. In cetane, Vold & Vold (*J. Phys. & Colloid Chem.* 52, 1424) found one additional phase of the soap at 130°C. which had no counterpart in the solvent-free system. Mardles' & Clarke's (*Trans. Faraday Soc.* 42B, 295) contributions to grease technology were swelling, surface tension, and adhesion data on the metal soaps, in hydrocarbons, and the effect of moisture and glycerol on the systems. Electron microscope observation on greases indicated that the calcium soaps were 1 $\mu$  long and consisted of fibers coiled in spiral forms or of two twisted together in a ropelike manner (Sprule & Pattended—*Can. J. Res.* 26F, 465). The addition of water to stabilize a dispersion of calcium soaps in grease was found to orientate the soap particles; and the shearing action associated with mixing a grease in its preparation caused the fibers to assume the spiral or twisted form. From similar work Birdsall & Farrington (*J. Phys. & Colloid Chem.* 52, 1415) reported that removal of moisture causes disintegration of the fiber or crystalline structure, and this in turn led to the separation of soap and oil. To preserve fiber structure water had to be present in a molar concentration equal to or greater than that of the soap.

The journal literature contained a contribution on manufacture of calcium soap grease (Baouman—*Industrie Chim.* 34, 211) and one on production of lithium grease (Fisher & Meyers—*Footprints* 19, No. 1, 9). The majority of new contributions on compounding lubricants appeared in patents (Ashburn & Puryear—*U. S.* 2,450,219-22; Beerbower *et al.*—*U. S.* 2,434,539, 2,449,580, 2,455,649; Bell—*U. S.* 2,444,720;

Bergman *et al.*—*U. S.* 2,450,224; Bondi—*U. S.* 2,445,935; Fraser—*U. S.* 2,455,892; Licata—*U. S.* 2,448,720-1; McCarty—*U. S.* 2,457,582; McGrogan—*U. S.* 2,457,586; McNulty & Zimmer—*U. S.* 2,433,861; Merker—*U. S.* 2,456,642; Puryear & Ashburn—*U. S.* 2,450,254-5; Roehner & Murray—*U. S.* 2,441,720; Smith *et al.*—*U. S.* 2,442,828; Thurman—*U. S.* 2,433,636; Zimmer & Morway—*U. S.* 2,436,347).

The so-called lubricant "additives" include many fat derivatives, which were added to lubricants in small amounts for various purposes, such as stabilizers, pour point depressants, viscosity modifiers, etc. General communications on this subject were prepared by Kaufman (*Inst. Spokesman* 11, No. 5, 4) and Yamaguchi (*Rpt. Aeronaut. Res. Inst. Tokyo Imp. Univ. No. 304*, 89). Krein *et al.* (*Neftyanoe Khoz.* 26, No. 6, 43) evaluated the generally known and Russian commercial detergent additives in regard to their oil dispersant properties. The products ranked as follows: Santolube 110, Lubri-Zol 738, and Cobalt naphthenate were best; Santolube 303A, Nox, Paranox 56A, and Voltol were intermediate; and organic derivatives of phosphorus and sulfur, and some Russian trade name products were poorest. Hattiangdi (*J. Phys. & Colloid Chem.* 52, 1481) recorded the effects of many additives on the properties of soap-hydrocarbon systems. Normal alcohols, chlorobenzene, bromobenzene, phenol, *o*- and *p*-cresols, methyl ethyl ether, anisole, phenetole, methyl ethyl ketone, and benzyl alcohol accelerated the synergetic process of sodium oleate-pinene gels, whereas isoalcohols and *m*-cresol had retarding effects. Alcohols increased opacity in the order of their increasing molecular weight. The per cent increase or decrease in setting time was related linearly to the atomic weights of the cations of the added soaps, and decreased with increasing atomic weight.

Among the newly patented lubricant additives the detergents were 2-stearoyl-4-amyphenol monosulfide (Cook & Thomas—*U. S.* 2,445,939), metallic derivatives of the thio ethers and disulfides derived from *o*-hydroxy derivatives of stearophenone laurophenone, palmitophenone, etc. (Evans & Elliott—*Brit.* 596,150), and amino fatty acid soaps (Bray & Russell—*U. S.* 2,435,734). The new rust inhibitor additives were sorbitan monooleate (Duncan—*U. S.* 2,434,490), reaction product of maleic acid and fatty alcohols (Snyder *et al.*—*U. S.* 2,436,272), and condensation products of dicarboxylic acids or anhydrides and unsaturated fatty acids or alcohols (Blair—*U. S.* 2,444,328). The new viscosity modifiers were certain phenol-formaldehyde resins (Mikeska—*U. S.* 2,429,479), glycol esters of dimerized fatty acids (Young & Sparks—*U. S.* 2,435,619), polymers of allyl laurate (Larsen & Marple—*U. S.* 2,441,023) and copolymers of isobutylene and butadiene (Hineline—*U. S.* 2,446,927). Chlorinated fatty acids were used as pour point depressors (Ridbo Labs. Inc.—*Brit.* 601,114). Sulfurized fat derivatives were patented as additives to improve film strength, oiliness, stability, and for other reasons (Lincoln *et al.* *U. S.* 2,433,853, 2,448,037; Musselman—*U. S.* 2,439,819; Musselman & Lankelma—*U. S.* 2,444,947; Reiff & Andress—*U. S.* 2,438,876). Lubricating greases containing petroleum sulfonates as rust inhibitors regained their water repellency by the addition of metal salts of 12-hydroxystearic acid (Butcosk—*U. S.* 2,445,936). Silicones when used in grease making

required special compounding and treatment to stabilize them within the finished product (Zimmer & Duncan—*U. S. 2,444,970*; Hain & Zisman—*U. S. 2,446,177*). Tetramethyldiaminodiphenylmethane was added to greases to modify the consistency (Detwiller—*U. S. 2,443,026*). Steam-cylinder oil was improved by the presence of a small amount of monoöleoyl malate (Salz & Marley—*U. S. 2,443,585*).

Newly reported lubricant materials were fatty diesters of azelaic acid (Zisman & Hain—*U. S. 2,448,567*), fatty acid esters of polyoxyalkylene diols (Fife & Toussaint—*U. S. 2,457,139*), and a polymerized olive oil product which was called "volatolyzed olive oil" (Vian *et al.*—*Combustibles* 5, No. 25/26, 3; 6, No. 33/34, 55).

The new metal cutting lubricants generally contained mineral oil, fats, certain fatty acid soaps, and a detergent (Carter & Coppock—*U. S. 2,433,646*; Showalter—*U. S. 2,438,461*; Myers & Muckerheide—*U. S. 2,443,833*; Lemmon & Schnuessler—*U. S. 2,436,046*; Larson—*Iron Steel Eng.* 24, No. 11, 73; Kadmer—*Petroleum Refiner* 25, No. 7, 351). A wire drawing lubricant contained zinc sulfide and calcium stearate—(Elder—*Can. 449,783*). Palm oil containing alkali salts of phosphoric and boric acids was patented for lubrication of steel during cold reduction (Hoelscher—*U. S. 2,430,400*).

Incomplete polyhydroxy alcohol esters of fatty acids and sulfonates of these were patented as tire cord lubricants (Standley & McLellan—*U. S. 2,436,978*).

### Deterioration

REVIEWS. The most comprehensive new review on fat spoilage was written from 726 references and included information on all aspects and their significance to economy and life (Schmalfuss—*Milchwirtschaft* 2, 335). Another general review treated methods of testing for spoilage and stability, with special reference to protecting fatty food by eliminating chemically active light rays and by refrigeration (Lunborg—*Festskr. J. Arvid Hedvall 1948*, 361). Two reviews treated antioxidants from the standpoint of natural and synthetic materials (Roy—*Indian Soap J.* 11, 203) and evaluation of antioxidants and synergists (McConnell—*Am. Perfumer* 50, 346). A paper on the stabilization of olive oil dealt with processing to preserve natural inhibitors and some information on suitable antioxidants (Frenquelli—*Olearia* 2, 675).

At various times during the year a card catalog of abstracts of the literature of antioxidants, originally published in 1936, was supplemented with abstracts of new literature (Anon.—*Quartermaster Food & Container Inst. Armed Forces* 600).

METHODS OF TESTING. Bates & Ast (*J. Am. Oil Chem. Soc.* 25, 42) suggested improvements in the design of the Swift Stability apparatus, which included steam heat, improved air regulation and distribution, and safety valves to eliminate leaks in the vapor condensing system.

Erdmann & Seelich (*Z. Anal. Chem.* 128, 303) proposed that peroxides be determined in fats by the oxidation of ferrous sulfate, inasmuch as the usual iodometric determination is complicated by the reaction of iodine with unsaturated, keto, diketo, and oxy compounds. In the proposed method ferrous sulfate was oxidized, and ferric iron determined colorimetrically with ammonium thiocyanate. Another color-

metric method for deterioration of fats was based on the production of yellow hexavalent titanium from titanium sulfate, under the influence of the peroxides formed in rancid fats (Staub—*Mitt. Gebiete Lebensm. Hyg.* 38, 292). Since animal fats on exposure to light gave a positive reaction much sooner than vegetable fat, the author suggested that this difference could be useful as a means of distinction.

MECHANISM OF DETERIORATION. Support has been given to the postulate of Farmer and of Boland and Koch, who proposed that during oxidation the initial attack on unsaturated fats was at a carbon in an  $\alpha$ -position to an ethylenic carbon and that the unsaturated bond was thus not the site of the initial addition of oxygen. Some of this work has already been cited in describing the mechanism of bodying of drying oils in the third section of this review. In addition, the observation of Chipault & Lundberg (1946-47, *Ann. Rept. Hormel Inst.* 9) supported the above theory. They found that in the oxidation of linoleates, all the stable peroxides formed in the earlier stages had an absorption at  $2325\text{\AA}$ , which indicated that conjugated diene groups were still present. This was also in harmony with Bergstrom's observation that hydrogenation of oxidized linoleate yielded 9- and 13-hydroxy stearates but no 11-hydroxy stearate. The authors suggested that some transitory intermediate was first formed, which became relatively stable 9- and 13-hydroperoxides containing diene systems. These might give rise to a conjugated diene ketone which could be converted to a triene system upon treatment with alkali. Dugan *et al.* (*J. Am. Oil Chem. Soc.* 25, 153) separated the oxidized products of methyl linoleate chromatographically and found that the conjugated constituents were oxidized first, and these linoleate peroxides still contained the diene system. Other work on oxidation of linoleates showed that positive and negative catalysts did not alter the composition of the products, but appeared primarily to affect the kinetics of the process (Lundberg—*Biol. Antioxidants, Trans. 1st Conf.* 1946, 26) and that the primary products of oxidation by autoxidation and by enzymes were the same (Holman—*Ibid.* 37).

Conversely, work on oleates indicated that the oxidative attack was at the double bond. Swift *et al.* (*J. Am. Oil Chem. Soc.* 25, 39, 52) presented evidence for this based on identification of the hydroperoxido compounds formed in the initial products, isolation of 9,10-dihydroxystearic acid, and identification of the aldehydes formed on further decomposition. In similar work Skellon (*J. Chem. Soc.* 1948, 343) suggested that from methyl linoleate a composition of  $C_{19}H_{30}O_6$  was formed.

Data on chemical oxidation of saturated acids were recorded by Paquot and de Goursac (*Compt. rend.* 226, 258; *Oleagineux* 2, 564). They concluded that  $\beta$ -oxidation principally occurred to produce progressively lower fatty acids, and in minor proportion stable lactones were formed by  $\gamma$ - or  $\delta$ -oxidation.

PHYSIOLOGY AND RANCIDITY. The fact that rancid or oxidized dietary fat decreased growth and fertility of animals was well known. However, according to Kennelly & Quackenbush (*Biol. Antioxidants Trans. 1st Conf.* 1946, 56), no such effects were observed when the oxidized fats were fed to rats three times weekly by dropper. This was interpreted to indicate that the oxidized fat destroyed some essential com-



ponent of the nonlipid portion of the diet. Kraybill & Nilson (*Com. Fisheries Res.* 9, No. 9, 8; No. 10, 7) found that the lipids of experimentally spoiled fish meal were not toxic to rats.

The depression of growth rate of rats whose dietary fat was rancid was also confirmed by Barnes (*Biol. Antioxidants, Trans. 1st Conf. 1946*, 49). He also showed that the stability of rat body fat was unaffected by feeding antioxidants, while very unsaturated dietary fat decreased stability and more saturated fats increased body fat stability. However, the stability of body fat of young rats on a vitamin E-deficient diet could be related to supplementation of the diet with tocopherols. This last observation was confirmed by Major & Watts (*J. Nutr.* 35, 103) in work with rabbits. Protection of the body fats occurred with high levels of tocopherols on experimental diets, but on ordinary ration the addition of tocopherol gave no protection.

In a preliminary report on fat rancidity in eviscerated poultry, Kummerow *et al.* (*Poultry Sci.* 27, 689) recorded the effect of diet on the characteristics of body fats of immature turkeys.

**STABILITY OF VARIOUS PRODUCTS.** In work on the keeping qualities of commercially produced armyration biscuits, Horne *et al.* (*J. Am. Oil Chem. Soc.* 25, 314, 389) observed a nearly direct relationship between the stability of soybean-oil shortening (Swift Stability Test) and the storage life of the corresponding biscuits. A 100-hour stability test shortening produced biscuits which could be stored up to 12 months at 100°F. The addition of N.D.G.A. to lard did not result in a significant increase in biscuit stability. Another test evaluated the suitability of stored commercial doughnut cooking fats (Overman *et al.*—*Ibid.* 434). In general, the desirability of the fat for doughnuts decreased after 2.5 years of commercial cold storage.

Experimental deodorization tests revealed that stabilities of the oils increased rapidly during the initial part of the deodorization, possibly because of destruction of prooxidants (Baldwin—*Ibid.* 33).

Chevallier *et al.* (*Compt. rend.* 226, 2098) found that calciferol gave marked acceleration of oxidation of fats, vitamin A a slight acceleration, folliculin a marked decrease of speed and dihydrofolliculin a slight decrease. Catalase inhibited oxidation; but, in the presence of manganese the inhibition was changed into an acceleration (Kiermeier—*Biochem. Z.* 318, 256).

Margarines stored for 538 days at 5°F. and -10°F. maintained their edible quality (Kiess *et al.*—*Food Inds.* 20, 716). Those stored at 28-45°F. were not marketable after this extended storage.

The deterioration of lipids in dairy products was discussed by Krukovsky *et al.* (*J. Dairy Sci.* 31, 961) from the standpoint of effect of pasteurization temperature, type of product, storage conditions, and exposure to light. Greenbank & Wright (*Ibid.* 698), in work on the preparation of dried milk, reported that heating deaerated milk preserved the substance which protected the fat more than did the same heat treatment in contact with air. Mulder *et al.* (*Netherlands Milk, Dairy J.* 1, 219, 225) observed that prooxidant metals considered to be responsible for the metallic taste in butter did not cause this off flavor when the butter was made from sweet cream. Otherwise, water-soluble antioxidants and pasteurization

inhibited the defect. Van der Waarden (*Research in Holland 1947*, 155) associated this defect of butter with the binding of the metal to phosphatides. Grant *et al.* (*Can. J. Res.* 26F, 105) reported data on changes in the characteristics and organoleptic quality of samples of butter stored in wrappers and cans at temperatures between 30 and 90°F. In general, decomposition of the serum and flavor deterioration occurred before changes appeared in the fat fraction.

Margarine containing five per cent sesame oil and fortified with vitamin A decreased in vitamin content on exposure to air more rapidly than margarine containing no sesame oil (Basu & Ray—*Sci. and Culture* 13, 73). The vitamin A content of oils from stored whale liver decreased more rapidly than that from crude oil extracted from fresh livers (Mori & Asakawa—*J. Agr. Chem. Soc. Japan* 17, 529). Similar work by Swain (*Fisheries Res. Board Can., Prog. Repts. Pacific Stas.* 73, 48) with dogfish livers indicated that storage of livers decreased the vitamin A content of the oil contained therein. Heimann (*Deut. Lebensm.-Rundschau* 43, 35) prepared a general discussion of the oxidative spoilage of fish liver oils, emphasizing the effect of various metals and of careless manufacture.

**ANTIOXIDANTS.** Experimental evaluation of known antioxidants was the text of several investigations. In work on nordihydroguaiaretic acid (N.D.G.A.) in cod-liver oil, best protection was afforded by 0.05% N.D.G.A. with 0.01% ascorbyl palmitate (Gisvold *et al.*—*J. Am. Pharm. Assoc. Sci. Ed.* 37, 232). For milk 0.0075% N.D.G.A. prevented development of oxidized flavor during five days' storage at 40°F. in the presence of 0.3 p.p.m. of added copper; in absence of copper, 0.00125-0.0075% N.D.G.A. retarded destruction of vitamin C (Stull *et al.*—*J. Dairy Sci.* 31, 449). Effects of packaging, pyrogallol, gallic acid, pyrocatechol, hydroquinol, oxalic acid,  $\alpha$ -tocopherol, and ascorbic acid for the protection of butter were evaluated by Mukherjee & Goswami (*J. Indian Chem. Soc.* 24, 239). In this work it was found that passing hydrogen into butter retarded hydrolytic and oxidative rancidity. Among natural dyes, kamala and tumeric had antioxidant properties, while annatto was prooxidant (Ramaswamy & Banerjee—*Ann. Biochem & Exptl. Med. India* 8, 55). Likewise, among carcinogenic aminoazo dyes some inhibited and some accelerated oxidation (Rusch & Miller—*Cancer Res.* 7, 730). Colamine, in amounts of 0.01-0.05 ml. per 30 g. fat checked the autoxidation of animal and plant fat and vitamin A; but in the presence of copper, colamine enhanced oxidation over that given by copper alone (Bunyatyan & Kamalyan—*Biokimiya* 13, 109). Both spontaneous and oxidase oxidation of fats was said to be inhibited by  $\beta$ -carotene (Herisset—*Bull. soc. chim. biol.* 30, 187). The protection of coconut oil in the kernel was believed to originate from reducing sugars and albumin (Roy *et al.*—*J. Indian Chem. Soc. Ind. & News Ed.* 9, 129). Antioxidant materials other than tocopherol were isolated from palm oil (Dubouloz—*Oleagineux* 2, 242). The effectivenesses of tocopherols were rated in the following order of increasing antioxidant potency:  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -tocopherol (Griewahn & Daubert—*J. Am. Oil Chem. Soc.* 25, 26). Rancidity in mackerel fillets was deterred by dips in cottonseed oil containing any of many antioxidants, and a second dip in Irish moss

extract containing ascorbic acid further enhanced protection in some cases (Stoloff *et al.*—*Food Inds.* 20, 1130).

Some of the newly patented antioxidants were an ethylene dichloride extract of soap stock (Buxton—*U. S.* 2,433,593), hydrogenated deodorizer scum (Hickman—*U. S.* 2,440,606), a mixture of N.D.G.A. and phosphoric acid (Kraybill & Beadle—*U. S.* 2,451,748), a mixture of phospholipids and fatty acid esters of ascorbic acid (Riemenschneider & Turer—*U. S.* 2,440,383), natural vitamins containing added ammonia (Buxton—*U. S.* 2,434,790; OPCO Chem. Co.—*Brit.* 591,511), divanillal acetone or isopropanol (Jarowski & Stiller—*U. S.* 2,455,254), diisoeugenol (Jarowski—*U. S.* 2,455,256), extracts from the leaves and stems of *Larrea divaricata* (Shipner—*U. S.* 2,457,741), polycyclic aromatic hydrocarbons of at least four condensed rings combined in the form of a pyrene nucleus (Evans *et al.*—*Brit.* 572,458), a mixture of an aliphatic hydroxy polybasic acid and an aromatic  $\rho$ -hydroxy monobasic acid (Penn—*U. S.* 2,444,307), hydrocaffeic acid and derivatives thereof (Elder & Levenson—*U. S.* 2,437,731), hydroxylamine (Scherr—*U. S.* 2,441,547), 5-pentadecyl resorcinol (Barnes—*U. S.* 2,448,207), organic sulfur compounds containing unsubstituted amino groups capable of enolizing to furnish sulfhydryl groups (Gyorgy *et al.*—*U. S.* 2,456,937) and biguanide  $\rho$ -tert-amyphenyl phosphates (Cook—*Brit.* 591,836). Lecithin was stabilized against rancidity by alkaline salts (Fitzpatrick—*U. S.* 2,444,984). Literature on the extraction of natural antioxidants included the concentration of N.D.G.A. (Gisvold—*U. S.* 2,444,346) and antioxidants from rice bran (Jarowski & Stiller—*U. S.* 2,455,255; Patterson & Williamson—*U. S.* 2,455,083),

and peanuts (Banerji & Mukherji—*Indian Soap J.* 13, 6). Vitamin A was rendered more stable by converting it into an ester (Embree & Shantz—*U. S.* 2,434,687; Basu & Sen Gupta—*J. Am. Chem. Soc.* 70, 413). Antioxidants were added to marine vitamin oils in order to preserve the therapeutic properties during their concentration (Buxton—*U. S.* 2,434,788-90). Prooxidant metals were precipitated from oils with  $\beta$ -mercaptopropionic compounds (Gribbins—*U. S.* 2,457,227).

**FLAVOR REVERSION.** A method for testing the reversion properties of hydrogenated soybean-oil shortenings was based on subjective organoleptic tests on samples that were heated to 140°C., rapidly cooled to  $\pm 5^\circ\text{C}$ . and rewarmed to 80°C. (Handschumaker—*J. Am. Oil Chem. Soc.* 25, 54). Semi-quantitative values were realized in the test when samples were compared with blends made from hydrogenated soybean and cottonseed oils. Moyer & Marmor (*U. S.* 2,454,937) claimed that materials that cause reversion in soybean oils could be removed by treatment of the oil with magnesium oxide which had previously been heated to 350-500°C.

Dutton, Schwab, and others (*J. Am. Oil Chem. Soc.* 25, 57, 385) produced evidence that the protection accorded to the flavor of soybean oil by organic acids and polyalcohols was due to their role as metal scavengers, for this was compatible with their known metal complexing properties. In the course of this work a four-sample glass laboratory oil deodorizer was designed.

Martin *et al.* (*Ibid.* 113) qualitatively analyzed the volatile materials from reverted soybean oil. They believed the flavor was due in part to carbonyl compounds, one of which was identified to be  $\alpha$ -heptenal.

## The Adsorptive Capacity of Cotton for Sodium Oleate

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THE retention of soaps by fabrics during washing and rinsing operations has long been of practical and theoretical interest to both the user and manufacturer of detergents. While the presence of a small amount of fatty matter is desirable as a fiber lubricant, the accumulation of lime soaps, especially in so-called "hard water" districts, makes white fabrics dingy and colors dull.

Several investigators (3, 6, 7, 9) have studied the adsorption of various detergents on wool, silk, and to a lesser extent on cotton, but insofar as the latter fiber is concerned, there appears to be little agreement regarding the nature of the adsorption mechanism or the character of the material adsorbed.

Thus Neville and Harris (9) have reported that while wool and silk exhibit a pronounced selective adsorption of alkali from sodium oleate solutions, cotton adsorbs equal and relatively small quantities of both alkali and fatty acid.

Colt and Snell (3), on the other hand, working with an 80% tallow to 20% coconut oil soap, found

that 19.5% of the total soap present in a 0.10% solution was adsorbed on cotton and that the amount was "somewhat greater at lower concentrations than at higher concentrations which is as should be expected." They also noted that the solutions in contact with the cloth decreased in pH: evidence of selective adsorption of alkali.

No one apparently has investigated the possible conversion of the adsorbed materials to lime soap in a hard water rinse or the effects which such conversion has on further adsorption. Since it was believed that the adsorption of sodium soaps and the "in situ" conversion of these to lime soaps during rinsing is largely responsible for the accumulation of the latter material, a further study of the mechanism by which a detergent is attracted to and maintained upon the fiber surface seemed desirable.

### Materials and Methods

The sodium oleate employed for this investigation was prepared by saponifying the fractionated methyl ester with NaOH. The product was thoroughly dried and stored in tightly stoppered bottles. Only after

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