

Report of the Literature Review Committee *

22nd Annual Review of the Literature on Fats, Oils, and Detergents. I.

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Introduction

ECONOMIC INFORMATION. The production data forecast for year beginning Oct. 1955, preliminary estimate for year beginning Oct. 1954, and data for the year previous (*Fats & Oils Situation 176*, 26PP) on fats and oils are:

| | For years beginning | | |
|--|---------------------|----------------|----------------|
| | Oct. 1 1953 | Oct. 1 1954 | Oct. 1 1955 |
| | mil. lbs. | mil. lbs. | mil. lbs. |
| Butter (actual weight)..... | 1,677 | 1,576 | 1,600 |
| Lard and pork fat..... | 2,208 | 2,588 | 2,800 |
| Edible beef fat..... | 255 | 269 | 270 |
| Edible vegetable oils (plus oil equiv. of seed exported)..... | 5,272 | 5,378 | 6,000 |
| Soap fats (inedible animal fats and marine oils)..... | 2,822 | 2,996 | 3,095 |
| Drying oils (linseed, tung, and castor oils)..... | 801 | 740 | 703 |
| Others (neats' foot, wool grease, fish liver oil, etc.)..... | 31 | 42 | 40 |
| TOTALS..... | 13,066 | 13,589 | 14,508 |

The figures indicate that a record supply of food fats will appear on the market in 1956. The consumption is expected to increase only in line with the population increase. However, exports of edible oils, not including soybeans, may increase 20% over the last fiscal year because of poor sunflower crop in Argentina, poor olive crop in the Mediterranean, and a lower price of lard encouraging greater export of this product. Butter export last year was four times as much as a year earlier because of various government programs, including relief. Such exports should continue at the same level. A good summary of the oils and fats situation and future outlook was prepared by Prichard (*Soap & Chem. Specialties 31*, No. 12, 54), who has analyzed the effect of production, price support, and export, and who favors the Government's method of handling the situation because they seem to be in the best position to develop foreign markets. Another communication on fats and oils outlook appeared earlier hence it pertained to marketing during the last half of the year 1955 (Andreas—*Ibid.* No. 6, 46).

The prices of fats and oils during 1955 were generally a little lower than in 1954 because of a reduction in support price by the Government. However, prices for the drying oils, linseed and tung oils, were higher principally because of greater demand for the former and a poor tung nut crop.

In the soap versus synthetic detergent industries, the growth of detergent sales has continued but at a greatly reduced pace and it has been predicted that in about 1960 it will capture 70% of the total market. At the middle of the year, 1955, the synthetic detergents were supplying 62.5% of the market for soaps and detergents (Assoc. Am. Soap & Glycerine Producers—*Chem. Eng. News 33*, 3710). Discussions on the trend in the industry were written by Macon (*Soap & Chem. Specialties 31*, No. 3, 41), and Price (*Chem. Week 77*, No. 17, 41). The status of the soap and detergent industry of Germany was reviewed by Harz (*Fette u. Seifen 57*, 763).

Comprehensive information has been published on many sources of oils to attract commercial interest to them. The oils treated in this manner were from: acorn (DeCastro—*Univ. Microfilm Ann Arbor Mich.* No. 10, 424, 16 pp.), babassu palm (Weghofer—*Fette u. Seifen 57*, 714), cacao bean shell (Kato & Tsuchiya—*J. Chem. Soc. Japan, Ind. Sect.* 57, 758), cottonseed of Pakistan (Wahhab & Hussain—*Agr. Pakistan 3*, 35), grape seed (Ekster & Osipchuk—*Vinodelic i Vinogradstvo 13*, No. 7, 21), fats and *Bassia* and *Shorea* species (*Illipe*) (Kaufmann & Thieme—*Fette u. Seifen 56*, 1001), kamala seed (Aggarwal—*J. Sci. Food Agr.* 6, 364), mandarin orange seed (Pruthi & Lal—*Bull. Central Food Tech. Res. Inst. Mysore 3*, 301), mbocaya palm (Markley—*J. Am. Oil Chemists' Soc.* 32,

405), Argentine blue poppyseed (Cattaneo *et al.*—*Anales direc. nacl. quim. Buenos Aires 6*, No. 12, 78), safflower (Knowles—*Econ. Botany 9*, 273), Indian teaseed (Chakrabarty—*Sci. & Culture, India 20*, 186), genus *Aleuritis* in Florida (Dickey *et al.*—*Univ. Florida Agr. Expt. Sta. Bull. No. 503*, 40 pp.), wool fat (Janecke—*Deut. Apoth. Ztg.* 95, 79; Dietrich—*Industrie parfum 9*, 375; Kawahara—*J. Japan Oil Chemists Soc.* 4, 134), ucuuba tree seed (Pinto—*Rev. quim. Ind. Rio de Janeiro 32*, No. 265, 12), *Crambe abyssinica* seed (Krzyszanski—*Roczniki Nauk Rolniczych Ser. 69*, 341) and seeds and bark of *Jatropha glandulifera* (Sheth & Desai—*J. Indiana Chem. Soc. Ind. News Ed.* 17, 197).

Some communications were reviews or general discussions that could not be classified in any one particular division which follow so are cited hereunder. These were on: the use of pilu oil as a substitute for coconut oil (Aggarwal—*Oils & Oilseeds, J., India 7*, No. 4, 5), research on peanut products (Basu—*Bengal Immunity Res. Inst. 1955*), commercial stearic acid in the cosmetic industry (Tillotson—*Am. Perfumer. Essent. Oil Rev.* 66, No. 2, 23), new methods in processing oil and fats (Kaufmann—*Olii minerali, grassi e saponi, colori e vernici 32*, 29; Schwitzer—*Chem. & Processing Eng.* 35, 204, 241), fats and oils of Japan and some undeveloped oil resources (Takei—*J. Chem. Soc. Japan, Ind. Sect.* 58, 235), fat industry in French over-seas territories (Anon—*Rev. franc. corps gras 2*,

TABLE OF CONTENTS

A. INTRODUCTION

Economic information, competing materials, new comprehensive literature.

B. PRODUCTION PROCESSES

Animal and fish fat production; vegetable oil extraction; byproduct fats; refining, bleaching, and deodorization; byproducts of refining; winterizing, splitting, and fractionating; hardening of oils; trans- and interesterification.

C. PRODUCTS (excepting detergents)

Household fats, emulsifiers and demulsifiers; esters, acids, alcohols, aldehydes, and other derivatives; defoamers, flotation, anticorrosives, drilling muds, quenching oils, water repellants, fire bombs, waxes and miscellaneous products; coatings, resins and plastics; plasticizers; lubrication, textile oiling, and metal working oil.

D. DETERIORATION OF FATTY MATERIALS

Reviews; tests for deterioration, stability and antioxidants; stability of fatty products, antioxidants.

E. NUTRITION AND BIOCHEMISTRY

Reviews, fat nutrition, intestinal absorption, intermediate metabolism, phospholipides, cholesterol, lipides under diseased states, lipides in microbiology and plants.

F. CHARACTERISTICS AND COMPOSITION

General and comprehensive, analysis of fat source, grading and vitamin tests, chemical characteristics, physical properties, detection of adulteration, composition.

G. DETERGENTS

Manufacture, chemical analyses, physical characteristics, performance testing.

* LITERATURE REVIEW COMMITTEE

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660), classification of the vegetable oils from Belgium Congo (Patzsch—*Seifen-Öle-Gette-Wachse* 80, 613, 638, 664, 699; 81, 3). Swedish oil seeds (Troëng—*Kgl. Lantbruksakad. Tidskr.* 94, No. 2 & 3, 125), component acids and glycerides of natural fats (Hilditch—*J. Sci. Food Agr.* 5, 557), and review of work concerning wool wax, human hair wax, South African pilchard oils of *Sterulia foetida* and others by the South African Council for Sci. and Ind. Research (Sutton—*J. Am. Oil Chemists' Soc.* 32, 16).

COMPETING MATERIALS. Information on materials which compete with natural fats and oils appears in sections on products and on detergents. As is evident, petroleum products are competing in detergent uses; organic silicones, silica gels, and resins are being recommended to replace metal soaps in lubricant greases; and various resins, plastics, and latexes are replacing drying oils in protective coatings and floor covering compositions. The new patents and literature from the petroleum industry also illustrate a continued interest in synthesizing fatty materials. Examples of these are: drying oils from petroleum (Block—*U. S.* 2,726,272-4; Albers & Gunzert—*Ger.* 848,815, Cl. 120), oleic acid substitute from paraffin oxidation (Luther & Reibnitz—*Ger.* 767,827, Cl. 23d), edible synthetic fats (Markische Seifen-Ind.—*Ger.* 767,825, Cl. 53h, *Ger.* 767,801, Cl. 23d), fatty acids from olefins (Thieme—*Ger.* 767,841, Cl. 120), and production and separation of fatty acids from paraffins (McLean et al.—*Brit.* 707,153; Wietzel—*Chem. Eng. Sci.* 3, *Spec. Suppl.*, 17; Man'kovskaye et al.—*Masloboino-Zhirovaya Prom* 20, No. 4, 15; Tsykovskii et al.—*Ibid.* No. 3, 17; Runge & Laske—*Fette u. Seifen* 56, 145; MacDonald et al.—*J. Applied Chem.* 5, 536).

It is possible that some time in the future fats may be commercially produced by microbiological means. This is reflected by a demonstration on production of fats from glucose and sucrose by the molds *Aspergillus nidulans*, *Penicillium javanicum*, and *P. spinulosum* (Gad & Walker—*J. Sci. Food Agr.* 5, 339) and by reviews on: microbiological technique for protein and fat synthesis Rieche—*Wiss. Ann.* 3, 705), mechanism of fat formation in *Fusarium lini* (Nord & Coleman—*Congr. intern. biochim. Resumes communs.* 2 congr. Paris 1952, 166), and chemical nature of fatty acids of microbiological origin (Tausig—*Univ. Microfilms Publ.* No. 11610, 144 pp.).

NEW COMPREHENSIVE LITERATURE. The previous review of this series was published in *J. Am. Oil Chemists' Soc.* 32, 255, 319. Several reviews of similar scope, collectively, appeared in *Rept. Progress Applied Chem.* 39, 377, 618. A series of reviews on this year's developments in unit process contained communications on alkylation, amination, esterification, halogenation, hydrogenation, isomerization, nitration, oxidations, polymerization, sulfonation, Friedel-Crafts reaction, paints and plastic, all of which should be of interest to fat and oil chemists (*Ind. Eng. Chem.* 47, Sept. Issue, Part 2). A symposium on applications of ultrasonic energy is also of interest because it contains papers on applications to liquid-liquid extractions, liquid-solid extractions, granular solid fluidization, convective heat transfer, solvation, and others (*Ibid.* 1152). Hutts' (*Nature* 175, 303) proposed classification and nomenclature of lipide should also be of general interest; as are also editorial comment (*Fette u. Seifen* 56, 909) and a communication on international relations in the field of fat and fat products (Kaufman—*Fette u. Seifen* 56, 910).

The new books that came to the reviewers' attention during the year were:

Fats-Oil-Detergent Yearbook 1954, Edited by B. F. Daubert. Interscience Pubs., New York, 1152 pp.

Die Gewinnung von Fetten und fetten Öle. 2nd Ed. By R. Lüde. T. Steinkopff Publ., Dresden, 299 pp.

Tekhnologiya pererabotki Zhirov (Fat Technology). By B. N. Tyukyunnikov et al. Gosudarst Isdatel'stvo Legkoi i Pishchevoi Prom., Moscow, 523 pp.

Khimiya Zhirov (Chemistry of Fats). By A. A. Zinov'ev. Pishchepromizdat., Moscow, 550 pp.

Pererabotka semyan khlopeatneca (Cottonseed processing). B. K. E. Leont'evskii. Pishchepromizdat., Moscow, 115 pp.

The Chemistry of Lipids of Biochemical Significance. By J. A. Lovorn. John Wiley & Sons, New York, 132 pp.

Symposium on Atherosclerosis. By Natl. Acad. Sci., Natl. Res. Council Publ. 338. Washington, D. C. 249 pp.

Principles of Emulsion Technology. By Paul Becher. Reinhold Pub. Corp., New York, 149 pp.

Contribution a l'etude de l'hydrolyse des corps gras, action catalytique de la silice hydratee. By Norber Duffaut. Bière, Bordeaux, 73 pp.

Standard Methods for the Analysis of Oils and Fats. By Soc. Ed. Enseignement Superieur, Paris, 117 pp.

Emulsions, mousses, detersion, les phenomenes des surface. By P. Cor. H. Dunod, Paris, 132 pp.

Savons et detergents. By J. Bergeron. A. Colen, Paris, 199 pp.

Textilhilfsmittel und Waschrohstoffe. By K. Linder. Wissenschaftliche Verlag, Stuttgart, 976 pp.

Moderne Wasch und Reinigungsmittel. Bd. V. Fettsäurekondensationsprodukte und nichtionogene Waschrohstoffe, 62 pp. Bd. VI. Alkylarylsulfosäuren und -sulfonate, 50 pp. By H. Manneck. Fachliteratur-Ermittlungs u. Berichtsdienst, Garmisch-Partenkirchen.

Industrial Detergency. By Wm. W. Niven Jr. Reinhold Pub. Corp. New York, 340 pp.

Chimie et technologie des agents tensio-actifs. By A. M. Schwartz and J. W. Perry. Dunod, Paris, 578 pp.

Series of lectures, equivalent to comprehensive books, have appeared in the journal literature on analytical techniques (*J. Am. Oil Chemists' Soc.* 32, 575), on chemistry, properties and uses of fatty acids (*Proc. Chem. Specialties Mfrs. Assoc. May 1955*, 131), on processing of cottonseeds (*Oil Mill Gaz.* 60, No. 2, 11; No. 3, 14), and of a short course on oil mill operation (*Ibid.* No. 4, 11; No. 5, 9; No. 6, 11). Some of these are available as separate booklets. Another series of papers, which has continued from a year earlier, is on fat and fat products and treats production and properties of all commercial fats and oils (Kaufman & Thieme—*Fette u. Seifen* 56, 1028; 57, 45, 133, 191, 285, 347, 441, 514, 615, 744, 807, 977).

The synthetic detergents of 150 distributors were tabulated, giving trade name, manufacture, class, formula, main use, concentration and some pertinent remarks (McCutcheon—*Soap & Chem. Specialties* 31, No. 7, 50; No. 8, 48; No. 9, 52; No. 10, 48). Similar information also appeared in another publication (Anon.—*Chem. Week* 77, No. 17, 46). These were available also as separate pamphlets.

Production Processes

ANIMAL AND FISH FAT EXTRACTION. The new descriptive communications on rendering processes pertained to a well mechanized batch-lot plant (Anon.—*Nat'l Prov.* 133, No. 13, 12) and to yields, quality and costs on dry versus wet rendering of inedible carcasses (*Die Fleischwirtschaft* 6, 459; 7, 107). Two rendering systems were patented; one is based on liberating fat by subjecting the tissue to repeated intense impacts delivered through a liquid medium (*Brit. Glues & Chem. Ltd.—Brit.* 722,311); the other comprises placing the finely ground tissue in water warmed to above the melting point of fat in a manner that the fat floats and a protein residue, suitable for sausage making, settles to the bottom (Kramer—*U. S.* 2,697,112-13). A Russian continuous renderer based on melting, drying, centrifuging, and cooling stages was investigated with regard to improving the stability of the fat produced (Drozdov & Materanskaya—*Myasnaya Ind. S.S.S.R.* 26, No. 5, 48). Since the drying stage is most detrimental, reducing the time of drying or replacing this stage with a demulsification process is suggested as a means of improvement. Fundamental data, such as the effect of moisture, particle size, miscella concentration, and temperature on extraction efficiency, have been recorded for solvent extraction of cooked meat and fish offal with trichloroethylene (Arnold & Arvidson—*J. Am. Oil Chemists' Soc.* 32, 25, 163). The mechanism of extraction in such systems was believed to be one of surface-washing with some diffusion.

A review on fish oil separation in the German fish-meal industry covered mainly the equipment in use (Dreesen—*Fette u. Seifen* 56, 224). Investigations on pigmentation of whale oils have indicated that the highly colored oils contained large amounts of iron and pyrrole compounds and that their presence was related to a high content of blood and aging of the blubbers (Mukai—*Bull. Japan. Soc. Sci. Fisheries* 20, 136, 242, 245, 610).

A literature review on the vitamin A content of cod-liver oil in relation to processing contains information on the influence on the yield of oil and vitamin A of rendering by steam, vacuum, enzyme, alkali, and alcohol; bleaching; hydrogenation; and presence of heavy metals and antioxidants (Woodsak—*Fette u. Seifen* 57, 491). A high potency vitamin A oil was extracted from whale livers by adding 7% sperm oil as a carrier, extracting with hexane, removing some of the lipides by precipitation with a solution of urea in methanol and recovering the vitamin A oil from the solvent (Tujii et al.—*Japan* 3977-'54). In the production of fish liver oils by alkali diges-

tion Kitamikado & Tanaka (*Bull. Japan Soc. Sci. Fisheries* 19, 1219) found that emulsification can be inhibited and greater oil yields attained if the separation and washing of the oil with a 0.2–0.3 M salt solution are done at 70°. With such a technique they obtained greater yields of the neutral oil than processing by solvent extraction followed by alkali refining (*Ibid.* 1223).

Mathematical equations were developed which related the transformation of cream into butter as a function of the peripheral speed of stirrers (Shuvalov & Vlodavets—*Kolloid. Zhur.* 16, 396). This work showed that blade stirrers are more efficient than cylindrical stirrers, possibly because they mix air into the cream and accelerate flotation of the fat. King (*J. Dairy Res.* 22, 328) observed microscopically, the appearance of fat on milk surfaces as affected by mechanical disturbance of the surface. At 30° the bursting of 10–15 air bubbles was enough to cover the milk surface with a continuous fat blanket, while at 20° globules and clumps occurred separately.

The history of development and the details of the continuous butter maker of the Cherry-Burrell Corp. have been described by Rishoi (*J. Dairy Sci.* 38, 109). An innovation in butter making comprises removing some of the aqueous portion of the raw material by freezing and separating the ice crystals, after which the remainder is churned (Toulmin—*U. S. Reissue* 23,988). A newly patented churn was designed to permit churning and washing of the butter within a minimum of time (Thorstenson-Rydberg—*U. S.* 2,726,069). Another patented system of butter making comprised a churning stage and a separate working stage for washing and adjusting moisture content (Nanz—*U. S.* 2,721,062). New equipment for shaping and packaging butter was also patented (Massmann—*U. S.* 2,705,835).

In instructions for making Russian butter oil it is recommended that the melted oils be separated and heated to 85–90° in the presence of at least 3% serum (Zhel'takov & Baulina—*Trudy Inst. Molochnoi Prom.* 1953, No. 13, 75; Smorodin—*Molochnaya Prom.* 15, No. 6, 38). The specific flavor of the product is developed from the aqueous portion during the heat treatment, and the presence of at least 3% serum during the process insures a good stability in the final product.

VEGETABLE OIL EXTRACTION. The general descriptive and review publications on vegetable oil production were written on the following subjects: recent advances in methods for production of vegetable oils and meals (Rao—*Bull. Central Food Tech. Research Inst. Mysore* 3, 249), processing mustard seeds in an expeller press (Kirakos'yan—*Masloboino-Zhirovaya Prom.* 19, No. 7, 7), expeller pressing of cottonseed (Burner *Oil Mill Gaz.* 59, No. 7, 11), quality of soybean oil from pressing plants and its refining (Morozov—*Masloboino-Zhirovaya Prom.* 19, No. 6, 8), wear and corrosion of machines for processing olives (Chelazzi—*Olearia* 9, 65), solvent extraction of vegetable oils (Grindrod—*Can. Chem. Processing* 38, No. 11, 60), improvements in design of solvent extraction plants (Hutchins—*J. Am. Oil Chemists' Soc.* 32, 698), and application of centrifuging in the fat and oil industry (Broadwell—*Chem. & Proc. Eng.* 36, 119).

Two patents dealt with heat treating oil seeds before their storage. One described heating the seeds in a tunnel with infrared lamps to reduce moisture to 1–3% and thus inhibit spoilage due to fermentation (Empresa Nac. "Calvo Sotelo" Combustibles Liquidos y Lubrificantes—*Span.* 207,997). The purpose in the other was to sterilize cottonseed infested with bollworm so as to eliminate spontaneous combustion during storage (Meaking—*U. S.* 2,704,869).

Optimum conditions for economical expeller pressing of cottonseed have been determined by Wamble & Harris (*Texas Eng. Expt. Sta. Bull. No. 136*, 70 pp.). A new seed oil press has three zones of pressure: (a) increasing pressure approaching oil expression level, (b) a pressure relieved zone, and (c) an oil expression zone (Hetzler—*U. S.* 2,724,327). The oil expressed in the last zone flows back and escapes through the material in the pressure relieved zone.

Alkali materials added to olive pulp during grinding or working facilitated liberation of oil, increased yields about 1.5%, and improved quality by reducing "fruitiness" and free fatty acids (Rousseau—*Oleagineux* 10, 183). In the method recommended for commercial operations, the olives were treated with 2% of a dry mixture of three parts trisodium phosphate and one part sodium bicarbonate. Treating olive pulp with pectinase also increased yields of the oil and ease of extraction (Pineda—*Ibid.* 9, 865; Lagua—*Anales bromatol., Madrid*, 6, 309). Marquezmy & Martinez (*Span.* 206,315), patented a process for extraction of olives under sterile conditions. In this process animal feed is prepared from the pulp, and sugars of value in fermentation processes are obtained from the

water pressed from the olives. Olives were also extracted with liquefied gases in a process in which moisture is frozen by partial evaporation of solvent, and the miscella removed and adjusted to conditions which release the oil (Ceni—*Ital.* 478,604).

In a process for converting coconuts to a flavoring extract and oil, the latter was removed by boiling in an alcohol-water solution, cooling, and removing the fat layer (Lopez-Irizarry—*U. S.* 2,712,502). The use of demulsifying reagents in displacing fat from vegetable materials by boiling in water was patented (Ranson & Rosello—*Fr.* 984,925).

Equipment has been arranged to process citrus fruit to peel oil, juice, seed oil, and residue (Toulmin—*U. S.* 2,708,627).

Material balance studies in a commercial tung oil mill indicated that losses were principally in particles of kernels occluded with separated hulls and in oil in screw press cake (Holmes *et al.*—*J. Am. Oil Chemists' Soc.* 32, 282). Wittka (*Olearia* 9, 55) investigated losses in the solvent milling of various seeds. The oil losses were 0.10–0.22%; total weight losses of materials were as high as 1.3%; and highest losses occurred with material of high protein content.

Nutritive value, toxicity, and flavor of oil milling products received attention by investigators of the industry. Arnold & Juhl (*J. Am. Oil Chemists' Soc.* 32, 151) report that use of trichloroethylene solvent in extraction reduces residual gossypol in flaked cottonseed meals, and because of the low temperatures involved the meal produced has a higher soluble protein content than a meal in which the gossypol is reduced by heat treatment. Jonassen & Demint (*Ibid.* 424) showed that on inactivating gossypol with ferrous compounds the iron displaces two sodium ions. In prepared animal mixed diets containing gossypol the components of the diet, the time and length of storage, and the concentration of the gossypol present, all influence the loss or inactivation of the added gossypol (Kupperman & Karon—*Ibid.* 54). A collaborative study on nutritional value of prepress-solvent cottonseed meals showed wide variation in protein efficiency numbers between laboratories. There was a negative correlation between total gossypol content and nutritional value, except in one test, and correlation coefficients indicated that solubility in 0.02 N sodium hydroxide was a better measure of protein quality than the solubility test with dilute hydrochloric acid (Chang *et al.*—*Ibid.* 103). Pons *et al.* (*Ibid.* 98) tested 26 sets of mill samples for the influence of milling on gossypol content and protein quality. In pressing mills gossypol was reduced in the cooking step whereas in prepress-solvent systems removal occurred through the extracted oils. Protein damage as measured by nitrogen solubility occurred mainly in cooking. The new analytical procedures for gossypol were a chemical method for use on cottonseed treated with dianilinogossypol (*Ibid.* 295), and a biological test based on gossypol discoloration of yolks of eggs from hens fed the cottonseed meal (Grau *et al.*—*J. Agr. & Food Chem.* 3, 864).

Losses in nitrogen solubility of the protein in salt and acid solutions during processing of soybeans were measured by Rzhekhin & Pogonkina (*Masloboino-Zhirovaya Prom.* 19, No. 6, 6). Greatest solubility losses or denaturation of the proteins occurred during cooking and pressing; these varied from 39% at 105° to 89% at 135°. Control of heat treatment in soybean processing is based on determination of urease activity. An apparatus and method for this purpose, based on splitting urea into carbon dioxide and ammonia, was described by Dangoumau & Debryne (*Rev. franc. corps gras* 2, 390). Two such methods whose last steps were based on pH and conductivity, respectively, gave concordant results (Croston *et al.*—*J. Am. Oil Chemists' Soc.* 32, 279). Uncooked soybeans yielded a solvent extracted meal whose nitrogen components were 90% dispersible in water at pH 6.5–6.7 and 98% with alkali (Smith *et al.*—*Ibid.* 274). In this work, eight components were identified among the proteins by means of electrophoretic patterns. A commercial means of treating seeds in oil milling to improve the nutritive value of the by-product meal comprises adjustment to a relatively high moisture content and to a pH which differs by at least 0.5 pH units from the original pH before the cooking step (King *et al.*—*U. S.* 2,726,155).

Fundamental information applicable to solvent extraction processes has been recorded. Othmer & Agarwal (*Chem. Eng. Progr.* 51, 372) found the rate of extraction of soybean flakes proportional to the 3.5 power of the oil remaining in the flakes at any time of the extraction, also that the rate decreases approximately as the flake thickness is raised to the fourth power. Thus increasing flake thickness three times decreases rate by 80 times. Equations were designed for calculating the number of extractions required for extracting grapeseeds (Moreno—*Quimica e ind. Bilbao* 1, 127) and for oil seeds in

general (Ellena—*Rev. fac. ing. quim.* 20, No. 34, 119). Nomo-graph (Graci—*J. Am. Oil Chemists' Soc.* 32, 109) and a laboratory test method (Kulkarni *et al.*—*Ibid.* 691) were designed for determining the extractability of oil seeds. With the latter it was shown that increasing the miscella concentration slowed initial extraction rates on all cooked flakes except those very thin; but from all flakes the degree of extraction was increased. With raw flakes the degree of extraction was increased only with the very thin flakes. Miscibility curves from temperature of complete miscibility and cloud temperatures to 0–10° were determined for cottonseed, peanut, sesame, and soybean oils in ethanol as fundamental data needed for application of ethanol for extraction of these oils (Rao—*Ibid.* 420; *Bull. Central Food Tech. Research Inst. Mysore*, 3, 221). A general equation relating density and composition of glyceride oil-solvent mixtures has been derived for application to simplify extraction control work (Skau *et al.*—*Ind. Eng. Chem.* 47, 1043). The value k , a constant necessary in calculation, has been determined at various temperatures for 23 solvents.

Innovations in equipment and methods for commercial solvent extraction were described. Improvements in bucket system continuous extractors dealt with distributing and maintaining a desirable amount of solvent in the individual buckets (Depmer *et al.*—*U. S.* 2,707,712) and with arrangement of buckets so that during extraction they were disposed vertically and while draining, horizontally (Hanke *et al.*—*U. S.* 2,722,474). In a system comprising a series of alternating leaching and centrifuging steps a new patented innovation dealt with complete separation of liquid in the first and last stage, whereas incomplete separation was achieved in the intermediate stages (Steinaecker—*U. S.* 2,715,094). Another patent on a similar system pertains to means of regulating transfer of material to the successive stages (Pascal—*U. S.* 2,714,551). The Kennedy system of countercurrent extraction in which the charge is mechanically swept through several leaching stages was improved to attain more efficient transfer of the material (Giese & Ludka—*U. S.* 2,703,274). Ultrasonic waves of 10^5 to 3 times 10^6 cycles per second applied for a period of a few seconds to several minutes improved efficiency of conventional extraction processes (Carpentier—*U. S.* 2,717,768). In testing such a method Thompson & Sutherland (*Ind. Eng. Chem.* 47, 1167) found that 60-volt-ampere per square centimeter ultrasonic intensity was equivalent to 1200 r.p.m. stirrer speed in extracting crushed peanuts with hexane. To remove settled solids from miscella, Depmer (*Ger.* 825,989 *Cl. 12c*) decanted clear miscella and recycled the lower layer and sediment to the extraction step. A combination solvent-pressure extraction system comprised repeatedly adding solvent just until gravity drainage occurs, and pressing (MacIlwaine—*U. S.* 2,689,857). A process of azeotropic distillation with fat solvent was recommended for removing water and extracting fat because a dustless dry residue is produced and the oil has minimum exposure to air or oxidizing conditions (Levin & Finn—*Chem. Eng. Progr.* 51, 223).

New descriptions and reviews on the "Filtration-Extraction" system also include discussions on new improvements (Spadaro—*J. Am. Oil Chemists' Soc.* 32, 160; Kulkarni & Vix—*Oils & Oilseeds J., India* 7, No. 7, 5). Bench scale apparatus to determine the extractability and filterability of oil-seeds for filtration-extraction was described (Graci *et al.*—*J. Am. Oil Chemists' Soc.* 32, 129) and demonstrated by details on determination of conditions necessary for extraction of peanut flakes (Pomenski—*Ibid.* 361, 565). In applying the method to cottonseed and rice bran oil production, the material was only mildly heated to prevent damage to protein and crisped by dehydration to yield relatively porous and incompressible granules (Gastrock *et al.*—*U. S.* 2,726,253; 2,727,914). Cost data for applying the system to processing cottonseed indicated that the process is economical (Graci & Bailie—*Oil Mill Gaz.* 60, No. 1, 9).

A new system of extraction is based on feeding material into the top of a column and the solvent, trichloroethylene, countercurrently through the bottom (Mitani—*Japan* 1991-54). The system is workable only with solvents of high density. The dark color of trichloroethylene-extracted oil has been related primarily to a function of the time and temperature of heating during processing (Arnold & Juhl—*J. Am. Oil Chemists' Soc.* 32, 444). The solvent did not appear to be the cause of high color in the oil. A review and new studies by Picken *et al.* (*Iowa State Coll. Veterinarian* 4, 137; *J. Agr. & Food Chem.* 3, 420) are reminders that trichloroethylene-extracted oil meals can lead to very toxic reactions when fed to cattle. In preliminary studies on the source of this toxicity, trichloroethylene epoxide, chloral, dichloroacetyl chloride, glyoxylic acid, and formic acid have been identified among the oxidation prod-

ucts of trichloroethylene (McKinney—*Ibid.* 413). Kaufmann & vom Orde (*Fette u. Seifen* 57, 399) recommended the use of 1,2,2-trifluoro-trichloroethane for the extraction of oilseeds because it combines the advantage of a solvent of low boiling point and low tendency to hydrolysis with good stability, low toxicity, low inflammability, and inertness toward metallic apparatus.

BYPRODUCT FATS. According to a patent, fatty acids may be recovered from tall oil skimmings by settling to remove lye, freeing the organic acids with mineral acids, bleaching and separating the rosin acids from the fatty acids by fractional crystallization (Thomsen—*U. S.* 2,720,515). New equipment (Spence—*U. S.* 2,724,709) and technique (Spangenberg & Culemeyer—*U. S.* 2,716,630) have been designed to separate the rosin from the fatty acids by distillation. From such processes a fraction rich in palmitic can be further purified to palmitic acid by conversion to soap, precipitation and washing with 85% alcohol (Elfström—*Swed.* 145,734). Experiments with urea-complex precipitation on tall oil have shown that fractions containing as much as 90% fatty acids can be segregated from the oil (Matsumoto & Tamura—*J. Japan Oil Chemists' Soc.* 4, 23). Sterols were produced from tall oil distillation pitches by neutralization of rosin and fatty acids, dilution, and cooling to precipitate the sterols (Albrecht *et al.*—*U. S.* 2,715,638-9).

A comprehensive review on production methods and uses for wool fats was prepared by Valee (*Rev. franc. corps gras* 2, 323). For producing lanolin free of fatty acids, he recommends centrifuging the wool scouring waters. An investigation on wool scouring agents has indicated that sodium carbonate at 0.3–0.5 concentration at 30°C. extracted the wool fat and caused less shrinkage of the wool than various other detergents (Yable & Susukida—*Natural Sci. Rept. Ochanomizu Univ.* 4, 227). Two new processes of degreasing wool were based on extraction with, respectively, tetrachloroethylene (Norman—*U. S.* 2,717,901) and methylene chloride (Norman—*U. S.* 2,723,281).

Recovery of fat from wool scouring waste by addition of 0.25–1.5% calcium chloride and centrifuging was considered suitable from the standpoint of industrial waste treatment (Taylor—*Sanitalk, Mass. Dept. Health*, 1, 13). Use of anionic and/or nonionic surface active agents in scouring was said to permit easy recovery of the wool fat by repeated centrifuging (Soc. Products Tensioactif *et derivs. Tensia—Belg.* 518,421). To remove wool grease from scouring solution by flotation, air was bubbled into it at about 40° to give a froth with about 70% moisture, which was further purified by settling and centrifugation (Bugard—*U. S.* 2,709,523; Anderson—*Chem. Ind. & Eng.* 3, No. 4, 10).

The olive oil constituent of recovered textile lubricant oils comprising mineral oil, olive oil and a nonionic emulsifier, was separated by adsorption on active carbon and surface-active resins, elution of mineral oil with petroleum ether, followed by elution of olive oil with acetone (Harker—*Chemistry & Industry* 1955, 592). A process for making good use of vegetable oil refining foots comprised processing to the fatty acids and refining these to solid and liquid acids by distillation and urea-complex segregation (Achaya *et al.*—*Indian* 51,816). Tests on three commercial methods have indicated that fatty acid recovery from refining foots was 84.5–90.4% complete (Sambuc & Desnuelle—*Rev. franc. corps gras* 2, 222). As alternate uses for soap stock, Paek & Goldblatt (*J. Am. Oil Chemists' Soc.* 32, 551) indicated how refinery cottonseed oil foots could be detoxified to serve in animal feeding or be used to prepare benzyl esters which may be useful as secondary plasticizers. In investigations on recovery of fatty material from used bleaching clays, the best treating solution was salt, monosodium phosphate, and water in the ratio of 12:2.5:100 and this permitted 90–92% recovery of the fatty material (Vasilevsky—*Oleagineux* 9, 869). Solvent extraction gave better yields but was difficult because of packing of the clays. A patented method for recovery of the fats in bleaching and filter earths comprises heat treatment with a caustic solution containing a wetting agent; the fatty material was recovered from the soaps formed (Chaloner & McNicoll—*U. S.* 2,706,201). Deodorizer sludge was hydrolyzed with acid, cooled to 10° to precipitate some sterols, and the remaining liquid was converted to methyl esters and distilled to yield fatty acid esters and tocopherols (Mattikow & Perlman—*U. S.* 2,704,764).

REFINING, BLEACHING, AND DEODORIZATION. Several descriptive communications on refining of fats and oils described existing equipment or methods. Short time mixing was emphasized in a description of one continuous method (Braac—*Ind. Chemist* 30, 523). In a discussion on the continuous

systems of Sharples and DeLaval, Loew (*Ind. y quimico, Buenos 16*, 526) considered these justified only in plants with high production. The methods used in investigating refining for application of Sharples equipment and description of the equipment were reported by Bradley & Smith (*Ind. Eng. Chem.* 47, 868). Other publications on such equipment were flow sheets of the Sharples system (Anon.—*Chem. Eng.* 62, No. 5, 326) and a demonstration showing that pressure system centrifugal refining with soda ash or ammonia results in a lower refining loss than that obtained by the laboratory cup test (Sullivan—*J. Am. Oil Chemists' Soc.* 32, 121). A comprehensive review on degumming of fats prior to refining was prepared by Merat (*Rev. franc. corps gras* 2, 614). Kaufmann & Schuppan (*Fette u. Seifen* 57, 402) drew attention to the natural waxes present in linseed oil. These may precipitate to cause costly difficulties during filtration or may cause turbidity in the oil and lack of brightness of films made therefrom. Means of eliminating waxes in production of the oil are suggested. Data have been presented to show that the color of refined cottonseed oil and the refining losses were reduced when the oil was cooled immediately after extraction and prior to refining (Tverdovskii & Umarov—*Masloboino-Zhirovaya Prom* 20, No. 2, 31).

A simple apparatus consisting of vats connected with siphons was designed to wash olive oil by forcing it successively into the bottoms of a series of vats containing water (Ciolli—*Ital.* 472,881).

Deacon & Wamble's (*Oil Mill. Gaz.* 59, No. 11, 45) studies on degumming of cottonseed oil showed that yields of degummed and final alkali refined oils from expeller oil were higher when the degumming was at 70° using 3% water than that at 40° or with less water, however refined colors were lower in runs at 40° using 3% water. Results with hydraulic expressed oil showed a gain in refined oil with degumming but the refining losses were greater than with the expeller oil. Similar work by Naudet *et al.* (*Rev. franc. corps gras* 2, 381) resulted in a record of the effect of degumming, stirrer speed, concentration of lye and the addition of salt with the lye on the losses during refining of solvent-extracted peanut oil. A preliminary degumming and use of salt with the lye reduced the refining losses. Smits (*Masloboino-Zhirovaya Prom.* 19, No. 8, 12) also reported that addition of salt to the refining lye reduced refining loss. He suggested that the improvement was due to demulsification effect of the salt.

Innovations for refining processes were described in patents and in the journal literature. One new continuous refining system is based on countercurrent flowing of an 8% aqueous caustic refining solution with a solution of the crude oil in 1-6 parts of hexane (Scott—*U. S.* 2,714,114). A preliminary treatment of crude oils with 0.1-0.4% of phosphoric acid reduced the subsequent alkali refining losses (Sullivan—*U. S.* 2,702,813). Adding various organic amines or sugar to rice oil when alkali refining reduced refining losses 32-55% depending on the additive (Cousins *et al.*—*J. Am. Oil Chemists' Soc.* 32, 561). From this work, sucrose and blackstrap molasses seemed most practical for commercial use. Ketones were removed from fatty acids by treatment with triethanolamine and washing with water (Barsky—*U. S.* 2,715,642). Glyceride oil recovered by steaming press residues was refined by treating with sodium silicate solution as the sole refining agent (Durkee—*U. S.* 2,701,810). Acid refining of fatty oils by proportioning the acid into a continuous stream of the oil avoids localized overheating and inhibits side reaction products such as sulfonates (Palmquist—*U. S.* 2,694,032).

Details have been recorded for refining some uncommon oils. Nahor and polang seed oils could be refined in two stages with 15-20% caustic sufficiently enough that soaps made therefrom did not discolor laundry (Kapadia & Aggarwal—*J. Sci. Ind. Res., India*, 13B, 732). Toxic alkaloids were removed from argemone oil by aerating in the presence of 1% manganese dioxide and adding 1-1.5% phosphoric acid (Roy—*J. Sci. Ind. Res. India*, 13B, 376). Excess acid was neutralized with chalk. Undi, malkanguni and pisa seed oils were refined sufficiently for soap making by washing with ethanol (Bhat *et al.*—*Indian Soap J.* 19, 279). In the same studies it was found that the color and odor of karanja oil could be improved with glacial acetic acid; whereas treatments with oxidizing agents or strong mineral acids were unsuccessful. Ethanol washing was also recommended for refining peanut and mowrah oils; and mutual solubility curves for the glyceride-fatty acids-ethanol systems have been determined as basic data for the process (Cama *et al.*—*Current Sci. India*, 23, 221). The methods suggested for refining highly acid rice oils comprised washing with a dilute solution of sodium hydroxide in ethanol (Hori—*Japan* 5532-54); and washing with dilute phosphoric acid (Inoue

et al.—*Japan* 3333-54) or oxalic acid solution (Mori—*Japan* 4785-54) followed by distillation of the free fatty acids under vacuum. Garcia (*Rev. cienc. apl., Madrid* 9, 130) demonstrated how highly acid sardine oils could be molecularly distilled to produce a neutral oil and various fractions of fatty acids having increasing iodine values from 102 to 278. In the process for refining highly acid oils by esterifying the acids with lower molecular weight alcohol and distilling the esters, Mattikow and Perlman (*U. S.* 2,721,872) found that washing the esters with dilute alkali prior to the distillation removed colored matter and insured permanently light colored oil and esters after distillation.

Data have been presented which indicate that the continuous countercurrent bleaching process gives better and more economical performance than batch-open kettle- or batch vacuum-bleaching systems (Singleton & McMichael—*J. Am. Oil Chemists' Soc.* 32, 1). In this process the adsorbent is added to the oil being bleached as a slurry that was made by mixing with fully bleached oil (McMichael *et al.*—*U. S.* 2,717,256). When oils are refined with a vacuum distillation step for removal of fatty acids partial bleaching with adsorbent can be done by adding the adsorbent to the still, and the bleaching can be completed at higher temperature after completion of the distillation (Metallgesellschaft A.G.—*Brit.* 707,455). Bleached oils were color stabilized by heating in an inert atmosphere with acylating agents such as acid halides or acid anhydrides (Blank & Artens—*U. S.* 2,727,051). Combining bleaching with hydrogenation by adding adsorbent to the hydrogenation mixture has been described in three patents and one literature item (Marsal—*Span.* 198,068; Delgado—*Span.* 207,877; Opie—*U. S.* 2,715,641; Mathur—*J. Indian Chem. Soc. Ind. & News Ed.* 17, 97). Centrifuges adapted for separating bleaching earth from oil were patented (Kjellgren—*U. S.* 2,711,854). The mechanical properties, chemical resistance, and heat setting properties of many synthetic filter fabrics with regard to use for filtration in the edible oil and other industries have been recorded (Essed—*Plastica* 7, 428, 482, 540; 8, 64). Clays indigenous to India (Rao & Krishnamurthy—*Bull. Central Food Tech. Res. Inst., Mysore*, 3, 196) and the Philippines (Cruz & Valencia—*Philippine J. Sci.* 83, 239) have been appraised for oil bleaching activity and procedures for their use in the industry issued. In bleaching tests with clays containing adsorbed water, animal and fish oils decolor best when active clays contained 15-18 or acid clays contained 10-12% adsorbed water (Yamada & Komatsu—*J. Japan Oil Chemists' Soc.* 4, 191). With vegetable oils optimum efficiency was obtained with a little less moisture.

Chemical oil bleaching processes were described in which the chemicals used were phosphoric acid (Aktiebolaget Separator—*Brit.* 714,160) and various oxidizing agents such as: air (Miyaji—*Japan* 4430-54), hydrogen peroxide (Tyutyunnikov & Man'kovskaya—*Masloboino-Zhirovaya Prom.* 19, No. 6, 23; Barsky—*U. S.* 2,705,722), *tert*-butyl peroxide (Tomiyama *et al.*—*Japan* 4431-54) and sodium chlorite (Rasch—*Seifen-Öle-Fette-Wachse* 81, 51; Corrato—*Ann. sper. agrar., Rome*, 8, 1393; Paquot & Paquot—*Rev. Française corps gras* 2, 217). Improvements mentioned in the chlorite bleaching process dealt with use of phosphoric acid or tin salts as bleaching activators.

New patents on steam deodorizing apparatus deal with arrangement of baffles in existing apparatus to inhibit foaming of oil during steaming (Brücke—*U. S.* 2,695,868) and on a continuous system in which oil flows downward through a plate column while steam enters at the bottom and successively bubbles through two inches of oil on each plate (Faulkner—*U. S.* 2,722,505). Experience gained in using a jet ejector for deodorizing fats and oil has been discussed by Zharskii (*Masloboino-Zhirovaya Prom.* 20, No. 2, 11).

BYPRODUCTS OF REFINING. Gums (phosphatides) obtained in the degumming of cottonseed oil were returned to the meal before desolventizing (Whittecar—*J. Am. Oil Chemists' Soc.* 32, 564). The process permitted efficient pelleting of the meal for livestock feeding. Sterol glycosides and inositol were recovered from vegetable oil phosphatides by treatment with lower alcohol, extraction of the sterol glycosides with pyridine, and the recovery of inositol from the residue by treatment with an acid (Perlman *et al.*—*U. S.* 2,691,011).

A wax ester obtained from the distillation of sperm whale oil was purified by recrystallization from petroleum naphthalene solvent (Nakajima & Kosuge—*Japan* 2982-54). The triglycerides in sperm oil were converted to fatty alcohol esters by partial saponification, removal of glycerol and reesterification of the free fatty acids with fatty alcohols (Grünthal & Mannes—*Ger.* 871,148 Cl. 120). Fatty alcohol esters of wool fat were concentrated by partial saponification, conversion of the free fatty acids to calcium soaps and separating the esters

(Gluzman *et al.*—*Masloboino-Zhironaya Prom.* 20, No. 4, 22). Cholesterol was prepared from wool grease by saponification, extraction of the unsaponified material with halogenated aliphatic solvents, and fractional crystallization of the extract (Ind. Quim. Lander S.A.—*Span.* 216,849).

Extraction of a carotene concentrate from palm oil by fractional crystallization to remove solid vegetable fat, methanolysis of the liquid oil, and fractional distillation of the carotene from the methyl esters was patented (*Inst. rech. huiles de palm et oleagineux*—*Fr.* 984,531). The economy of such a system was discussed by Jorand (*Oleagineux* 10, 99, 193, 269). Another process of recovery of carotene from oil was based on a novel technique of fractional crystallization (de Witte—*U. S.* 2,717,210).

Recovery of vitamin A from fish oils by molecular distillation can exceed 100% yields because during the process the kitol present in the oil decomposes to produce additional vitamin (Hirao *et al.*—*Bull. Japan Soc. Sci. Fisheries* 15, 615). Whale liver gave as high as 166% yields of vitamin A based on the amount analytically determined in the original oil. Acid contaminants of vitamin A esters were removed with the use of anion exchange material (Bentel—*U. S.* 2,712,515).

A method designed for the production of vitamin E from wheat-germ oil involved converting the oil to methyl esters and fractionally distilling in a molecular still (Martin & Cardona—*Anales real soc. espan. fis. y quim. Madrid*, 50B, 911).

WINTERIZING, SPLITTING, AND FRACTIONATION. Physical-chemical data has been presented for use in solvent winterizing of crude cottonseed oil in 85-15 acetone-hexane mixture as has been previously published for several other oils (Boucher & Skau—*J. Am. Oil Chemists' Soc.* 32, 497). Passino (*U. S.* 2,728,707) patented a winterizing method based on solvents in which solubility of stearin decreases with increasing temperature. After critical temperatures are reached overhead stearin is removed.

Equilibrium diagrams were developed for use of acetone-water mixtures as selective solvents for segregating linseed and soybean oils into components of high and of low iodine value (Young & Sallans—*J. Am. Oil Chemists' Soc.* 32, 397). Solubility curves of peanut oil-oleic acid systems in acetic acid and in furfural at 40° have shown that the oleic acid has an affinity for the oil phase in either solvent (Venkataraman & Laddha—*Ind. Eng. Chem.* 47, 1272).

Of two reviews on splitting of fats one pertained to a "contact" method of splitting (Rozhdvestvenskii—*Masloboino-Zhironaya Prom.* 20, No. 2, 15) and the other to both splitting and esterification (Paquot—*Rev. franc. corps gras* 2, 475). The steam splitting process of *Italian patent 484,620* has been described and illustrated, and processing data has been recorded (Martinenghi—*Ibid.* 773; *Fette u. Seifen* 5, 570; *Riechstoffe, Parfums, Seifen* 1955, No. 8, 8; *Olearia* 9, 13).

An improvement for the batch splitting process was based on autoclaving new batches with concentrated glycerinated water derived from a previous splitting (Raffaeta—*Ital.* 469,565). Use of waste sulfuric acid from DDT preparation as a splitting reagent was patented (Kurokawa—*Japan* 1843-54). The mixed splitting agent dibutyl-naphthalene-sulfuric acid was less efficient with dioxane solvent, than without the solvent (Fukuzumi—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 448). Twitchell-reagent splitting was applied for the recovery of free fatty acids from their methyl esters (Goebel—*U. S.* 2,714,603).

A review on separation of fatty acids contained information on fractional distillation and crystallization, chromatography, selective extraction, and urea fractionation (Rigamonti—*Fette u. Seifen* 56, 1). A review on fatty acid distillation was principally on the role of steam in the process (Schlenker—*Seifen-Öle-Fette-Wachse* 81, 285). A multicolumn still designed with a saving in expensive acid-proof material made use of porcelain material in the first column which distilled corrosive acids (C₁-C₅), while the other four columns were metal and designed according to variables as temperature and vacuum (Dobrowolski—*Przemysl Chem.* 9, 419). Oleic acid was separated from a mixture of liquid acids by reacting the polyunsaturated components with maleic anhydride and fractionally distilling the mixture (Yatani *et al.*—*Japan* 4281-54).

Solvents were used to fractionate fatty acids by various methods. In the process comprising graining fatty acids, followed by pressing, better separation of liquid from solid components occurred when a small amount of organic solvent and water were present during graining. Alcohol (Stein & Hartmann—*Ger.* 825,839 *Cl.* 120) and acetonitrile (Hoerr—*U. S.* 2,705,723), respectively, were the organic solvents involved in two patents on such a method. Another method comprises saponifying the acids with potassium hydroxide while in a mixture of isopropyl alcohol and a small amount of water and

cooling to precipitate soaps of the higher melting acids (Union chim. belge, Soc. Anon.—*Belg.* 525,262). The acids are released from the solid and the liquid fractions with sulfuric acid. A similar process comprises extracting the sodium soaps of the acid with lower alcohols or ketones (Notevarp *et al.*—*Brit.* 719513). Mixed fatty acid of tallow can be emulsified in water with the use of a capillary-agent and centrifugally separated into a liquid and a solid phase (Henkle & Cie G. m.b.H.—*Brit.* 724,222). Another method for tallow fatty acids comprises completely solidifying, shaving into thin flakes, and extracting at -30° with trichloroethylene (Yokoi & Furukawa—*Japan* 5805-54). The solubilities of elaidic, oleic, stearic, linoleic, arachidic, eicosenoic, palmitic, behenic, erucic, and brassidic acids in methanol, ethyl acetate, ether, acetone, toluene, and *n*-heptane were recorded for various temperatures between -70 and 10° to serve as fundamental information for design of analytical or commercial processes to separate fatty acid mixtures by fractional crystallization (Kolb & Brown—*J. Am. Oil Chemists' Soc.* 32, 357). Limited studies were also made with eight other hydrocarbon solvents. The increase in solubility introduced by the presence of a double bond was greater the farther the point of unsaturation was removed from the carboxyl group. The change of a *cis*-bond to *trans* reduced solubility of the acid.

Experimental results from fractionating fatty acids with urea in methyl alcohol as the solvent were recorded for the fatty acids from the oils of menhaden, herring, tuna, seal, salmon eggs, heads and viscera (Domart *et al.*—*J. Am. Oil Chemists' Soc.* 32, 481), dalda seed (Mehta *et al.*—*J. Chem. Soc. Ind. & News Ed.* 17, 177), shark-liver (*Ibid.* 182), sesame (*Ibid.* 15, 97), linseed (*Ibid.* 97; Loury & Heliot—*Rev. franc. corps gras* 2, 488), and cottonseed (Kats and Vlasova—*Doklady Akad. Uzbek S. S. R.* 1953, No. 6, 48). The method was also used for separating erucic acid from mustard oil fatty acids (Pathak & Aggarwal—*J. Sci. Ind. Res. India*, 14B, 229) and ricinoleic acid from castor oil fatty acids (Mehta—*J. Indian Chem. Soc., Ind. & News Ed.* 17, 23). In the use of the method on fatty monoglycerides, diglycerides and diglycol esters it was noted that the diglyceride-urea complexes had entirely different physical structures (Martinex-Moreno *et al.*—*Fette u. Seifen* 57, 652). Hypothetical structures based on x-ray observations were designed. A special technique for separation of the fatty acids of peanut oil with urea-alcohol solution was patented (Achaya *et al.*—*Indian* 48,934). Finer separations of fatty acids were said to be obtained by dissolving the acids in benzene and precipitating with aqueous solutions of urea (Urakami & Sakuri—*Japan* 3687-54; Sakuri—*J. Oil Chemists' Soc. Japan* 3, 263, 265) or with solid urea suspended in a saturated aqueous solution of urea (Regamonti & Riccio—*Ann. chim., Rome* 44, 288; Rigamonti—*Ital.* 484,045).

Data useful in designing commercial urea complex separations were recorded. In a process using ethanol-water media, the formation of the complexes from linseed and safflower oil fatty acids has been determined as functions of water dilutions and urea concentrations (Narayan & Kulkarni—*J. Sci. Ind. Res., India* 13B, 9). The equilibrium constant of the formation of complexes with C₁ to C₁₈ saturated acids, linoleic acid, and elaidic acid was developed for use in designing a semicontinuous method for separation of a mixture of 2 or 3 fatty acids (Regamonti & Riccio—*Gazz. chim. Ital.* 85, 521). In another similar study the effects of different solvents were also studied (Sakurai—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 277). Segregation of stearic and oleic acid mixtures was easier when applied to the methyl esters of the acids rather than to the free acids (Sakurai—*Ibid.* 50). A new technique of urea fractionation comprised passing solutions of fatty acids through columns containing mixtures of crystalline urea and silica (Martinez-Morena *et al.*—*Anales real soc. espan. fis. quim.* 49B, 539). Thiourea resembles urea with regard to forming fatty acid complexes (Schlenk *et al.*—*J. Am. Chem. Soc.* 77, 5437).

HARDENING OF OILS. Studies were recorded on the kinetics and mechanism of hydrogenation reactions. Data on the total percentage of *cis*, *trans*, and saturated acids present at various time intervals during the hydrogenation of pure triolein were used to develop rate rules governing the reactions and effectiveness of the catalyst (Swicklik *et al.*—*J. Am. Oil Chemists' Soc.* 32, 69). The kinetic study substantiated the existence of an equilibrium between *cis* and *trans* isomers over part of the reaction. At 125° the hydrogenation reaction was of the first order; but at higher temperatures it became more complex. Equations were also developed for calculating rates of hydrogenation from experimental data on various fats (Zinov'ev and Potapova—*Gizlegpisheprom.* 1953, 37). Studies on hydrogenation of oleic acid have shown that in the isomerization

reactions, migration of the double bonds takes place equally in each direction (Allen & Kiess—*J. Am. Oil Chemists' Soc.* 32, 400). In this work a partial hydrogenation-dehydrogenation theory was suggested to explain the simultaneous formation of both positional and geometric isomers. In another work on isomerization during hydrogenation, sunflowerseed, cottonseed, rapeseed, and soybean oils were partially hydrogenated, the isoacids isolated and their principal Raman spectra lines determined (Artamonov—*Zhur. Priklad. Khim.* 28, 775). In similar work on linolenic acid and linoleic acid, methyl esters, it was found that ease of hydrogenation at the double bonds in the former were $\Delta^{15} > \Delta^9 > \Delta^{12}$ and with the latter partial hydrogenation mainly produced isoöleic acids (Ueno & Hidaka—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 73, 133). Lecithin was found to hydrogenate at 90–100° and 90–100 atmospheres pressure; above 100° it decomposed (Jacini—*Olii minerali grassi e seponi, colori e vernici* 32, 101).

The descriptive communications on commercial hydrogenation were written on the Russian continuous process plants, respectively, at Salolin (Vengerova & Ashkinazi—*Masloboino-Zhirovaya Prom* 19, No. 7, 16) and at Kharkov (Zharskii et al.—*Ibid.* 18) on equipment for drying and circulation of hydrogen for hydrogenation (Fainberg—*Ibid.* 19, No. 6, 13) and on hydrogenation of highly acid olive seed oil (Ayerbe—*Grasas y Aceite* 5, 154). Two new patents were on continuous hydrogenation; one involved passing oil and hydrogen through a mass of catalyst while inducing a high frequency alternating current in the catalyst (Dunmire—*U. S.* 2,724,689), and the other patent was on equipment and controls by which hydrogen, oil, and catalyst are exposed to reaction for the same length of time and pressure, and distribution of components are uniformly maintained to produce products of uniform melting point (Bregman—*Brit.* 723,887). Studies on solvent extracted olive drupe oils has indicated that the principal hydrogenation inhibitors in the oils are sulfur compounds (Mareno & Ayerbe—*Oleagineux* 9, 697).

Hydrogenation catalysts comprising specific nickel-copper and nickel chromium mixtures on kieselguhr were patented (Empresa Nac. "Calvo Sateo"—*Span.* 212,632, 215,121). A carrierless catalyst was made by reduction of nickel hydroxide with hydrogen at 80–150° while in an aqueous dispersion (Kern—*U. S.* 2,726,151). New methods for recovery of spent catalyst contained economical means for removal of iron (Bijawat et al.—*J. Sci. Ind. Res., India*, 13B, 572). Analytical methods were published for determination of nickel in hydrogenated fat and in catalysts which also contained iron and copper (Kul'berg et al.—*Masloboino-Zhirovaya Prom.* 20, No. 1, 19). The use of radio-active cobalt in the catalyst has been proposed so that it can serve as a tracer for determination of residual catalyst in hardened fats (Kaufmann & Brouër—*Fette u. Seifen* 57, 407).

A method of hardening fats by elaidization in which liquid sulfur dioxide is used as a catalyst was described (Waterman & Dahmen—*Chemie & Ind.* 64, 558), and it was demonstrated with experimental data on hardening sesame, olive, soybean, and perilla oils (Dahmen, et al.—*Ibid.* 560). Elaidinization under anhydrous conditions with alkali metabisulfites as catalyst was patented (Wittka—*Ger.* 894,559 Cl. 120).

TRANS- AND INTERESTERIFICATION. The reaction of glycerol with triglycerides for the manufacture of mono-glyceride emulsifiers was investigated. Mehta's et al. (*J. Am. Oil Chemists' Soc.* 32, 478) tests showed that equilibrium of the reaction was attained quicker with peanut oil than with mustard oil, and production of monoglyceride with the peanut oil was greater. Rossi et al. (*Chimica e ind.* 37, 356) reported that there was an induction period for the reaction which may differ considerably even among different samples of an individual oil. The reactions proceeded at the same rate after the induction period. Various acids were reacted with excess glycerol in a study on directing the glycerolysis to formation of monoglycerides (Chaudhury et al.—*Sci. & Culture, India* 20, 344). Greater yields of the latter were obtained with the lower mole weight fatty acids.

Partial glycerol esters for use as emulsifiers were made to fit various physical specifications by manufacture from fatty acids of an oil, stearic acid, and glycerol in ratios compatible to meet each specification (Schlüter—*Brit.* 712,747). The presence of ethylenediaminetetraacetic acid during the transesterification preparation of monoglycerides improved the stability of the product (Kuhrt—*U. S.* 2,714,113).

Various means were described to increase the monoglyceride content in commercial partial glycerides. In applying urea-complex separation technique to the reacted mixtures, the separations were first on the basis of saturation and secondly on the basis of the degree of esterification of glycerol (Heckles &

Dunlap—*J. Am. Oil Chemists' Soc.* 32, 224). This technique was patented for the separation of monoglycerides of soybean fatty acids into fractions of low and of high iodine values (Bradley—*U. S.* 2,700,036). Commercial monoglycerides were concentrated by extraction with absolute methanol (Basu—*Sci. & Culture, India*, 20, 395) and with methanol-water mixtures (Kuhrt & Welch—*U. S.* 2,727,913). Glycerol monoricinoleate was prepared from the acid and glycerol with phosphoric acid as the catalyst and purified by washing with water and extracting with ethanol (Bozzola—*Boll. chim. farm.* 93, 199).

Solubility curves of monostearin in acetone, hexane, and various alcohols have been determined by Ward & Singleton (*J. Am. Oil Chemists' Soc.* 32, 172). The countercurrent distribution curves (Craig apparatus) between petroleum ether and methanol have been determined for eight monoglycerides and a diglyceride (Perry & Brokaw—*Ibid.* 191). Increase in chain length increased partition coefficient and the β -monoesters had lower coefficients than the corresponding α -forms. The apparatus was used to show that commercial partial esters contain 5–8% β -isomers (Brokaw et al.—*Ibid.* 194). The β -monoglycerides segregated in this work appeared equivalent to α -forms for cake baking utility.

Acetoglycerides were prepared by interesterification of fatty materials and triacetin and the properties and uses of the products were discussed (Mellier—*Oleagineux* 10, 335).

The ethanolysis of many oils using sodium hydroxide as the catalyst was comprehensively studied by Chowdhury & Mukherji (*Sci. & Culture* 20, 48, 200; *J. Indian Chem. Soc.* 31, 794; *Indian Soap J.* 18, 233; 19, 47). In general, saturated acids interesterified more rapidly than unsaturated; among saturated acids the reaction was faster the lower the molecular weight; and among the unsaturated acids the rate in decreasing order was ricinoleic, oleic, linoleic, linolenic, eleostearic, and erucic. A method devised for alcoholysis of wheat-germ oil as a step in distillation production of vitamin E contained the stipulations of dehydrating the ethanol with copper sulfate, using a 2:1 ratio of alcohol and oil, and 1.6% sulfuric acid catalyst (Garcia—*Rev. cienc. apl., Madrid* 8, No. 41, 522). Continuous methods of alcoholysis were based on passing oil-lower alcohol mixtures over zinc silicate at high temperature and pressure (Braconier & Hermesse—*U. S.* 2,727,049, *Belg.* 527,076), spraying oil heated to 170° into a tower countercurrent to vapors of methanol (Kida & Motonaga—*Japan* 4932-54) or glycerol (Santelli—*Ital.* 480,063). Chrysalis oil was interesterified with glycerol and methanol using an alkali catalyst to produce useful products having free hydroxyl groups (Toyoda—*Japan* 1290-54).

Products (Excepting Detergents)

HOUSEHOLD FATS. New details have been published on development of a margarine fat, so called "global spread," which is spreadable in both warm and cold climates. The fat is a tempered composition of 80–90% vegetable fat and 10–20% mono- or diglyceride, and may also contain minor proportions of polyalkylene glycol esters (Jones et al.—*U. S.* 2,718,468). The additional presence of very small amounts of soybean phosphatides and tempering at 44° for 24 hours inhibited progressive hardening or firming of this spread during storage (Lancaster et al.—*J. Am. Oil Chemists' Soc.* 32, 9). The development of the tempering procedure resulted from microscopic, ultracentrifuge, and X-ray diffraction studies of the crystal structure and solubility studies of monoglycerides in vegetable oil which have indicated that the hardening resulted from recrystallization of solid components (Hellman et al.—*J. Am. Oil Chemists' Soc.* 32, 110, 489). The tempering caused recrystallization into more perfect ordered and sharply defined crystals. For this work the high speed centrifuge was applied to separate liquid from solid phases of the spread (*Ibid.* 73). Best separation occurred when centrifuging with a layer of aqueous alcohol of density intermediate to the oil and solids; however, the separation was not quantitative.

A newly patented margarine, containing about 0.05% of the alcohol-insoluble moiety of whole vegetable phosphatides, was substantially free from spattering and development of a layer of foam on its surface when heated to frying temperatures (Julian—*U. S.* 2,724,649). Another patent dealt with packaging margarine in rectangular or square slabs (Heidrich et al.—*U. S.* 2,705,203).

General information on margarine appeared in the foreign literature: Knollenberg (*Fette u. Seifen* 57, 449) reviewed application of the "Votator" and other new equipment for the industry. For the Polish margarine industry, Berens (*Prace Głównego Inst. Przemysłu Rolnego i Spoywczego* 4, No. 1, 19) reviewed emulsifying agents; Czapliski et al. (*Ibid.* 1) issued

instructions on how to refine and hydrogenate rapeseed oil intended for margarine making; and Krolkowski *et al.* (*Ibid.* 3, No. 3, 24) demonstrated the use of the Richardson-Holde penetrometer for laboratory control of the consistency of the product. The latter group (*Ibid.* 40) reports that small amounts of lactic acid induce more desirable flavors in margarine than citric or tartaric acids. Because the former is prooxidant such margarines must be consumed soon after manufacture. Blends of vegetable and animal fats and oils containing less than 18% high melting solid fractions were recommended for manufacture of margarine from Russian raw materials (Palladina & Styazhkina—*Maslobaino-Zhirovaia Prom.* 20, No. 3, 9).

A few improvements in deep fat frying were discussed. Periodically filtering the frying fat for potato chips and continuously filtering for fried onions yielded better looking, tasting, and storable fried products (Grim—*Food Eng.* 27, No. 6, 113). New automatic equipment which involves heating frying oil by repeatedly circulating it from the fryer through a heat exchanger has also cured some deep fat frying faults (Smith & Freeman—*Ibid.* No. 3, 60). Vegetable chips, similar to potato chips, made from beets, carrots, parsnips, and pea and lima bean chunks have been described giving frying conditions, protein and oil content, storage, flavor, and commercial possibilities (Kelley & Baum—*Food Tech.* 9, 388).

Mixed "acetin" fats made by random interesterification of various common fats with triacetin were described and their potential food uses reviewed (Feuge—*Food Tech.* 9, 314; *Proc. 7th Res. Conf. Am. Meat Inst.* 1955, 86). Solubility data of pure acetin fats prepared in this manner and of "butyro" products in tristearin and in hydrogenated cottonseed oil have been recorded graphically for use in development of new uses and products (Ward *et al.*—*J. Am. Oil Chemists' Soc.* 32, 316). Their specific heats, heats of fusion, accumulated heat contents, and heats of transition upon changing polymorphic form were also determined (Ward—*J. Phys. Chem.* 59, 4). A nutritional comparison of "acetin" versus normal fats has shown that the former were better utilized than the glycerides consisting entirely of long chain fatty acids (Mattson—*Fed. Proc.* 14, 443).

A compounded fat made from Polish raw materials contained 60% beef tallow and 40% rapeseed oil (Rutkowski—*Przemysl Rolny i Spozyczy* 8, 87). Raw materials that did not blend easily such as very hard fat and liquid fat, yielded satisfactory blends on adding 5-25% rapeseed oil and/or rice oil (Ginn—*U. S.* 2,721,303). This product was intended for greasing pans which are used in commercial bakeries. Lard was converted to a "high ratio" shortening by mechanically and thermally working with gas and phosphatides to give a smooth blend (Griffin—*U. S.* 2,728,674-5). Lard, molecularly rearranged for shortening use by transesterification treatment, had much smaller crystals which were in a looser order of packing than normal lard (Hoerr & Waugh—*J. Am. Oil Chemists' Soc.* 32, 37).

Several communications dealt with fats and fat derivatives in the baking industry. Recipes for fancy breads, pastries, buns, and cakes incorporating lecithin have been published (Stewart—*Food Manuf.* 30, 370). Histological technique has been used to observe fat distribution in cake batter (Hunt & Green—*Food Tech.* 9, 241). The fat distribution was markedly affected by emulsifiers. A new bakery emulsifier was made by esterifying polymerized glycerol with lactic acid, and submitting some of this product to transesterifying conditions with polymerized triglycerides (Aktieselskabet Grindstedvaerket—*Brit.* 731,934). Another product for the same purpose was produced by reacting glycol with a fatty acid and then with an aliphatic tricarboxylic acid (Gooding *et al.*—*U. S.* 2,701,203). Several pharmacological studies have indicated that the polyoxyethylene ester emulsifiers as used in baking are not physiologically harmful (Janowitz *et al.*—*Gastroenterology* 24, 510; Smyth *et al.*—*J. Am. Pharm. Assoc. Sci.* 44, 227; Graham *et al.*—*J. Pharm. & Pharmacol.* 6, 534; 7, 126).

Fats or oils were involved in the preparation of other household products. Peanut butter which is stabilized against the separation of oil was prepared by roasting peanuts in hydrogenated peanut oil, draining the oil and thereafter grinding the nuts to form peanut butter (Cochran & Carter—*U. S.* 2,708,634). Either isomerization or hydrogenation prevented "bloom" in cacao butter (Newman—*Food Manuf.* 30, 286). This bloom of natural cacao butter was said to arise from some fat constituent with a high melting point (Easton & Moler—*Zucker- u Susswaren-wirtschaft.* 7, 261). A substitute for the grained coconut oil, "hard butter," of the confectionery industry was made by blending various oils to certain ratios of acids of various chain length and subjecting to hydrogenation and molecular rearrangement (Cochran & McGee—*U. S.*

2,726,158). A patented composition for coating frozen cuts of meat comprised meat-basting fat, water, edible gelatin, and cellulose gum (Shinn & Childs—*U. S.* 2,721,142).

Fats and oils were studied in regard to production of pharmaceuticals. Janot & Ruoss (*Pharm. Acta Helv.* 30, 8, 15) reviewed the preparation of oily injectable solutions, selection of the oils, and control of their sterility. Vitamin A oil emulsions made with anionic surface active agents, adjusted to pH 5.0, and containing additions of ascorbic acid and vitamin E were of suitable stability (Ito *et al.*—*Ann. Rept. Takamine Lab.* 6, 41). Banker & Lee (*J. Am. Pharm. Assoc. Pract. Ed.* 16, 169) determined and recorded a list of emulsifiers which produce clear elixir emulsions. Igarashi *et al.* (*Japan* 5092-54) patented the use of a mixture of sorbitan monooleate and sorbitol as an edible emulsifier. Acylating wool fat to form some acetate esters improved its properties for cosmetic and pharmaceutical uses (Conrad & Motiuk—*U. S.* 2,725,334).

EMULSIFIERS AND DEMULSIFIERS. General descriptive communications on emulsifiers were written on: emulsifiers for agricultural pesticides (Brown & Riley—*Agr. Chemicals* 10, No. 8, 34), emulsifying, gelling and dispersing agents and their uses (Kappeller—*Deut. Drogisten-Ztg.* 5, 10), use of fatty acids in emulsifiers (McCaulliff—*Rev. franc. corps. gras* 2, 3), fat derivatives of sugar (Sisley—*Ibid.* 305), lecithin (Ghatak & Krishna—*J. Sci. Ind. Res., India* 14A, 285), and "AMP" as an emulsifying agent in polishing waxes (Frump—*Soap & Chem. Specialties* 31, No. 2, 153).

Alkali salts of sulfoaromatic fatty acids, such as sodium sulfophenylstearate, were patented as general emulsifiers (DeGroote—*U. S.* 2,716,126). A patented wax emulsion contained a nonionic emulsifier derived from ricinoleic acid and protein (Holzinger—*U. S.* 2,711,378). A combination of protein and surface active agent was also used to emulsify asphaltic compositions (Day—*U. S.* 2,714,582), and for elastomeric moisture proof coating material (Herzog & Gilchrist—*U. S.* 2,709,689). Another emulsifier for asphaltic material was made by reacting aliphatic polyamines with tall oil- or fish oil-fatty acid pitch (Kalinowski *et al.*—*U. S.* 2,723,632). Emulsifiers were used to impregnate leather with elastomeric material and plasticizers (Cheronis—*U. S.* 2,721,145). When using ultrasonic waves along with emulsifiers, soap was the best of six emulsifying agents, followed in order by polyethylene glycol 400, monostearin, polysorbate 80, acacia, sodium dodecyl sulfate, and tragacanth (Beal & Skauen—*J. Am. Pharm. Assoc.* 44, 487).

Rosin soap which was treated with potassium hypochlorite was a suitable emulsifier in the emulsion polymerizations in which a hydroperoxide initiator was used (Uraneck & Landes—*U. S.* 2,679,497). Ultramicroscopic particle count of latexes prepared by emulsion polymerization with soaps and one synthetic surface active agent has confirmed concepts of the action of nuclei and micelles formation determined previously by X-ray photography (Wintgen & Neveling—*Kolloid-Z.* 138, 142). In studies on effect of aliphatic detergents on the mechanical stability of polystyrene latex, potassium palmitate was more effective than the laurate, and combinations of the former with a nonionic detergent produced more stable latex than with either alone (Roe & Brass—*J. Colloid Sci.* 10, 194).

The properties of several emulsions were studied. With emulsions prepared with mineral oil and aqueous phases containing various glycols or glycerol, neither the viscosity of the internal phase nor the ratio of the viscosity of the phases directly affected the emulsion viscosity (Sherman—*Kolloid-Z.* 141, 6). In this work, an increase in viscosity brought about by addition of fine carbon was attributed to absorption of carbon by the emulsifier. An increase in viscosity induced by glycol ricinoleate emulsifiers over that of the nonhydroxy esters was attributed to formation of a gaseous film at the oil-water interface with the former (Sherman—*J. Colloid Sci.* 10, 63). Higher alcohol- or ester-water emulsions made with potassium ricinoleate were more stable than those made with sodium oleate (Kazi & Desai—*J. Indian Chem. Soc.* 31, 765). The addition of very low concentrations of bivalent metal ions to lecithin sols caused a considerable increase in the surface force (Elworthy & Saunders—*J. Chem. Soc.* 1955, 1166).

Gelatinized emulsions of benzene with sodium, ammonia, and triethanolamine soaps as emulsifiers were studied with regard to stability, inversion, particle size, etc., as affected by the type of soap and the fatty acid radical of the soap (Kremner & Kuibina—*Kolloid, Zhur.* 16, 358, 425; 17, 34). Emulsions stabilized with the triethanolamine oleate were more stable than comparable soap of sodium or ammonia; but with a shorter fatty acid, octanoate, the triethanolamine soap emulsion became unstable. The disruption or inversion as produced

by various concentrations of different salts was also recorded. In work on capacity of ammonium oleate, sodium naphthenate, and sodium butylnaphthalene sulfonate solubilization of oil, various critical mixtures of these had the best efficiencies (Spivakova—*Ibid.* 17, 131).

Among a series of discussions on coagulation, papers were read on: stability and electrophoretic deposition of suspensions in nonaqueous media (Koelmans & Overbeek—*Discussion Faraday Soc.* 18, 52), theory of heterocoagulation, interaction and adhesion in emulsions (Deryagin—*Ibid.* 85), kinetics of coagulation of emulsions (Lawrence & Mills—*Ibid.* 98), the flocculation and coagulation of different systems (Dervichian—*Ibid.* 231), soap-water-amphiphile systems (Hyde *et al.*—*Ibid.* 239), surface potential of long-chain sulfates and their relation to dispersion stability (Pethica & Few—*Ibid.* 258), and surface and interfacial viscosity of soap solutions (Blakey & Lawrence—*Ibid.* 268). The conditions governing the phase continuity of oil-water dispersions stabilized with soap and alcohol were reviewed (Bowcott & Schulman—*Z. Elektrochem.* 59, 283).

Emulsions containing Lissapol N, salt, and lanolin, mineral oil or olive oil were separated quantitatively by adsorption on a column containing a mixture of Zeokarb 225 and De-Acidite FF and eluted first with 50% aqueous ethanol and then with trichloroethylene (Green *et al.*—*Nature* 174, 659; *Analyst* 80, 470). A procedure for the determination of polyethyleneglycol monooleate emulsifier depended on formation of a blue complex with ammonium cobaltothiocyanate and extraction of this complex into chloroform (Brown & Hayes—*Analyst* 80, 755). A method for polyethylene oxide dispersing agents in general was based on precipitation with ferrocyanic acid from hydrochloric acid solution (Schönfeldt—*J. Am. Oil Chemists' Soc.* 32, 77).

The "petroleum oil displacement efficiency" (petroleum emulsion demulsification), composition, type form, surface tension, cloud point, and manufacture were tabulated for 105 commercial surface active agents (Johansen *et al.*—*Soap, Chem. Specialties* 31, No. 10, 41; No. 11, 53). The nonionic products had the highest displacement efficiencies and the lowest surface tension. Except for heavy anionics and the "Ethomeens," anionic and cationic products were generally ineffective for oil displacement, silicates and polyphosphate builders were moderately effective, and polyamine acetates were effective only in basic solution. The newly patented surface active agents for use as demulsifiers in the production of petroleum were derived from fats or fatty acids (Brainerd—*U. S.* 2,721,174, 2,724,439; DeGroot—*U. S.* 2,695,882-90, 2,723,241; Hughes *et al.*—*U. S.* 2,700,024; Smith—2,713,559; Fischer & Nowak—*U. S.* 2,708,974). A product useful in petroleum refinery desalting operations was a condensation product of polymerized drying oil acid, alkylolamine, polyhydric alcohol, and polycarboxy organic acid (Kirkpatrick *et al.*—*U. S.* 2,723,960).

ESTERS, ACIDS, ALCOHOLS, ALDEHYDES, AND OTHER FAT DERIVATIVES. Pure symmetrical diglycerides were made from dihydroxy acetone and allyl alcohol (Barry & Craig—*Can. J. Chem.* 33, 716) and from 2-*o*-benzylglycerol (Porek & Craig—*Ibid.* 1286), and α,β -unsaturated glycerides were made from 1-*o*-benzylglycerol (Fray & Polgar—*J. Chem. Soc.* 1955, 1802) in order to study the properties of the pure compounds. Ethyl stearate was condensed with ethylbenzoate in the presence of sodium to yield ethyl α -benzoylstearate which decomposed to stearophenone (Teramura *et al.*—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 64). A 45:75 mixture of adipic acid monomethyl ester and palmitic acid electrolyzed in absolute sodium methylate yielded triacontan 16%, methyl cerochidate 41.5%, and dimethyl sebacate 17% (Fuchs & Dickersbach-Baronetzky—*Fette u. Seifen* 57, 675). Higher fatty acid esters of acetals were prepared for use as intermediates, plasticizers, solvents, and surface-active agents (Harvey—*U. S.* 2,691,026).

Ricinoleic acid (Crombie & Jacklin—*J. Chem. Soc.* 1955, 1740), α -eleostearic acid (Crombie & Jacklin—*Chemistry & Industry* 1955, 1186) and 11-dodecenoic acid (Rowntree & Smith—*Ibid.* 1954, 190) were synthesized to study the properties of the pure compounds. A series of 15 keto acids were prepared from 15,16-dihydroxypalmitic acid and their infrared absorption characteristics were described (Crossley & Craig—*Can. J. Chem.* 33, 1426). 2-Methyl-2-eicosenoic, 2-methyl-2-hexacosenoic, and 2,4-dimethyl-2-pentacosenoic acids have been prepared to be tested biologically with the physiologically active C_{22} -phthienoic acid (Cason & Kalm—*J. Org. Chem.* 19, 1836). Chain extension by anodic synthesis was used to prepare cis- and trans-octadec-11-enoic and eicos-11-enoic acids (Bounds *et al.*—*J. Chem. Soc.* 1954, 4219; Linstead *et al.*—*Ibid.* 1955, 1097). The properties of the former support the contention that natu-

ral vaccenic acid is a mixture in which the trans acid is the main constituent. Properties of the other preparation suggest that the natural eicos-11-enoic acid is in the cis-form. The ω -hydroxystearic acid obtained from kamala seed oil was converted to 17-octadecenoic acid by chlorination and dechlorination and this product was oxidized with potassium permanganate to yield 1,15-pentadecane dicarboxylic acid (Gupta—*J. Sci. Ind. Res., India*, 13B, 885). Commercially prepared fatty acids were improved with regard to color stability by adding to molten caustic and recovery with inorganic acid (Logan—*U. S.* 2,727,916).

Methyl oleate, oleic acid, and ethyl linoleate were chlorinated and the characteristics of the chlorinated compounds were recorded (Lyness & Quackenbush—*J. Am. Oil Chemists' Soc.* 32, 520). To produce 1-bromoheptadecene and 1,8,9-tribromoheptadecane directly from oleic acid, Maekawa (*Bull. Nagoya Inst. Tech.* 5, 310) recommended that the silver salt be prepared and the bromination be conducted in carbon tetrachloride at below 0°. Appropriate conditions for bromination of unsaturated fatty acids with *N*-bromosuccinimide were a stoichiometric amount of reagent, 80° temperature, and 1-2 hours' time (Oyamada *et al.*—*J. Chem. Soc. Japan, Ind. Sect.* 57, 200). An investigation on alkaline materials suitable for dechlorination of the products has indicated that pyridine, potassium carbonate or ammonia reacting at 170-5° were most effective (*Ibid.* 202). In another dechlorination study cobalt compounds were preferred (Naudet & Desnuelle—*Bull. soc. chim. France* 1955, 563).

Various reactions were used to convert unsaturated acids to hydroxy acids. As high as 31% conversion of oleic acid to dihydroxystearic acid was obtained by oxidation with air at 120° for eight hours in the presence of 2% manganese dioxide (Moreno & Lopez—*Anales real. soc. espan. fis. y quim.* 50B, 489). Autoxidation techniques plus subsequent reduction were investigated for the same purpose (Coleman & Swern—*J. Am. Oil Chemists' Soc.* 32, 221). Autoxidation of the oleic acid or its ester beyond the peak of peroxide value followed by hydrogenation gave monohydroxystearic acids in high yields. Much of the peroxides were converted to carbonyl compounds rather than the anticipated hydroxy compounds. The oils of camellia, rapeseed, soybean, linseed, rice bran, castor, whale, and cuttle fish were treated in an autoclave with carbon monoxide and then with hydrogen in the presence of cobalt and thorium catalyst and the products analyzed for hydroxy acids, saturation and carbonyl compounds (Kodama *et al.*—*J. Chem. Soc. Japan Ind. Sect.* 57, 395). Hydroxymethylation occurred at one double bond, and where two double bonds had been present the remaining one was hydrogenated. Heating elaidic acid with peracetic acid in ether yielded elaidic acid oxide which was converted to 9-amino-10-hydroxystearic acid by treatment with ammonium hydroxide (Pigulevskii & Kuranova—*Zhur. Obshchei Khim.* 24, 2006). This compound could be oxidized to pelargon-aldehyde and azelaic acid. A review on hydroxylation of fatty acids and their derivatives was prepared by Naudet (*Rev. franc. corps gras* 2, 781).

Oxidation of oleic acid with nitric acid under pressure produced the dibasic acids: succinic, glutaric, pimelic, and suberic, and C_2 to C_6 monobasic acids (Kobayashi—*Science & Ind., Japan* 29, 40). Dibasic acids and other materials were produced from sperm oil fatty acids by oxidation with a mixture of oxygen and ozone (Kobayashi & Miyazaki—*Japan* 5079-'54).

A review of the various chemicals obtained by different methods of fission of castor oil was published (Henderson—*Can. Chem. Processing* 38, No. 10, 94). In an investigation of many catalysts for the preparation of 10-undecenoic acid by pyrolysis of castor oil, best yields were obtained with the presence of polyvinyl chloride (Li—*J. Taiwan Pharm. Assoc.* 6, 21). The residual oil from alkali fission of castor oil after removal of sebacic acid, 2-octanol, and methylhexylketone was fractionally distilled to heptonic, undecylic, oleic and C_8 - C_{15} saturated acids and their polymers (Kobayashi—*Science & Ind., Japan* 27, 104).

A successful procedure for the *in situ* epoxidation of unsaturated fatty acid esters has been developed employing acetic acid and hydrogen peroxide with sulfuric acid as the catalyst (Gall & Greenspan—*Ind. Eng. Chem.* 47, 147). Another new process for the preparation of peroxy fatty acids consisted in reacting fatty acids with 0.5-2.0 moles of 50-65% hydrogen peroxide in concentrated sulfuric acid solution (Parker *et al.*—*J. Am. Chem. Soc.* 77, 4037). Manufacture of fatty peroxides by contacting refined liquid unsaturated fat with oxygen and chlorophyll in visible light free of ultraviolet light was patented (Carter—*U. S.* 2,727,857).

The literature on manufacture of fatty alcohols included reduction of fatty materials with hydrogen and with sodium.

Factories and commercial procedures for the hydrogenation method were described (Bernard—*Chimie & ind.* 72, 919; Anon.—*Chem. Eng.* 62, No. 3, 124; Thompson—*Ibid.* No. 5, 108). In studies on conversion of oils native to India into alcohols by hydrogenation, coconut oil was converted to the extent of 70%, kokum, makua, white damar, and *Actin daphne hookeri* fats 45–75%, pongam oil 15%, and margosa oil was unconverted (Kane & Kulkarni—*J. Sci. Ind. Res., India* 13B, 890). In this work Co-Cu chromite catalyst and hydrogen pressures of 2500 lbs./sq. in. were used. Pure acids isolated from coconut oil were easily hydrogenated to alcohols in a vibrating autoclave with catalyst prepared from copper sulfate, sodium dichromate, ammonia and water (Matsuda—*J. Japan Oil Chemists' Soc.* 4, 10). "Lanocerine," a product obtained by high pressure hydrogenation of lanolin principally to alcohols, had better properties for many uses than the original lanolin (Rivera & Fayaud—*Riv. ital. essenze, profumi, olii, saponi* 36, 539). For preparation of alcohols from tall oil, the oil was first hydrogenated at 120°, the spent catalyst removed and the oil rehydrogenated to produce the alcohols (Hoffman & Montgomery—*U. S.* 2,727,885). Lanolin was also reduced to alcohols by treatment with sodium in xylene solution (Eisner et al.—*J. Am. Oil Chemists' Soc.* 32, 556). Here, larger quantities of the solvent are needed than are necessary when glyceride oil is reduced. Refined sardine, cottonseed, and poppy seed oils, respectively, were reduced to alcohols with sodium while dissolved in three parts of xylene or toluene and the products were fractionated to various saturated and unsaturated alcohols by vacuum distillation and precipitation as urea complexes (Masuyama—*J. Agr. Chem. Soc. Japan* 26, 524). A comparison of sodium reduction of glycerides and partial glycerides in the presence of glycerol or butanol has shown that the diglycerides do not require the presence of glycerol or butanol to bring about a rapid reduction to fatty alcohols (Ayerbe et al.—*Anales real soc. espan. fis. y quim.* 50B, 427). When the sodium reduction of fatty acid esters was made in the presence of furfural the latter could be separated pure as a lower layer on cooling to below 50° (Utiel—*Span.* 204,373).

Nitrogen derivatives of fatty acids, such as amines, amides, nitriles, and surface-active agents, were reviewed by Schwitzer (*Ind. Chemists* 31, 340). When laurionitrile and stearonitrile were hydrogenated with Raney-nickel catalyst about 19% secondary amines were obtained in addition to the primary amines (Sakakibara—*J. Chem. Soc. Japan, Ind. Sect.* 56, 497). When the hydrogenation was done in the presence of bases, such as ammonia, furfurylamine, aniline, and others, the development of secondary amines was depressed. Reacting fatty acid nitriles with maleic anhydride in an autoclave at 200–50° yielded products which may be useful as plasticizers for polyvinyl chloride (Komori et al.—*Ibid.* 885). Many pure fatty and rosin amines have been prepared and their properties recorded (Zvejniaks—*Svensk Kem. Tidskr.* 66, 316). A mixture of 9- and 10-hydroxyoctadecylamines was made to serve in the manufacture of wax-like compounds and quaternary ammonium compounds (Vander Wal et al.—*U. S.* 2,712,558). The rate of decomposition of ammonium palmitate and of simultaneous formation of palmitamide were determined and represented by equations to serve in the design of a suitable reaction vessel for continuous manufacture of fatty amides (Hollo & Gal—*Yearbook Inst. Agr. Chem. Technol. Univ. Budapest, Hung.* 1952–III–1954–VIII–18). Liquid hydrogen cyanide has been reacted at the double bonds of oleic, 10-hendecenoic, and ricinoleic acids in 85–95% sulfuric acid to yield the corresponding formamido-compounds and these were refluxed with dilute sulfuric acid to give the corresponding amino acid sulfates (Roe & Swern—*J. Am. Chem. Soc.* 77, 5408). In investigations on preparation of pungent materials from fatty materials, the morpholides of C₇–C₁₂ acids were strong pungents, whereas other amides as the pyrrolidides and the hexamethylenimide were devoid of pungency (Rice et al.—*J. Am. Chem. Soc.* 76, 3730). Thiocyanate fatty acid esters of methyl alkyl ketone cyanohydrins were manufactured for use as insecticides (Martin—*U. S.* 2,716,626). The 2- α -aminoacyl-1,3-dilurins, -dipalmitins, and -distearins have been prepared representing a combination of acidic constituents of protein and fat in one molecule (Huber—*J. Am. Chem. Soc.* 77, 112). These are oil-like water-soluble materials. Proteins acylated with fatty acid radicals to 50% of the weight of the original protein yielded products suitable as paint additives, paper size, leather waterproofers, and detergents (Keil—*U. S.* 2,723,759, *Brit.* 736,584).

DEFOAMERS, FLOTATION, ANTICORROSIVES, DRILLING MUDS, QUENCHING OILS, WATER REPELLENTS, FIRE BOMBS, WAXES, AND MISCELLANEOUS PRODUCTS. In a discussion on foaming

and foam destruction it was pointed out that the best defoamers are able to form surface films and are insoluble in the solution media (Dervichian—*Z. Elektrochem.* 59, 290). An investigation into the defoaming activity of fatty materials for fermentation liquors has indicated that among oils those containing free fatty acids are most efficient; among free fatty acids, capric acid is best and oleic, linoleic, and ricinoleic acids are very good; and among fatty alcohols those of 8–12 carbon atoms are effective (Motoyoshi—*Rept. Food Research Inst., Tokyo* 5, 87). Among fatty derivatives of diamides, ureas, and urethans the long-chain diamides proved to be effective anti-foaming agents (Agre et al.—*J. Org. Chem.* 20, 695). The newly patented compositions for defoaming use were: a mixture of mineral wax, monoglyceride of monohydroxystearic acid and an ester of polyethylene glycol (Snook—*U. S.* 2,715,614), pentaerythritol monostearate (Gibson—*U. S.* 2,715,613), a mixture of lecithin, polyoxyethylene glycol-400 dilaurate, and polyoxyethylene glycol-40 diester of lower organic acid (Jurisch—*U. S.* 2,727,009), and emulsions of fat derived polyacylated polyamines with salts of amines (Jacoby—*U. S.* 2,723,959).

A composition for inhibiting moisture accumulation on surfaces (defogging) contained polyoxyethylene sorbitan-monooleate, -monolaurate, and -monostearate, and polyoxyethylene sorbitol pentaoleate in organic solvent (Iorio—*U. S.* 2,726,962).

The use of fatty acids and their derivatives in the flotation of ores has been reviewed (Blaziot—*Oleagineux* 10, 473). The flotation of galena, pyrite, and sphalerite was intensified by adding sodium oleate to the usual agents, xanthates and butyldithiophosphate (Glembotskii & Pikkat-Ordynskaya—*Inst. Gornogo Dela. Akad. Nauk S.S.S.R.* 1, 235). The newly patented fat derived flotation agents were: a complex of oleic acid and sodium salts of mixed petroleum sulfonic acids (Pryor et al.—*U. S.* 2,698,088), and condensates of tall oil with polyalkylene polyamines containing hydroxyethyl groups (Carpenter—*U. S.* 2,710,856).

The maleic anhydride adducts of oleic acid were more effective anticorrosive additives for commercial turbine oil than were sebacic acid, castor oil fatty acid or stearic acid (Sato—*J. Oil Chemists' Soc. Japan* 3, 149; 4, 14). The newly patented fat-derived anticorrosion compounds were: reaction products of alkanol amines with the non-volatile material remaining from vacuum distillation of the acids obtained in the preparation of sebacic acid from castor oil (Lytle—*U. S.* 2,723,333), and alkaline earth metal salts of sebacic and azelaic acid (Jones—*U. S.* 2,726,215), some other patented rust inhibitors were organic materials with a small amount of emulsifier as the only fat derivative present (Fales—*U. S.* 2,701,206; Paxton—*U. S.* 2,716,611; Howell & Waddey—*U. S.* 2,724,654).

Patents were issued on several oil well drilling fluids or "muds" which contained soaps or fat derived surface-active agents as emulsifiers (Freeland—*U. S.* 2,702,787; Wilson—*U. S.* 2,698,833; Tailleux—*U. S.* 2,713,032; Fischer & Scheffel—*U. S.* 2,717,239; Fischer—*U. S.* 2,721,841; N. V. Bataafsche Petrol. Maatschappij—*Dutch* 76,028). The preparation, properties and applications of drilling emulsions was also the subject of two reviews (Henkes—*Proc. 3rd World Petrol. Cong. Hague* 1951, Sect. II, 351; Wilson—*Ibid.* 360).

A quenching oil for high temperatures was made from rice oil by deacidification and heat treating to 300° (Koyama—*Japan* 5389-54). A high specific heat was induced in such oil by addition of 3% sulfur and polymerization with air (Koyama—*Japan* 1844-54). Investigations on tinning oils have shown that with low polyunsaturation there is low consumption of oil and higher prime plate (Kubie & Werle—*J. Am. Oil Chemists' Soc.* 32, 83).

A study of wetting and emulsifying agents and fat liquor products on water absorption of leather has shown that use of oleate soap and condensation products of fat acids with protein in fat liquoring induced slower wetting and lower water absorption in the leathers than use of sulfated compounds in the process (Herfeld et al.—*Ges. Abhandl. deut. Lederinsts.* No. 11, 35). This publication contains much information on the effect of various surface-active agents and fat liquors on the properties of the leather. A water repellent boot grease and leather preservative contained menhaden oil, pine tar and beeswax (Schmid—*U. S.* 2,668,773). A water-repellent composition for textile fabrics was prepared from *N*-(hydroxymethyl)-amides of higher fatty acids mixed with quaternary nitrogen base emulsifiers (Cross & Mayhew—*U. S.* 2,692,837).

Incendiary bomb gels were prepared using, respectively, aluminum soaps of mixed iso-octic acids (Cohen—*U. S.* 2,718,462) and lanosterols (Vaterrodt—*U. S.* 2,719,782) as gelling agents.

Of two reviews on metal soaps, one contained general information on the products (Torrella—*Affinitad* 31, 349, 396), the

other was on uses in floor waxes and in shoe creams (Kselik—*Seifen-Öle-Fette-Wachse* 81, 222). Hydrocarbon-soluble zirconium compounds were prepared by heating $Zr(OR)_4$, where R is an alkyl group of 1-12 carbons, with 0.5-4.0 equivalents of the fatty acids of linseed oil (Balthis—*U. S.* 2,681,922). The product is useful as a paint ingredient, as a rust inhibitor, and as a textile water-repellent. The tin soap of ricinoleic acid was found to be more soluble in organic solvent than those of aluminum, barium, calcium, magnesium, and zinc, and it did not undergo phase separation, swelling, nor thixotropy (Merz—*J. Am. Oil Chemists' Soc.* 32, 177). Amines dissolved lead and zinc soaps in the following order: secondary > primary > tertiary (Chatterjee & Palit—*J. Indian Chem. Soc.* 31, 421). This work suggested that the diethanolamine solutions of the soaps are suitable for treating textiles.

A simulated snow coating contained 12% thermoplastic material, 12% stearic and/or palmitic acids dissolved in a solvent propellant (Bunting—*U. S.* 2,716,637).

COATINGS, RESINS, AND PLASTICS. The general informative communications on these subjects were written on: liquid oiticica oil and its industrial uses (Huffman—*Vernici* 7, No. 3, 31), tobacco seed oil (Rao—*Paintindia* 2, No. 1, 57), Indian tobacco seed oil for varnish and paints (Kapadia & Aggarwal—*J. Sci. Ind. Res. India*, 13B, 352), fish oil in the varnish industry (Salvi—*Pitture e vernici* 11, 37), tall oil in the paint industry (Brushwell—*Am. Paint J.* 38, No. 48, 48; No. 51, 60; 39, No. 6, 80), history and uses for dehydrated castor oil fatty acids (Rowe—*Paint Technol.* 19, No. 210, 79), research and future markets for drying oils (Wilhelmy & Barr—*J. Am. Oil Chemists' Soc.* 32, 204), autoxidation and oxidative polymerization (Lumberg—*Ibid.* 207), problems in modification of drying oils (Terrill—*Ibid.* 208), problems in using drying oils in protective coatings (Fitzgerald—*Ibid.* 210), mechanism of stand oil formation (Berger—*Peintures, pigments, vernis* 30, 1019), structure of bodied oils (Petit—*Paint Varnish Production* 45, No. 2, 37), pentaerythritol in synthetic oils and resins (Schlenker—*Fette u. Seifen* 57, 87), review on alkyl resins (Meziva & Hanzlik—*Chem. Prumysl* 4, No. 29, 138), nomograph for formulation with alkyls (Wangness *et al.*—*Paint Oil & Chem. Rev.* 117, No. 24, 80), properties of modified alkyl resins as related to glycerolysis (Kiselev & Belyaeva—*J. Appl. Chem. U.S.S.R.* 26, 1037), fatty acids for manufacture of alkyl resins (Earhart—*Rev. franc. corps gras* 1, 541), alkyl resins (Robinson—*Can. Chem. Processing* 39, No. 3, 38; No. 4, 100), kamala seed oil alkyl resins (Sharma & Aggarwal—*J. Sci. Ind. Res. India* 13B, 791), problems in copolymerization (Scheiber—*Fette u. Seifen* 57, 81), analytical study of polymerized linseed oils (Vaillant—*Rev. franc. corps gras* 2, 21, 159), vinyl stearate plastics (Port *et al.*—*Ind. Eng. Chem.* 47, 472), cost of vinyl stearate (Redfield *et al.*—*Ibid.* 1707), polyamide-epoxy resin products for protective coatings (Witteoff *et al.*—*Fette u. Seifen* 56, 793), and plasticizers derived from fats (Swern—*Rev. franc. corps gras* 2, 75).

A new concept on mechanism of autoxidation of unsaturated fatty acids was based on collision of oxygen at the three carbon system of a double bond, development of a certain activated state, electron transfer, hydrogen atom transfer, and development of six membered rings (Kahn—*J. Chem. Phys.* 22, 2090; *Can. J. Chem.* 32, 1149). Since the ideas involved did not agree with the current theories of Farmer they were polemically discussed (Bateman—*J. Chem. Phys.* 22, 2090). A kinetic study of polymerization of eleostearate has shown agreement with second order reaction as for a bimolecular Diels-Alder addition (Pasche & Wheeler—*J. Am. Oil Chemists' Soc.* 32, 469). The all *trans*-eleostearate reacted faster than the *cis,trans,trans*-linolenate in agreement with known *cis,trans* effects on diene activity. The polymerization of linolenate followed a first order reaction. In continuing this work with a study of color formation from eleostearic acids, it was suggested that this involves dehydration to ketones of the hydroperoxides formed, enolization to conjugated trienes, cyclization to a cyclic ketone, and polymerization of this to colored products (*Ibid.* 473). Thus it was indicated that color in commercial products arises from arachidonic acid and acids of five and six double bonds.

Some studies on mechanism of autoxidation were based on spectroscopic observations. Such work by Privett (*Ann. Rept. Hormel Inst.* 1954-55, 9) indicated that *trans* double bonds and *trans-trans* conjugation produced in linoleate autoxidation arise from concurrent oxidation of the hydroperoxides. *Cis-trans* diene conjugated hydroperoxides were formed in addition to *trans-trans* isomers in the autoxidation of methyl linoleate indicating that *trans* double bonds invert to the *cis* configuration upon shifting into a conjugated position. Wolffs' (*Peintures, pigments, vernis* 31, 612) spectrophotometric stud-

ies were on bodying of linseed oil. He pointed out the variations caused in the ultraviolet by formation of peroxides, ketones, conjugation, etc., and how these were influenced by heat treatment and decolorizing with earths. Crecelius *et al.* (*Ind. Eng. Chem.* 47, 1643) made similar observations in the infrared region on the drying of films of linseed oil and dehydrated castor oil.

A study of catalysis of the autoxidation has suggested that the primarily developed hydroperoxide is an autocatalyzer and that metal compounds accelerate radical formation from hydroperoxide (Kern & Willersinn—*Angew. Chem.* 67, 573; *Makromol. Chem.* 15, 1, 15, 36). A study of catalytic polymerization of 1,4-pentadiene was interpreted to indicate that quinones catalyze the isomerization step by a free radical mechanism and sulfur dioxide and alkali by a polar mechanism (Grummitt & Chudd—*J. Am. Oil Chemists' Soc.* 32, 454). In this work the quinones and sulfur dioxide catalyzed formation of high polymers, but sodium hydroxide catalyzed formation of both polymer and dimer. In similar work on drying oils, the influence of 15 catalysts and 15 inhibitors were determined (Sims—*J. Am. Oil Chemists' Soc.* 32, 94). Materials such as sulfonic acids, chloroacetic acid, and halogens increased polymerization 20-fold at 240° and 3- to 4-fold at 310°. Quinones, certain alkylxyaryl amines, mercaptans, and commercial resins were also effective. A comparison of uncatalyzed and catalyzed polymerization of methyl linoleate has suggested that the function of the catalyst was to abstract an α -methylene hydrogen atom to give rise to radicals that produce dimers or conjugate to an isomer (Rushman & Simpson—*Trans. Faraday Soc.* 51, 230, 237). Lead salts were very effective for drying of conjugated oils, whereas the effect was small for non-conjugated oils (Kaufmann & Gulinsky—*Fette u. Seifen* 57, 677). The catalytic activity of lithium, copper, silver, magnesium, zinc, lead, and other metal soaps of erucic and petroselinic acids has been recorded (Skellon & Andrews—*J. Applied Chem.* 5, 245). These results were correlated with valence and position of the metals in the periodic system.

Chlorides of aluminum, titanium, iron, and bismuth caused solutions of tung oil in organic solvents to gel (Petit & Cazes—*Bull. soc. chim. France* 1954, 1428). Adverse results in catalyzing polymerization of drying oils with boron trifluoride were inhibited by adding the catalyst diluted with nitrogen (Petit & Cazes—*Peintures, pigments, vernis* 30, 823) or by introducing the catalyst only after the charge has undergone considerable oxidation and polymerization (Kiebler *et al.*—*U. S.* 2,717, 332). The conventional drying catalysts can be replaced by complexes of the metals with diamines or difunctional amines possessing resonant structures and by certain amines of large steric requirements (Zettlemoyer & Myers—*Ind. Eng. Chem.* 46, 2220). Linseed oil was bodied with various common driers and comparisons were made based on the properties of films produced (Montequi & Morales—*Anales real soc. espan. fis. y quim.* 50B, 859). Most of the common driers induced rapid drying, hardness, and resistance to cold water, hot water and alkali; with sulfur catalysts the films dried slowly but were exceptionally resistant to alkalies. When drying of oil films was accelerated by addition of organic peroxide an initial weight loss occurred before the film gained weight (Bartosik—*Farbe u. Lack* 61, 368). The weight losses were found to be due to loss of acrolein, fatty aldehyde, and fatty acids which could be collected on a sharply cooled glass plate above the drying film. Antioxidants inhibited weight increase of drying oil films in the following order of effectiveness: pyrogallol > pyrocatechol > naphthol > hydroquinone > resorcinol > thymol > diphenylamine > p-toluidine (Toyama & Hirabayashi—*Mem. Fac. Eng. Nagoya Univ.* 6, 59).

Tung oil, linseed oil, cottonseed oil, and pentaerythrol esters of the fatty acids were isomerized and polymerized and the characteristics of the products compared (Drinberg & Chervinskaya—*Zhur. Priklad. Khim.* 27, 983, 1307). Varnishes from tung oils dried fastest and the pentaerythrol esters of the cottonseed acids were next best. However, the pentaerythrol esters had a tendency to retain some tackiness. The blowing of linseed oil studied with respect to characteristics of the final films has indicated that oils intended for quick-drying finishes should be blown at low temperature without catalyst so as to produce a high peroxide content; whereas oils to be used with polar film formers should be blown with cobalt drier so as to have a high hydroxide content (Wilborn & Morgner—*Fette u. Seifen* 57, 178).

Data have been recorded to show the relationship of the viscosity of heat-polymerized linseed, safflower, and tung oils to the polymerization time and percentage of polymeric glycerides (Sims—*Ind. Eng. Chem.* 47, 1049). Tung oil contained the least and safflower the most polymer for a given viscosity.

Viscosity of linseed oil during polymerization has been related to the disappearance of linoleic and linolenic acids (Vaillant—*Rev. franc. corps gras* 2, 394). At the beginning linoleic disappeared more rapidly until one poise viscosity, then linolenic acid disappeared more rapidly and even disappeared at a rate seven times that for linoleic.

Attempts to use solubility in furfural to follow the oxidation during bodying was unsuccessful because solubility was augmented by formation of polar groups and simultaneously lowered because of condensation and polymerization (Angelescu & Esanu—*Acad. Rep. Populare Rom. Studii Cercetari Chim.* 2, 27). Fluorescence of heated and unheated linseed, safflower, tung, and oiticica oils has been recorded (Sims & Cooper—*J. Am. Oil Chemists' Soc.* 32, 381). The relationships among these data could not serve as a comparison for extents of polymerization.

The properties of dried films were used as criteria to evaluate some oils. Oil thickened by air blowing dried much faster and adhered to glass test plates much better than oils thickened without access to air (Taniewski—*Przemysl Chem.* 9, 461). The swelling of test oil films in water was found to be related to the composition of the oils, their treatment, and their quality, and was used to compare Danish linseed oils with foreign products (Singer—*Farbe u. Lacke* 60, 189, 261, 298, 342, 391), to determine the effects of conjugation of oils and additions of rosin-modified phenolic resins to the oils (von Mikuseh & Mebes—*Farbe u. Lack* 61, 9), and to evaluate films made from drying oils obtained by chlorination and dechlorination (Wekua & Bergmann—*Ibid.* 324). The yellowing of films depended on the nature of the acid constituents of an oil, in the following order of increasing yellowing: oleic, linoleic, eleostearic, and linolenic; and the order of decreasing gloss was: linolenic, linoleic, oleic, eleostearic (Johnston & Fitzgerald—*Offic. Dig. Federation Paint Varnish Production Clubs* 27, 280). Presence of natural waxes in drying oils caused turbidity and opaqueness in films (Kaufmann & Schuppan—*Fette u. Seifen* 57, 402). The wrinkling of films was explained thus: a surface film formed by rapid polymerization becomes swollen by monomer until the expansive forces cause a folding of the swollen skin which appears as a wrinkle (Burrell—*Ind. Eng. Chem.* 46, 2233).

Several means were used to convert non-drying and semi-drying oils to drying oil usage. Heat treatment with polybasic organic acids was the method used on oils from the Ongokea species (Kaufmann—*Swed.* 143,349), and cuttle fish oil (Marumo *et al.*—*J. Chem. Soc. Japan Ind. Sect.* 58, 424, 430, 432). Film formation properties were induced into cottonseed oil by oxidative bodying with pentaerythritol and rosin (Ivanova—*Zhur. Priklad. Khim.* 28, 718) and bodying and mixing with tung oil (Osnoš & Il'ina—*Masloboino-Zhirovaya Prom.* 20, No. 4, 12). Soybean oil treated to induce conjugation was said to yield films with better water repellency than those of linseed oil (Arimune—*Japan* 5390-54). A process used on chrysalis oil involved concentrating the unsaturated acids by urea-precipitation technique, isomerizing these, and bodying (Maruta & Suzuki—*J. Chem. Soc. Japan Ind. Sect.* 27, 582). A paint panel test of four years' duration has shown that products made from soybean oil that was chlorinated and dechlorinated to increase unsaturation can be used successfully as a drying oil in paint making (Lewis *et al.*—*J. Am. Oil Chemists' Soc.* 32, 300). Mixed esters of aromatic monocarboxylic acids, rosin acids, and fatty acids of soybean oil were patented for protective coating usage (N. V. Bataafsche Petrol. Maatschappij—*Dutch* 76,235). Nonconjugated unsaturated fatty acids were converted to conjugated products by reacting their soaps with hypochlorous acid to form the chlorohydrin, reacting the chlorohydrin with acetic anhydride, acetic acid, and sodium acetate to form the diacetate, and pyrolyzing to the conjugated acid (Arnold—*U. S.* 2,698,857). Oleic acid was converted to an elastic film by heat treatment at 160° (Taranenko—*Zhur. Priklad. Khim.* 27, 1024). Accordingly it was used as a substitute for linseed oils in the manufacture of coated woven brake bands.

The methods for converting castor oil into a drying oil product involved dehydroxylation by heat in the presence of a catalyst. Operational details with the following catalyst were published: sulfuric acid (Yasuhara & Kobayashi—*Sci. & Ind., Japan* 28, 42), sodium bisulfate (Sirasamban *et al.*—*J. Sci. Res., India* 13B, 349) and combinations of clays and acid (Chen & Chang—*Chemistry, Taiwan* 1, 35; Nakajima & Kosuge—*Japan* 2837-54). Continuous operation by passing the oil and catalyst through a heating zone was patented (Carter *et al.*—*U. S.* 2,711,416). Castor oil was partially converted to fatty acid estolides and then dehydrated to yield material suitable for coating compositions (Polly & Cunningham—*U. S.*

2,681,921). Heat treatment of dehydroxylated oils with alkaline earth oxide at 400° stabilized the color of the products (Humm—*U. S.* 2,727,047). The conjugated acid, ximenynic or santalbic, was prepared from castor oil by dehydroxylation and other steps so that it may be compared with the natural acid (Grigor *et al.*—*J. Chem. Soc.* 1955, 1069).

Products ranging from improved drying oils to resinous solids were made by copolymerizing fatty material with: styrene (Crofts—*J. Appl. Chem.* 5, 88; Slanky—*Paint Manuf.* 25, 54; Dyer & Weissgerber—*U. S.* 2,698,840; Bradshaw & Evans—*U. S.* 2,698,839; Munday & Malvan—*Brit.* 711,141; Chem. Werke Albert—*Brit.* 721,938; Seado Kunsttharsind. N.V.—*Dutch* 75,341, vinyl compounds (Port *et al.*—*Ind. Eng. Chem.* 47, 472; Eeky *et al.*—*J. Am. Oil Chemists' Soc.* 32, 185, 350; McNabb—*U. S.* 2,689,834; Ropp—*U. S.* 2,727,871-3; Lewis Berger & Sons Ltd.—*Brit.* 714,432), butadiene polymer (Koencke & Mahan—*U. S.* 2,709,662), allyl compounds (Chu *et al.*—*Chemistry, Twain* 1, 25; Swern—*U. S.* 2,715,132), styrene and cyclopentadiene (McKenna—*U. S.* 2,639,231), styrene and vinyl hydrocarbons (Wakeford—*Brit.* 713,328), styrene, methacrylates, and alkyds (Beavers & Urban—*U. S.* 2,727,870), allyl and vinyl ethers (Giammaria—*U. S.* 2,704,277), styrene, allyl compounds, and alkyds (Cadwell & Petropoulos—*U. S.* 2,713,039), unsaturated hydrocarbons (Block—*U. S.* 2,719,164; Mundy—*J. Oil & Colour Chemists' Assoc.* 38, 219), alkyd resins (Mleziva *et al.*—*Chem. Prum.* 4, No. 29, 442; Levasseur—*Peintures, pigments, vernis* 30, 44, 134; Park—*Can. Paint & Varnish Mag.* 29, No. 5, 30; Council Sci. & Ind. Res.—*Indian* 50,758, and epoxy compounds (Tess—*J. Am. Oil Chemists' Soc.* 32, 291; Korphage—*Fette u. Seifen* 57, 696; Theile & Colomb—*Ibid.* 686; Greenlee—*U. S.* 2,694,694; Crecelius—*U. S.* 2,698,308; Osdal—*U. S.* 2,703,765; Renfrew *et al.*—*U. S.* 2,705,223; Witteoff—*U. S.* 2,707,708; Narracott—*U. S.* 2,709,690; Fisch—*U. S.* 2,712,535). Resinous material was also made from ω -(2-furyl) substituted fatty acids (Moldenhauer *et al.*—*Ger.* 825,272), condensation of resoreinal and *m*-cresol with tung oil (Mehta *et al.*—*Paintindia* 4, 29), reacting protein, ligno-cellulose, and fatty oil (Rao *et al.*—*U. S.* 2,702,754) and polyamide derivatives of fats (Witteoff—*U. S.* 2,728,737).

Ultraviolet spectrometric data on styrenated fatty acids and alkyd resins has been recorded to serve in the analysis of styrenated alkyd resins (Hirt *et al.*—*Anal. Chem.* 27, 226). A graphical method for the analysis of styrenated linseed oils was based on the refractive index and density of the sample (Boelhouwer *et al.*—*Anal. chim. acta* 11, 74). Polymer distribution in drying-oil-modified alkyd resins was determined by a solvent separation system (Wilson & Robson—*Off. Dig. Federation Paint Prod. Clubs* 27, 111). In this work improved paints were made by using alkyds after removal of the very high and the very low polymers. Investigations on determination of pentaerythritol in alkyd resins have indicated that some of the pentaerythritol was thermally decomposed during manufacture of the resin (Mleziva—*Fette u. Seifen* 57, 691). Attempts to devise a procedure for estimating the phenolic hydroxyl groups in resins evolved in the discovery that phenols can be directly esterified with fatty acids (Aelony—*J. Am. Oil Chemists' Soc.* 32, 170). Hypothetical suggestions made regarding the deterioration of alkyd films include oxidation of unsaturated oil during baking, decomposition of conjugated carbonyl groups in sunlight to produce carbon monoxide, and ultimate decomposition of the glyceryl phthalate to volatile products (Fitzgerald—*ASTM Bull.* No. 207, 65).

PLASTICIZERS. The fat derivatives recommended for use as plasticizers were: glycol esters of dimerized linoleic acid (de Surville—*J. rech. centre natl. Lab. Bellevue, Paris*, No. 30, 169), arylstearonitriles (Watanabe & Masuzawa—*J. Chem. Soc. Japan, Ind. Sect.* 57, 154), esteramides prepared from fatty acids and amino alcohols (Silverstein *et al.*—*J. Am. Oil Chemists' Soc.* 32, 354), reaction products of β propiolactone and α - and β -eleostearates (Hoffmann *et al.*—*Ibid.* 533), acetylation products of compounds obtained by the sodium reduction of castor oil (Komori *et al.*—*J. Chem. Soc. Japan, Ind. Sect.* 57, 740), epoxy esters of fats and fatty compounds (Witnauer *et al.*—*Ind. Eng. Chem.* 47, 2304), water-insoluble metal soaps (Vennels—*Plastics, London* 20, 93), tetrahydrofurfuryl oleate, methoxyethyl oleate, phenoxyethyl oleate, and oleoyl diacetyl glyceride (Murai & Akazome—*J. Japan Oil Chemists' Soc.* 4, 125).

FATTY MATERIAL IN LUBRICATION, TEXTILE OILING, AND METAL WORKING. General informative communications pertaining to fatty lubricants were written on: recent advances in grease technology (Wakana—*J. Oil Chemists' Soc., Japan* 3, 247), and lubricating greases as disperse systems (Vinogradov—*Trudy V.S. Khim. i Pererabotke Nefti* 1953, 151).

Considerable physical data on lubricants or lubricant consti-

tients were recorded and are being cited in the following with brief annotation so that brevity is maintained in this review. Typical grease-like soap-oil dispersions passed through three major structure types as their temperature was increased: microcrystalline paste, gel, and solution (Hotten & Birdsall—*Ind. Eng. Chem.* 47, 447). Electron microscopic observations on calcium and sodium greases showed no definite structure, whereas addition of calcium acetate induced submicroscopic structures (Vinogradov *et al.*—*J. Appl. Khim. U.S.S.R.* 28, 52). The viscosity and thixotropic behavior of lubricant mixtures of ceresin, synthetic petroleum wax, and petroleum oil were recorded (Lebedov & Vinogradov—*Kolloid Zhur.* 17, 38). The above characteristics and shear stresses were determined on several commercial greases (Keil & Presting—*Chem. Tech., Berlin*, 6, 436). Syneresis of high consistency lubricants was found to be highest at low soap concentrations (Klimov—*Neftyanoe Khoz.* 32, No. 11, 62). Viscoelastic behavior of greases has been related to structure of its fibers and aggregates (Hutton & Matthews—*Proc. 2nd Intern. Congr. Rheol.* 1953, 408). A linear equation has been derived which related apparent viscosity and rate of shear to mineral oil viscosity, worked penetration, and soap content (Dreher *et al.*—*NLGI Spokesman* 18, No. 10, 8). Equations have also been designed for the rates of production of three types of deformation in greases by application of stress (Velikovskii—*Kolloid Zhur.* 16, 406). Length-width ratio of soap fibers calculated before and after shearing did not correlate with mechanical breakdown of grease consistency (Renshaw—*Ind. Eng. Chem.* 47, 834). The shear resistance of films of potassium palmitate, iron stearate and sodium soaps were measured (White—*Lubrication Eng.* 10, 340). The effect of adding several fatty acids to the moistened surface of a friction tester was examined at 20 to 140° and the variation of dynamic and static frictional coefficients of fatty acid with temperature thus obtained was discussed (Sakurai *et al.*—*J. fuel Soc. Japan*, 31, 554).

The observation that heat was given off when soaps were added to vasoline was interpreted to indicate that formation of addition compounds was involved (Demchenko *et al.*—*Ukrain. Khim. Zhur.* 20, 635; *Dopovidi Akad. Nauk. Ukr. R.S.R.* 1952, 284). The conductivities at 25° and other properties of toluene solutions of oleates of zinc, copper, lead, magnesium, and calcium show a gradation from zinc, which is almost nonpolar to calcium oleate which appears to be wholly ionic (Nelson & Pink—*J. Chem. Soc.* 1954, 4412). The conductance increased with increase in concentration and decrease in temperature. The effects were attributed to association of molecules and ions into aggregates. The data are pertinent to use in transformer oils.

X-ray diffraction studies of built-up multilayers of strontium stearate and palmitate showed duplication, indicating that two phases are present (Bisset & Iball—*Trans. Faraday Soc.* 50, 421). Other soaps of bivalent metals, such as barium, calcium and magnesium soaps did not show this pattern.

Spectrographic methods were designed for analyzing lubricating oils for additives (Gunn—*Anal. Chem.* 26, 1895), for analyzing lubricating greases for metals (Key & Hoggan—*Ibid.* 1900), and for study of impurities and decomposition of metal soaps of phenylstearic acid (Kagarise—*J. Phys. Chem.* 59, 271). The detergency of lubricating oils was assessed by the photometric determination of the amount of carbon black remaining in suspension after diluting with kerosene and by centrifuging a sample of oil to which carbon black was added (Faust—*Lubrication Eng.* 10, 345).

Homogenizing under high pressure and sudden release of pressure induced lower penetration and higher dropping points in lubricant greases (Armstrong—*U. S.* 2,704,363). A system of melting a grease and rapidly cooling while subjecting to mechanical treatment was said to lead to efficient use of the gelling soaps (N.V. Bataafsche Petrol. Maatschappij—*Dutch* 76,475).

Three patents on manufacture of greases pertained to drying the metal soap so that it would dissolve or gel better when mixed with the oil components (Ashley—*U. S.* 2,702,792; Cunder & Licata—*U. S.* 2,716,073; Morway—*U. S.* 2,719,122). An all-purpose grease contained soaps of calcium mixed with soaps of barium, magnesium, and/or strontium (Forster—*U. S.* 2,708,659). A product of improved mechanical stability was made with complex soap thickener of both high and lower molecular weight acids (N.V. Bataafsche Petrol. Maatschappij—*Dutch* 75,559-60). Thixotropic (Morway & Bruggmann—*U. S.* 2,710,838) and very stiff greases (Lux & Parker—*U. S.* 2,699,428) were made of mixed soaps of fatty and polycarboxylic acids. Greases containing special combinations of soaps of hydroxy and non-hydroxy acids were patented (Culnane *et al.*—*U. S.* 2,721,844; Mikeska—*U. S.* 2,712,527). One new

grease comprised di-2-ethylhexyl sebacate thickened with the lithium salt of the high temperature and pressure reaction product of butyl oleate with carbon monoxide and hydrogen (Mikeska & Morway—*U. S.* 2,719,124).

In some of the newly patented greases part of the soap thickener was replaced by other materials. These substitute thickeners included silica aerogels (Hughes *et al.*—*U. S.* 2,711,393; Puddington & Sirianni—*U. S.* 2,714,091; N.V. Bataafsche Petrol. Maatschappij—*Dutch* 75,308, bentonite-resin polymer mixtures (McCarthy—*U. S.* 2,704,276, *U. S.* 2,710,837), organic silane compounds (Orkin—*U. S.* 2,701,803), phenylene diamides (Hotten—*U. S.* 2,709,157), certain resinous residues of propane extraction of paraffins (Morway *et al.*—*U. S.* 2,723,957), waxy polymers of fluoroethylene compounds (Conner—*U. S.* 2,706,715; Benning & Hill—*U. S.* 2,695,880), and aryl-carbamyl resins (Swakon & Brannen—*U. S.* 2,710,839-41).

Greases, mainly lithium soap greases, were rendered non-corrosive by additions of small amounts of alkylene dicarboxylic salt (Merker—*U. S.* 2,722,516), alkyl benzene compounds and their sulfides (Dilworth *et al.*—*U. S.* 2,690,998, 2,721,845), and soluble metal alkyl salicylate (Culnane—*U. S.* 2,714,092). A sulfurized fatty additive for lubricants was rendered noncorrosive by heat treating with olefinic hydrocarbons (Waddey *et al.*—*U. S.* 2,703,318).

Anti-wear characteristics of aluminum soap greases were enhanced by dispersing calcium oxide into it (Hotten—*U. S.* 2,719,826). A grease for blast furnace equipment lubrication was based on lithium soap and had a very high dropping point (Jenkins—*Iron Age* 175, No. 6, 104). A lubricant for facilitating mounting and demounting of auto tires consisted of mahogany soap, and aluminum stearate in a major portion of lubricating oil (McGrogan—*U. S.* 2,698,834). A lubricant for marine engine and machinery encountering large amounts of water contained a major portion of petroleum oil, with small amounts of glycerol esters of oxidized petroleum and lecithin (Francis & Shoemaker—*U. S.* 2,718,502).

Lubricating oils were improved with various fatty derivative additives. The compounds used to depress pour point and/or improve viscosity index were: alkylated aromatics compounds (Dean *et al.*—*U. S.* 2,688,643), esters of fatty alcohol and tripolymers of acyclic unsaturated hydrocarbon (Linsk & Scantley—*U. S.* 2,710,282-3), esters of polycarboxylic acids, fatty alcohols, and vinyl compounds (Popkin *et al.*—*U. S.* 2,721,877), copolymers of maleic anhydride, vinyl compounds and fatty amines (Giammaria—*U. S.* 2,698,316, *U. S.* 2,704,277), hydrogenated castor oil (Vaughn—*U. S.* 2,712,518), polymerized ester of alkyl alcohol and alcohols obtained by hydrogenating coconut oil (Bartlett—*U. S.* 2,718,504), and aluminum soap along with fatty acid salts of alkylamines (Sakurai & Koike—*Japan* 5232-54). The patented additives for gear lubricant oils were: reaction product of sulfurized sperm oil, phosphorus trichloride, and ethylene oxide (Smith *et al.*—*U. S.* 2,722,517) a mixture of lead naphthenate, sulfochlorinated sperm oil, and chlorinated paraffin wax (Sokol & Coppoe—*U. S.* 2,701,237), a mixture of isopropyl oleate and tributyl phosphate (Lowenstein-Lom—*U. S.* 2,699,429), and sulfurized unsaponifiable portion of wool grease (Sunde—*U. S.* 2,710,836). A condensate of phthalic anhydride, glycerol, and stearic acid was used as an antifricition additive (Sirianni & Puddington—*U. S.* 2,689,224). Addition of fatty acid sugar esters to lubricant oils inhibited harmful piston deposits (Clayton *et al.*—*U. S.* 2,700,022). The surface active agents patented for addition to lubricant oils were: certain fat derived quaternary ammonium compounds (Stayner & Stayner—*U. S.* 2,697,656-7), and tall oil pitch-phosphorus reaction products (Hook & Beegle—*U. S.* 2,717,241).

A hydraulic transmission fluid contained mineral oil, methacrylate ester polymer, and sulfurized fatty material (Heisig & Murphey—*U. S.* 2,710,842).

In a symposium on metal-working oils review papers were presented on: mechanism of friction and lubrication in metal working (Bowden & Tabor—*J. Inst. Petroleum* 40, 243), effectiveness of chlorinated hydrocarbon compounds as cutting-oil additives (Wolfe *et al.*—*Ibid.* 253), physical factors involved (Stabler—*Ibid.* 256), mechanical testing of the oils (Morton & Tourret—*Ibid.* 261), economical application of cutting fluids (Grisbrook—*Ibid.* 269), and evaluation of cutting fluids (Chisholm—*Ibid.* 271). A petroleum base cutting oil was improved by addition of a partial fatty ester of sorbitan and polyoxyethylene (Oathout—*U. S.* 2,689,222).

A patented textile lubricant contained mineral oil, alkyl phenol, low molecular weight esters of castor oil acids, sulfonated fatty oil, fatty acids, and alkyl phosphate (Duke & Hohing—*U. S.* 2,727,860).

Deterioration of Fatty Materials

REVIEWS. The reviews and general information communications pertaining to deterioration of fatty materials were written on: autoxidation of methyl oleate (Swern & Coleman—*J. Am. Oil Chemists' Soc.* 32, 700), oxidation processes in butter (Fredholm—*Tek. Tidskr.* 85, 339), stability of pound-packaged butter (Peterson—*Fette u. Seifen* 57, 268), rancidity and use of antioxidants (Smith—*Am. Perfumer Essent. Oil Rev.* 66, No. 2, 61), rancidity and its estimation (Hajek—*Prumysl Potravin* 4, 437), spectrophotometric studies on rancid oils (Wolff—*Parfumerie mod.* 46, 53), antioxidants and determination of stability (Högl & Wenger—*Mitt. Lebensm. Hyg.* 45, 335, 364), stabilization of fats (Bauer—*Dept. Lebensm.-Rundschau* 50, 109, 146, 173, 192, 218, 259), antioxidants and their detection (Janecke—*Ibid.* 51, 121), natural and synthetic antioxidants (Smith—*Am. Perfumer Essent. Oil Rev.* 65, No. 4, 54), use of antioxidants (Ruys—*Tidskr. Hermetikind.* 41, 244), application of gallic acid esters as antioxidants (Sabalitschka—*Seifen-Öle-Fette-Wachse* 80, 542), antioxidants for fats (Hofman—*Prumysl Potravin* 6, 376), antioxidants for vitamin A (Mori—*Vitamins, Japan* 8, 193), ascorbic acid and its derivatives as antioxidants (Herisset—*Publ. by Impr. Moderne, Angers* 1954), and testing stability of textile processing oils (Kehren & Scharroba—*Meiland Textilber* 36, 735).

TESTS FOR DETERIORATION, STABILITY, AND ANTIOXIDANTS. The thiobarbituric acid reaction for fat oxidation paralleled other spoilage tests, such as peroxide value, aldehydes or Kreis test, when testing linolenates or linoleates but was negative for oleate oxidation (Kenaston *et al.*—*J. Am. Oil Chemists' Soc.* 32, 33). It was 30–80 times more sensitive for linolenate than for linoleate of the same peroxide value. That this color reaction is due to the condensation of thiobarbituric acid with aldehydes present in the oxidized fats has been confirmed by the above work and the work of Jennings *et al.* (*Food Res.* 20, 13). In a procedure developed for the application of the test to cereal and baked products, the red compound of the reaction was separated from colored interfering natural materials by adsorption on cellulose (Caldwell & Grogg—*Food Tech.* 9, 185). The α,β -unsaturated aldehydes which are considered responsible for the oxidized flavor of dairy products react in this test (Patton & Kurtz—*J. Dairy Sci.* 38, 901). The intensity of the test and the development of aldehydes, oxidized flavor, and thiobarbituric reaction in milks were intensified when traces of copper were present.

New suggestions were made for improvement of the peroxide value procedure. To obtain fat for the test from dairy products, the samples were demulsified by warming in aqueous solutions containing sodium salicylate and butanol and then centrifuging (Pont—*Australian J. Dairy Tech.* 10, 72). The procedure could be simplified by colorimetric determination of the free iodine rather than titrating the iodine in the test (Siddigi & Tappel—*Chemist Analyst* 44, 52). A rapid colorimetric peroxide procedure was based on using filter paper as the sample carrier and spraying with a special ferrous sulfate-ammonium thiocyanate reagent (Täufel & Vogel—*Fette u. Seifen* 57, 393). In the colorimetric indophenol method the need for heating was eliminated by addition of ferric compounds to the reagent (Glavind & Hartmann—*Acta Chem. Scand.* 9, 497). Also, with this modification plus the presence of magnesium chloride, phospholipides may be successfully analyzed for peroxides.

Epoxides may develop in fats during certain cooking operations because of excess heating. The methods recommended for measuring such epoxides were based on a color reaction with 2,4-dinitrophenol or with trimethylamine-hydrochloride (Seelkopf—*Fette u. Seifen* 57, 111).

Thomas (*Iowa State Coll. J. Sci.* 29, 517), in studies on measuring spoilage of milk fats, found that the differences between the hydrogenation iodine value and the same value determined with reagents increased as the flavor score decreased. Similar work with margarine has indicated that titratable acidity, the Lea peroxide value, and amount of volatile reducing material correlate best with organoleptic evaluation (Schoeneich & Streich—*Rozniski Panstowego Zakladu Hig.* 5, 227). The acidity and peroxide value were considered to be the most significant tests for measuring the degree of freshness of butter (Cerutti—*Ann. sper. agar., Rome*, 8, 1715). A Brazilian decree stated that butter must be considered rancid if its oxidizability index is 15 or more (Vas Pereira—*Rev. quim. e farm. Rio De Jan.* 20, No. 1, 33). The oxidizability index is a measure of the permanganate oxidizable material in a dilute sulfuric acid extract of the sample.

An apparatus and method designed for measuring degree of reversion and rancidity of edible oils was based on the amount

of carbonyl compounds diffused from a sample into a stream of nitrogen under specific conditions (Chang & Kummerow—*J. Am. Oil Chemists' Soc.* 32, 341). The carbonyl compounds were trapped and determined spectroscopically.

The fluorescence of soybean lecithin increased in a linear fashion with increase in browning of the product (Scholfield & Dutton—*J. Am. Oil Chemists' Soc.* 32, 169). The fluorescence measurement was suggested as a simple index of browning of the product.

Two communications were on improvements of a method for the determination of water-insoluble acids which are a measure of the quality of butter or cream. The method for butter was hastened by using water warmed to 55–60° in the extraction step (Ensminger—*J. Assoc. Off. Agr. Chemists' 38*, 183). The method was simplified for application to cream and applied to the study of the effect of storage conditions and lactic acid on the development of the water-insoluble free fatty acids (Crowe—*J. Dairy Sci.* 38, 969).

A test on using glass versus iron tubes in the Swift accelerated oxidizability test in testing vegetable oils has shown that the iron tubes cause destruction of tocopherol and yield lower stability values (Luckman & Melnick—*J. Am. Oil Chemists' Soc.* 32, 175). Presence of isopropyl citrate greatly retarded tocopherol destruction and protected the oils. This accelerated oxidizability test was modified for application to solid fatty foods such as potato chips, peanuts, etc. (Hilton—*Food Eng.* 27, No. 4, 7). A new accelerated oxidizability test was based on observation while aging of sample spread over glass beads. The expanded oil surface thus obtained permitted greater exposure to air which accelerated the oxidation (Spruyt—*Ibid.* 197). The test was especially recommended for the study of the stability of vitamin A oil used in feed mixtures, tablets, etc., because it simulated commercial conditions. The stability of carotene in the hydrogenated oil of commerce in India was directly related to the color intensity produced in the Baudouin test for sesame oil (Roy—*J. Indian Chem. Soc. Ind. & News Ed.* 15, 171). Indian law requires the presence of sesame oil in hydrogenated fat because such fats may easily be traced when used to adulterate Indian butter. This sesame oil thus serves as a tracer, as a preservative for carotene, and through the Baudouin test as indication of the stability of the carotene. Lack of dissolved oxygen in oils and fats stored in open containers is said to indicate that the samples are in a rapid stage of deterioration (Hirano & Kurobe—*J. Chem. Soc. Japan Ind. Chem. Soc.* 57, 624). Stable oils contain some dissolved oxygen.

A study of the stabilities of refined soybean and rapeseed oils has indicated that the beginning of rancidity coincided with the beginning of the rapid rise in carbonyl content (Nikkilä & Linko—*Suomen Kemistilehti* 28B, No. 3, 113). This work contained a comparison of peroxide value and carbonyl value for studying rancidity and stability of the oils.

The details for the Mackey test for evaluating the stability of textile lubricating oils was published in the French literature (Anon.—*Rev. franc. corps gras* 2, 653).

Spectroscopic methods based on readings at four wave lengths have been designed for determination of butyl hydroxyanisole and propyl gallate in food antioxidants (Whetsel *et al.*—*J. Am. Oil Chemists' Soc.* 32, 493). Paper-chromatographic detection methods based on color developers and on R_f values have been developed for the antioxidants: ethyl gallate, butyl gallate, dodecyl gallate, nordihydroguaiaretic acid, propyl gallate, quercitrin, ascorbyl palmitate, α -tocopherol, and others (Gander—*Fette u. Seifen* 57, 423). Similar tests were also developed for detecting the margarine preservatives, benzoic acid and dehydroacetic acid (Clemens—*Ibid.* 109).

ACCELERATORS OF DETERIORATION. The relationships of hydroperoxide and active oxygen content to total active oxygen observed during autoxidation of methyl oleate have been plotted and equations developed to represent these relationships (Saunders *et al.*—*J. Am. Oil Chemists' Soc.* 32, 79). The major portion of active oxygen compounds formed were hydroperoxides, but a small but significant amount of nonhydroperoxide-peroxide was formed concurrently. In continuing this work with methyl oleate (Knight—*Ibid.*, 135), by use of urea complex separations, it was found that the active oxygen containing fraction can be fractionated before peak peroxide value was attained, but after this peak, the oxygenated concentrate obtained has very little peroxide content. The important secondary products of the autoxidation were α,β -unsaturated carbonyl compounds. Similar work based on polarographic observations has indicated that peroxides were formed in considerably larger proportions in oils than in methyl esters of similar acid radical compositions (Kalbag—*Ibid.* 271). This peroxide was reduced at more positive potentials than the

hydroperoxide. In the presence of cobalt dryers negligible amounts of peroxide appear in the oils. Polarographic technique was also used to elucidate reactions of *tert*-butylated hydroxyanisole with oxygen and thus its reaction mechanism as an antioxidant (Baltes—*Fette u. Seifen* 57, 656).

In the oxidation of unsaturated fats catalyzed by hematin compounds it was suggested that a lipid peroxide-hematin compound forms which then decomposes into free radicals that propagate chain reaction oxidation (Tappel—*J. Biol. Chem.* 217, 721). The fragmentation of fatty acids in this mechanism runs concurrent with destruction of the hematin catalyst. Data from infrared studies of fat autoxidation with and without catalyst have been interpreted to indicate (a) isomerization and other changes occur only in oxidized products of the fatty acid, (b) geometric isomerization occurs in the intermediate activated stage involving energy transfer and leading to formation of monohydroperoxide, (c) activity is at the α -methylene group; and (d) hydroperoxides are absent at C_{11} in autoxidized linoleate as well as at C_{11} or C_{14} in the autoxidized linolenate products (Khan—*Biochim. et Biophys. Acta* 16, 159). Analysis of lipoxidase-catalyzed oxidation products of sodium linoleate has shown that the enzyme was inactive to the *cis*-9,*trans*-12-, and *trans*-9,*trans*-12-isomers, and that the products formed, *cis,trans*-conjugated monomeric monohydroperoxides and polymers, substantiate a previously proposed mechanism of Tappel and coworkers in which the enzyme is considered to be involved in the formation of each peroxide molecule (Privett *et al.*—*J. Am. Oil Chemists' Soc.* 32, 505).

New studies on the offensive smelling compounds of the fatty materials were recorded. Normal undecanal and *n*-undecenal were isolated from rancid corn oil (Buss & Mackinney—*Ibid.* 487). The bitter and beany-odor substances obtained by steam distillation of soybean products contained ketones, carboxylic acids, esters, phenols and some neutral compounds (Teeter *et al.*—*Ibid.* 390). In similar work with ill-smelling chrysalis oil, aldehydes and acids of 1-5 carbon atoms have been isolated (Maruta—*J. Chem. Soc., Japan Chem. Sect.* 74, 805). Various unconjugated and conjugated unsaturated aldehydes were isolated from oxidized milk products by Forss *et al.* (*J. Dairy Res.* 22, 345), and by Tamsma (*J. Dairy Sci.* 38, 487). In studying these compounds the latter suggested that the carbonyl group and unsaturation were both essential for oxidized flavors. Forss *et al.*, who have isolated C_5 - C_{11} 2,4-dienals and C_4 - C_{11} 2-enals in this work, showed that these compounds in dilutions of 10^{-7} to 10^{-9} induced oxidized-like flavors in skim milk.

FACTORS AFFECTING STABILITY OF FATS AND OILS. Various influences which hasten deterioration of fats and oils were studied. Spetsig (*Acta Chem. Scand.* 8, 1643, 1648), considered that the accelerating action of water on the autoxidation of methyl linoleate was due to the moisture interfering with the reactions initiating the autoxidation prior to the formation of the peroxides. In the same work it was found that the efficiency of ascorbic acid as a synergistic antioxidant in the presence of moisture decreased with increasing pH. The solubility of water and the vapor pressure of the water dissolved in various fats and oils have been determined as basic information in relating stability of oil to presence of moisture (Loucin—*Fette u. Seifen* 57, 413). Chlorophyll with sunlight increased the peroxide development in almond and Brazil nut oils ten- and five-fold, respectively. But, such acceleration was inhibited by addition of carotene (Lee—*Nature* 176, 463). High-energy irradiation of fats, oils, or fatty derivatives with β - or γ -rays resulted in the formation of carbonyl compounds and decreased palatability (Chipault *et al.*—*Ann. Rpt. Hormel Inst.* 1954-5, 21). In the presence of oxygen peroxides were also formed.

Copper-proteins formed by binding copper with conalbumin, serum albumin, or caseinate were more effective catalysts for linoleate oxidation than copper alone (Tappel—*J. Am. Oil Chemists' Soc.* 32, 252). This was attributed to the easier formation and greater stability of the intermediate complex of linoleate peroxide-copper-protein. Ease of acceleration of autoxidation of an oil with copper metal was related to the velocity of formation of copper soaps from metallic copper dipped into the oils (Bitto & Inaba—*Kagaku* 24, 575). This ease of formation of copper soaps was characteristic of each type of oil; it was not related to the acid value; and was retarded by antioxidants. The storability of peanut oil was adversely affected by various metals in the following increasing order: silver, stainless steel, aluminum, iron, zinc, tin, brass, copper, and lead (Husaini & Saletore—*Indian Soap J.* 18, 192).

Flour of 80% extraction contained about 0.6 p.p.m. of catalase which was considered sufficient to cause autoxidative bleaching of any carotene present (Hawthorn & Todd—*Chem-*

istry & Industry 1955, 446). Equations were designed for predicting the color of macaroni from wheats and semolinis based on the amount of carotene and the activity of the lipoxidase present (Irvine—*J. Am. Oil Chemists' Soc.* 32, 558).

STABILITY OF FATTY PRODUCTS. The course of development of free fatty acids and peroxide value in the inner skin fats of frozen chicken and geese stored 9 months at -10° and in unfrozen samples stored at 0° for 13 days were recorded (Gorizontova—*Myasnaya Ind. S.S.S.R.* 26, No. 2, 13). Free fatty acids rose to as high as 2.4% and peroxide value to 0.30. Supplements of 5% tallow, 5 and 10% soybean fats, and 5 and 10% hydrolyzed cottonseed fat substituted for corn in broiler rations did not adversely affect the storage quality of poultry at 0°F. or lower for nine months (Darrow & Essary—*Poultry Sci.* 34, 427). A study of rancidity of bacons has shown that in cured and smoked bacon the acidity increased very rapidly; whereas in pickled or salted bacon acidity remained normal, but peroxide value increased rapidly (Bronisz & Raciborska—*Roczniki Panstworvego Zagladu Hig.* 5, 143). The characteristic odor of oleo oil and edible tallow could be removed and the stability of the fats improved by slight hydrogenation of high selectivity under atmospheric pressure (Chang & Kummerow—*J. Am. Oil Chemists' Soc.* 32, 547). The process raised the melting point by less than 2° but substantially decreased the linolenic and arachidonic content. A kinetic study of stability of rendered fats has confirmed that vacuum rendering and absence of metals (rendering in glass) was conducive to better stability (Emanuel *et al.*—*Myasnaya Ind. S.S.S.R.* 26, No. 5, 44).

Ethyl oleate whose peroxide index had become higher than permitted for pharmaceutical uses was acceptable after treatment with alumina (Ponci—*Il Farmaco, Pavia, Sci.* 9, 539).

Improvement of flours with gaseous oxidizing agents reduced the stability of the flour lipides (Moran *et al.*—*Nature* 174, 449).

Studies on the reddening or rusting of fish oils during storage has confirmed that this occurs simultaneous with autoxidation and that the presence of ammonia or basic nitrogen compounds (decomposed proteins) was necessary for the development of the discoloration (Nonaka—*Bull. Japan Soc. Sci. Fisheries* 15, 805; 19, 1001; Nonaka *et al.*—*Ibid.* 20, 40, 46, 319; Ando—*Ibid.* 19, 1069; Suzuki—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 660). It was suggested that the nitrogen bases partaking in the discoloration did not function to produce ammonia compounds in the oils, but that they behaved as catalyzers for the formation of colored oxidation products.

A comparison of stabilities of dried whole milk with dried "filled" milks showed that: oxidized off-flavor develops within one month in the whole milk even when vacuum packaged; "filled" products in which the butterfat is replaced with hydrogenated cottonseed, peanut, or soybean oils or lard had poor flavor stabilities, whereas vacuum packed "filled" milks made with coconut fat retained acceptable flavor qualities after six months' storage at room temperature (Herald & Patton—*J. Dairy Sci.* 38, 640).

Fat oxidation during storage of unsalted and highly salted butters was much lower than butters of normal salt content (McDowell—*J. Dairy Res.* 22, 349). Antioxidants added to the butters retarded oxidation and development of storage flavors. A study of peroxide value changes that occurred during the storage of butters has indicated that when the value remained below 0.8-1.0 during 70-75 days' storage at -10° , the butter did not become fishy or tallowy in continuing the storage to six months (Piroux *et al.*—*Bull. inst. agron. et stas. rech. Gembloux* 22, 76). Studies on storage of Russian butters have indicated that fresh butter was best stored at temperatures below 1° ; butter oil was best held at -5° ; milk fat and refined butter could be stored for two years at temperatures between -5 and $+6^\circ$, and dry butter stored in hermetically sealed containers stayed fresh 12 months when kept at $18-20^\circ$ (Titov—*Trudy Inst. Molchnoi Prom.* 1953, No. 13, 39). Indian butter oil, "samna," made from the cream of goat's milk was more stable than that from the milk of buffalo, cow, or sheep (El-Sokkary & Zaki—*Indian J. Dairy Sci.* 6, 217).

The stability of some fats were investigated with regard to retention of fat soluble vitamins. Loss of vitamin A during storage was more rapid in butter made from raw than from boiled milk. However, butter oil "ghee," prepared at 115° deteriorates at the same rate whether the butter had been obtained from raw or boiled milk (Lalitha & Dastur—*Indian J. Sci.* 7, 1). A more comprehensive investigation on stability of vitamin A and carotene in fortified ghees has shown that: stability was improved with high supplements of green grass in the rations of the dairy animals and storing the ghee in aluminum, glass or tinned containers; souring the milk with

starter had no effect on the vitamin A content; and heating at temperatures over 125° in manufacture or storage of the ghee in mud pots was detrimental (Narayanan *et al.*—*Indian J. Dairy Sci.* 6, 189; 7, 76; Shroff *et al.*—*Ibid.* 159). Among components of margarines, skim milk, casein, or other proteins inhibited oxidation of vitamin A; lecithin, starch, or agar were without effect; whereas monoglyceride emulsifiers promoted oxidation of the vitamin (Naito & Mori—*J. Agr. Chem. Soc. Japan* 27, 265, 268). Disappearance of the yellow color, β -carotene, and appearance of olive tint in stored beef fat was inhibited with addition of alkaline salts (K_2CO_3 or $NaOAc$); while additions of ascorbic or citric acid had no influence (Lyaskovskaya *et al.*—*Myasnaya Ind. S.S.S.R.* 26, No. 3, 49). The loss of vitamin A in fish oils was more influenced by the total amount of unsaturated molecules in the oils than by the number of double bonds in the unsaturated molecules (Abe & Ihara—*Bull. Japan. Soc. Sci. Fisheries* 19, 95). Vitamin A acetate in peanut oil was protected by hardening the oil, addition of ethyl gallate, or both (Roy—*J. Sci. Ind. Res., India*, 13B, 496). Carotene extracted with vegetable oils from the albumin sediment that settles from carrot juice was very stable and was suitable for coloring margarine (Ruhowicz & Jarmolowicz—*Prace Glownego Inst. Przemyslu Rolnego i Spozyczego* 3, No. 3, 1). Addition of animal fats or vegetable oil to dehydrated alfalfa meal to reduce dustiness increased the stability of carotene therein (Bickoff *et al.*—*J. Agr. & Food Chem.* 3, 67). But, poorer oils such as salmon body oil or acidulated cottonseed soapstock reduced the carotene when an antioxidant was not added (Mitchell & Silker—*Ibid.* 69). Both animal fats and antioxidants acted as effective stabilizers for xanthophyll concentrates that were added to feeds (Livingston *et al.*—*Ibid.* 439).

ANTIOXIDANTS. Many natural antioxidant materials were studied. The unsaponifiable extract of *Mortierella* species of mold contained an effective antioxidant (Tatarenko *et al.*—*Mikrobiologiya* 24, 217). An antioxidant extract obtained by successive extractions of rosemary with methanol, petroleum ether, and ether protected edible oils better than did propyl gallate (Rac & Ostric—*Kemiya e Ind., Zagreb*, 3, 301). Spices were generally more effective antioxidants in emulsions than in plain fat or baked pie crust, but the order of effectiveness was different for different substances (Chipault *et al.*—*Food Res.* 20, 443). In 0.5% concentrations three melanoidins tested in margarine inhibited an increase in Lea values more markedly than did 0.01% additions of dodecyl gallate, tetraethylthiuram disulfide, nordihydroguaiaretic acid, or 1,7-naphthalenediol (Franzke & Iwainsky—*Deut. Lebensm-Rundschau* 50, 251). Meals of wheat, barley, and oats were preferred over chemical antioxidants for stabilizing certain fats and fat-containing food products during storage (Korobkina—*Voprosy Pitaniya* 13, No. 5, 33). Wood tars from the woods of broad leaf trees, needle-leaf trees and pine roots were effective antioxidants in decreasing order as listed (Mori & Naito—*J. Japan. Soc. Food Nutr.* 4, 179). A mechanism proposed for the synergistic action of α -alanine with phenolic antioxidants involved the deamination of the amino acid to yield pyrroacemic acid and ammonia and the pyrroacemic acid reduces the oxidized phenolic antioxidant (Heimann *et al.*—*Z. Lebensm.-Untersuch. u. Forsch.* 102, 1).

Anders (*Deut. Lebensm.-Rundschau* 51, 104) favored use of citrates and citraconic acids as antioxidants for fats because "they fit into the human metabolic scheme, the citric acid cycle." Roy (*J. Indian Chem. Soc. Ind. & News Ed.* 17, 135) found citric and tartaric acids equivalent as antioxidants for peanut oils, and combinations of both acids were more efficient than either alone. Data by Ramos (*Oleagineux* 10, 177) on palm oils containing metallic impurities show that citric and phosphoric acids were efficient stabilizers, and ascorbic acid was not. Ascorbyl palmitate was a less active antioxidant in peanut and olive oil than carotene initially but the antioxidant effect of the former appeared to increase in effectiveness with time of storage (Herisset—*Trav. lab. matiere med. et pharm. ecole med. et pharm. Angers No. 1*, 4 pp.; *No. 2*, 4 pp.).

Forty-two bisphenol derivatives have been tested for the protection of carotene in oil and in alfalfa meal (Bickoff *et al.*—*J. Am. Oil Chemists' Soc.* 32, 64). Alkyl substitution in the reactive *o*- or *p*-positions improved efficiency of the compounds studied, and bisphenols linked by methylene or sulfur were highly active. In tests on several commercially used phenolic antioxidants in edible animal fats, propyl gallate either alone or in combination with butylated hydroxy-

anisole or butylated hydroxytoluene produced the highest stability (Gearhart & Stuckey—*Ibid.* 287, 386). In yellow grease, citric acid was synergistic for the above antioxidants. The above antioxidants were also recommended for increasing the shelf life of cereals (Stuckey—*Food Tech.* 9, 585). Desirable combinations of butylhydroxyanisole with various other antioxidants and/or synergists have been worked out for the protection of lard, olive oil, margarine, and butter, respectively (Pulgar—*Univ. Chile, fac. quim. y farm., Thesis*, 5, 247). Butylhydroxyanisole was recommended for preventing oxidation of fish oils and fish products (Otani *et al.*—*Bull. Japan Soc. Sci. Fisheries* 19, 947; Matsubashi—*Ibid.* 20, 497). Butylhydroxyanisole, ethyl gallate, nordihydroguaiaretic acid, and di-*tert*-butyl-*p*-cresol are destroyed at about 200° and hence become ineffective when preserved fats have been used for frying (Kapadia & Magar—*J. Indian Chem. Soc. Ind. News Ed.* 17, 101). The antioxidant, 2,4,5-trihydroxybutyro-phenone, was effective in lard and peanut oil; less effective in cottonseed, corn, castor and sesame oils and fallows; and in greases, palm oil, and sperm oil it was only moderately effective (Knowles *et al.*—*J. Am. Oil Chemists' Soc.* 32, 158).

Of 20 antioxidants studied for the stabilization of kamalaseed oil, hydroquinone was most effective (Kapadia & Aggarwal—*J. Sci. Ind. Res., India*, 14B, 186). Cosmetic creams containing eugenol essence were stable for six months when stored in aluminum tubes, and when stored in glass addition of 0.15% sodium benzoate and 0.3% cinnamic alcohol is necessary to preserve them for the same period (Moldavskaya & Dmitrieva—*Masloboino-Zhivovaya Prom.* 20, No. 5, 18). Phenothiazine, phenylhydrazine, α -naphthol inhibited catalytic activity of plant lipoxidase and of hemolyzates of human erythrocytes in the oxidation of linoleates (Collier & McRae—*Can. J. Biochem. & Physiol.* 33, 773).

Some blue discolorations of stabilized fats have been traced to changes undergone by the antioxidants used. The antioxidants 2 *tert*-butyl-4-methoxyphenol, 2,6-di-*tert*-butyl-*p*-cresol, and α -tocopherol were found to dehydrogenate to deep blue free radicals (Baltes—*Fette u. Seifen* 56, 984). Some of the blue products from these antioxidants have been isolated and identified (Baltes & Volbert—*Ibid.* 57, 660).

The toxicity of several antioxidants was investigated. Booth & DeEds (*Food Res.* 20, 582) found phytic acid-stabilized soybean oil non-toxic to rats. Grahams' & Grieces' work (*J. Pharm. & Pharmacol.* 7, 126) indicated that propyl gallate and butylated hydroxyanisole are non-toxic at concentration many times those used in preservation of fats. Roy (*Indian J. Med. Res.* 41, 201) reported that rats receiving diets containing ethyl gallate in oil, in concentrations 100 times the dose necessary for antioxidant action, showed no symptoms of toxicity. The LD₅₀ of ethyl gallate for rats was found to be 581 mg. per 100 g. body weight.

Tests on corrosive action of solutions of antioxidants in 1:1 mixtures of castor oil:ethanol on iron and copper have shown that the antioxidants depress corrosion and formation of metallic soap (Bito—*J. Chem. Soc. Japan, Ind. Chem. Sect.* 57, 718).

Patents have been issued on the following stabilizers for fats and oils: aliphatic hydrocarbon-mercaptans, -sulfides and -polysulfides in combination with organic amines (Harle—*U. S.* 2,718,501), 2,2'-alkylidenebis (4-alkoxy-6-vinylphenols) (Bell & Knowles—*U. S.* 2,688,625), mixtures of glycine and phosphoric acid (Kuhrt—*U. S.* 2,701,769-70), 5-(1,2-dithiolane-3-yl)pentanoic acid (Searle—*U. S.* 2,706,158), citric acid dissolved in a monoglyceride (Brown *et al.*—*U. S.* 2,699,395), combinations of phenolic antioxidant, alkali metal phosphate and ascorbic acid (Lehmann & Watts—*U. S.* 2,707,154), ortho-substituted, hydroquinones (Gaydasch & Gleim—*U. S.* 2,681,371), N,N'-bis(hydroxyphenyl) amidine (Chenicek—*U. S.* 2,687,962), 1-hydroxy-4-alkoxy-5,8-di- and -5,6,7,8-tetrahydro-naphthalenes (Chenicek & Thompson—*U. S.* 2,692,202) alkylated flavone compound having at least one hydroxy substituent (Gleim—*U. S.* 2,694,645), flakes comprising 80% 3-*tert*-butyl-4-hydroxyanisole and 20% 2-*tert*-butyl-4-hydroxyanisole (Chenicek—*U. S.* 2,704,746), and 2,4,6-trialkylphenol (Rosenwald—*U. S.* 2,721,804). Appearance of streaks in unhydrogenated vegetable shortening was inhibited by reducing the peroxide value to zero in vacuum, cooling, adding small amounts of propyl gallate and citric acid, steaming to dissolve these antioxidants, and then removing the oils from the vacuum (Newby & Guidry—*U. S.* 2,727,159).