

the peroxide reaches 10 which is used in the A.O.M. method as the end point for the induction period.

Table 6 shows the variation in effectiveness of various samples of commercial tannins. Neither the color, the flavor, nor the odor of the lard was adversely affected by treatment with any of these tannins.

### Summary

The literature on the use of tannins as antioxidants for fats is reviewed. A process is described for the improvement of the keeping quality of edible fats by treatment with tannin in which the tannin and/or tannin compound is removed by filtration. Data are presented for various types of animal and vegetable fats and oils which were treated with U.S.P. tannic acid by the process described. The process is particularly effective on lard and beef fats. Data are presented which show the effects of varying the temperature at which the treatment is made. A method for testing the effectiveness of removal of the tannin is

described. The improvement value  $I_V$ , is introduced and is defined as the increase in keeping quality of a fat attributable to a process. It is analogous to the  $I_A$  value which is defined as the increase in induction period of a fat due to the addition of an antioxidant.

### REFERENCES

1. Winton, A. L. and Winton, K. B., Structure and Composition of Foods, Vol. 1, Page 13.
2. Lea, C. H., Rancidity in Edible Fats, Part V, Deterioration of Fats by Atmospheric Oxidation.
3. Moureu, C. and Dufraisse, C., Chem. Reviews 3, 113 (1926-27), Compt. Rend. 186, 196-9 (1928).
4. Olcott, H. S. and Matill, H. A., J.A.C.S. 58, 2204-2208 (1936).
5. Heffer-Schönfeld, Chemie und Technologie der Fette und Fettprodukte, Zweiter Band Verarbeitung und Anwendung der Fette, p. 22.
6. Musher, S., U. S. Patent 2,233,142—2-15-41.
7. Musher, S., U. S. Patent 2,282,811—5-12-42.
8. Verbeck, B. J., U. S. Patent 2,354,719—8-1-44.
9. King, Roschen and Irwin, Oil & Soap 10, 105 (1933).
10. Meat Insp. Regulations of U. S. Dept. of Agriculture, Regulation 1, Section 1, paragraph 1.
11. Readings on By-Products of the Meat Packing Industry.
12. Pharmacopoeia of the U. S., 12th Edition, p. 31-32.
13. Lips, A., and McFarlane, W. D., Oil and Soap, 20, 193-6 (1943).
14. Riemenschneider, R. W., Turer, J., and Ault, Waldo, Oil and Soap 21, 98-100 (1944).
15. National Provisioner 110, p. 19 (2-19-44).

# Review of Literature on Fats, Oils and Soaps

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## Report of the Literature Review Committee

### Part 1

#### Introduction

Domestic production of fats and oils during 1945 amounted to about 9.5 billion pounds compared with 10.8 billion pounds in 1943 and in 1944. Exports to the Allied countries were decreased about 53% as compared to the previous year, and imports tapered off to the smallest volume in many years. Stocks on hand toward the end of the year were being depleted to the lowest since 1936.

The effect of the fat situation on civilian consumption was such that the food fat supplies in 1945 were 41 to 42 pounds per capita (as compared to an average of 48 pounds in 1936-39) in the face of a potential demand of at least 50 pounds per capita. Technical fat users also felt a more or less corresponding deficiency of raw material. Soapmakers were additionally affected by short rosin supplies. Early in the war period, soapmakers were required to increase the percentage of rosin in soap to conserve fats. However, use of rosin was simultaneously expanded in the manufacture of ester gum, synthetic rubber, and miscellaneous chemicals to such an extent that the demand exceeded supplies. Beginning with the second quarter of 1945, the use of rosin in civilian soap was limited by WPB Order M-387 to 25% of the quantity used in civilian soap in the corresponding quarter of 1944.

All predictions suggest that no improvement is expected until mid-1946; for the year as a whole there should be about a 4-pound per capita increase in food fats available for civilian consumption. Demands from our armed forces and allies should decrease. Imports should begin to alleviate the deficiencies in the paint and soap industries, for in normal times these industries were the consumers of those spe-

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cial types of oils principally obtained from foreign sources. This trade should now begin to adjust itself to prewar channels. Whaling is expected to begin again and will aid in the relief of the universal shortage of fat. Changes expected during 1946 in domestic production of the leading fats are increases of lard, butter, peanut oil, and linseed oil and slight decreases of cottonseed and soybean oils.

Because of excessive demand and OPA regulations the prices of oils and fats did not vary much, remaining close to their ceilings. The average was slightly greater than that of the year previous because a five-cent increase in the price of butter was allowed.

The above information was obtained from several recent issues of the Bureau of Agricultural Economics' publication, "The Fats and Oils Situation." The Bureau of Foreign and Domestic Commerce of the U. S. Department of Commerce also compiled data on the subject. Two of their recent publications (*Ind. Ref. Service* 3, Pt. 5, No. 13; *Animal and Vegetable Fats and Oils, Years 1940-44*) contain many statistical data and trade discussions. Several journal communications reviewed and discussed limited parts of the fat and oil field; Lehberg (*Oil & Soap* 22, 46) reviewed the Canadian fat and oil industry; Chatterjee (*Indian Soap J.* 10, 61) described the seed crushing industry of India, and soybean oil was the subject of general papers by Alderks (*Chem. Eng. News* 23, 1168; *Oil & Soap* 22, 232), Brown (*Soybean Digest* 5, No. 11, 35), Smith and Cowan (*Ibid.* 43), and Henson (*Ibid.* 47). The latter two papers were, respectively, on research developments in soybeans at the Northern Regional Research Laboratory and the southern soybean program of the U. S. Regional Soybean Laboratory.

In the activities on the interchangeability of fats and the search for new sources, the work on fish oils has produced abundant information characterizing many new oils. The aim in many of these was to find new sources of vitamin oils to supplement those obtained from soupfin shark liver. The soupfins have been so intensively hunted that this source is becoming exhausted. In this connection Setna (*J. Sci. & Ind. Res., India* 3, 303) classified 41 species of sharks and rays with emphasis on the therapeutic value of the liver oils. The work of Rapson *et al.* (*J. Soc. Chem. Ind.* 63, 340, 367; 64, 5, 7, 47, 114, 139, 140, 172) included the analysis of the liver, body, head, and intestinal oils of numerous fish caught near South Africa. Cunningham and Scott (*New Zealand J. Sci. Tech.* 26B, 21) surveyed the potencies of vitamin A and D in New Zealand fish capable of large scale production. There were indications of similar work, though unpublished, being done in the fishing industries of various localities.

Other communications fostering new sources of oils were on degermination of feed corn (Goltz—*Deut. Molkerei- u. Fettwirtsch.* 1, 138; Conti—*Ilii minerali, olii e grassi, colori e vernici* 22, No. 6, 28), milkweed seed oil (Lanson, Habib and Spoerri—*Ind. Eng. Chem.* 37, 179), tobacco seed oil (Rao—*Indian Farming* 5, 359), sunflower seed oil production in Great Britain (Hurt—*Chemist and Druggist* 143, 46), and use of fish oils in paint (Mann—*Am. Paint J.* 29, No. 14, 22). The recovery of fat from sewage continued to be intensively developed in Germany. Keller (*Fleischwirtschaft* 23, No. 4, 47), Bourmer (*Deut. tierärztl. Wochschr.* 1942, No. 9/10, 119), and Korn-

messer (*Gesundh.-Ing.* 65, 24) discussed the progress of this activity giving methods, description of the most efficient equipment, and statistics on amount of grease recovered on the basis of population in cities and per animal (beef and hog) slaughtered in the packinghouses. A new grease trap for industrial waste water was designed by Langdon (*U. S.* 2,370,974).

The literature references on fat synthesis which became available during the year were principally general discussions or reviews on the subject (Rosen-dahl—*Z. kompr. fluss. Gase* 38, 25, 37, 49; Lindner—*Fette u. Seifen* 50, 396; Wittka—*Seifensieder-Ztg.* 1943, 50, 68). A rich source of information on this subject were the reports of the Office of the Publication Board, Department of Commerce, prepared by American scientists and technicians who visited the industries of Axis nations. It was reported that the products resulting from the oxidation of paraffins were fractionated into divisions of different chain lengths and those between C<sub>10</sub> and C<sub>15</sub> were used for manufacture of soap and food fats. During the last year of production the output of synthetic food fat in Germany amounted to 440,000 pounds per month. Samples tasted by various individuals were found to be excellent in quality; some six-month old margarine made from the synthetic fat was only slightly off taste.

Among new books in the oil and fat field, the comprehensive text entitled, "Industrial Oil and Fat Products," 735 pp., by Bailey (Interscience Publishers, Inc.) was most welcome for it presented much more information of technical nature on the subject that was heretofore available in a book in the English language. It contains much new information and treats subjects such as shortening and bakery products which were ignored in the older books. Several recent German books (Möllering, Lüttgen and van der Werth—*Seifen-Herstellung*, 466 pp.; Gnam—*Fettchemie. I. Lösungsmittel und Weichhaltungsmittel* 4th ed., 516 pp.; Lüde—*Gewinnung von Fetten und fetten Ölen*, 224 pp.) were made available in the United States by the Alien Property Custodian. A symposium, "Medical Uses for Soap," was published (Lippincott Company) in book form. A book by Young and Coons, "Surface Active Agents," (Chemical Publishing Company) contained information on the theoretical aspects, a description of commercial preparations, and a discussion of their uses. Leffingwell and Lesser reviewed in book form (Chemical Publishing Company) the uses and potential uses of glycerol. The agronomic, physical, chemical, economic, and industrial aspects of soybeans were briefly outlined in a pamphlet by Shollenberger and Goss (*U.S.D.A., Bur. Agr. & Ind. Chem., A.I.C.* 74). A review on advances in the chemistry of fats by Daubert (*J. Am. Pharm. Assoc.* 33, 321) contains 72 references.

At this time of writing, three issues of a new journal (*Industries des corps gras* 1) have been received. This will be the official journal of L'institut Technique d'Etudes et de Recherches des Corps Gras of Paris. Judging from the material already published, this journal should become one of the leading publications for the industry. Another new journal, "Corps Gras Savons," originated during the war and published by Presses Documentaires of Paris has only recently become available in America.

### Production Processes

The use of alkalis in rendering processes was evident in three industries. Novelty in a process and apparatus for rendering meat products was patented by Kernot and Silberstein (*U. S. 2,368,028; Belg. 444,345*). It comprised the addition of a small amount of alkali, a special stirring device, and a means of skimming fat. Anderson (*Fishery Market News* 7, No. 4, 4) recommended that salmon cannery trimmings, *i. e.*, head and collar sections, be rendered by digestion at 92-93° in dilute caustic solution. A digestion with alkalis was also recommended in a process for extracting avocado oil by Love (*U. S. 2,383,398*). The final recovery is by skimming, but for greater efficiency, filter presses, solvent extraction, and centrifuges may be used in the final stages of the process. Two other rendering processes were designed to give special products. Ratner (*U. S. 2,388,284*) expressed oleo oil from fresh suet for margarine manufacture in a hydraulic press at 20-25°. The oil was said to have a better taste and odor than that commonly produced at 28-32°. According to Blumenthal (*Brit. 555,299*), bones for the production of glue and gelatine can be rendered by treatment with acetone and ethyl alcohol. The solvents removed fat and water from the bones at low temperature.

General papers in the vegetable oil field included a review of pressing plant equipment by Leont'evskii (*Pishchevaya Prom* 1, No. 2, 15) for Russian technicians, and a brief, comprehensive treatise on oil seed processing by Geisler (*Prog. Fortschr. deut. Tech.* 8, 441). They recommended that material of high oil content should be prepressed to less than 30% oil and then solvent extracted. Gordon (*Chem. Met. Eng.* 52, No. 11, 106) described a unique plant for processing tung and peanut oil. Its isolated location on a high plateau in the interior of the island of Madagascar necessitated the design of complete facilities for generating electric power, process and heating steam, and machinery for making cans from tin plate. A patent issued to Upton (*U. S. 2,369,192*) dealt with special bars designed for a cage oil press to allow passing heat exchange fluid through the bars.

Some work was carried out on the storage and handling of oilseeds. Milner and Geddes (*Cereal Chem.* 22, 477, 484) recorded results of experiments on soybean storage. The work on air movements confirmed some older work on the subject. However, it was observed that carbon dioxide was carried by convection currents in the interseed air from zones of heating to the upper and cooler regions of the soybeans. The movement of water vapor, from heating zones to cool areas immediately above, increased the relative humidity of the air in the cooler regions and promoted mold growth at the successively higher levels. Mold proliferation was positively correlated with respiratory activity, with degree of aeration up to an optimum, and with increases in temperature to 40°. Only slight increases of acid value of the oil extracted from soybeans appeared in samples respiring under nitrogen. A patented process of treating oil seeds by Altschul and Karon (*U. S. 2,376,568, 2,376,852*) comprised treating with a volatile base, such as ammonia or morpholine, at least one week before extraction; such seeds yielded a considerably lighter-colored oil.

Hutchins (*Oil & Soap* 22, 165) recorded data on the effect of bean damage, splits, off-color varieties,

moisture, and foreign material on the soybean oil produced. At seed moistures above 10%, oil quality deteriorated sharply. The oil from wet or water damaged soybeans was greatly improved by drying the beans. An investigation on pressing cottonseeds developed information on the economical optimum pressing times for hydraulic oil presses (Baskerville and Wamble—*Univ. Tenn. Eng. Exper. Sta. Bull.* 13, 21 pp.). The most economical cycle varied from 36-57 (av. 47) minutes. At present, commercial presses operate at a cycle of 30 minutes; an increase to 45 minutes would require a 50% increase in number of presses and would give an average increase in oil output of 8%.

Several solvent extraction innovations were patented. Berry (*U. S. 2,381,965*) designed a counter-current system using either a "U" or "V" shaped container. Bonotto (*U. S. 2,370,138*) introduced clarifying filters for extraction of miscella in a counter-current system. Böhm's (*U. S. 2,370,614*) horizontally rotating mounted cylindrical extraction vessel was improved by adding filtering means in the interior and by imparting oscillatory movement to the vessel. Jones and Bath (*U. S. 2,370,315*) strained the liquid from the solids with centrifuges. Dinley and McCracken (*U. S. 2,377,135-6*) injected the uncondensed recovered solvent into the unextracted new charge. They (*Can. 428,374*) also recovered some solvent by passing extracted meal through a forward moving supply of dry unextracted meal, whereby the latter adsorbs and absorbs uncondensed solvent. Both batch and continuous processes were designed by Singer and Deobald (*U. S. 2,377,975-6*) for producing "nonbreak" soybean oil. A mixture of 75% ethanol and 25% isopropanol was used as the solvent; on cooling, the oil separated and the phosphatides were recovered from the solvent layer by use of a salting out agent, *i. e.*, calcium chloride solution. Two communications on extraction of seeds with dichloroethylene presented data to demonstrate the potentialities of the solvent (McCracken—Iowa State Coll. *J. Sci.* 19, 47; Gil'tan—*Pishchevaya Prom.* 1, No. 2, 25).

Recorded data on corrosion by fat acids and physical data on solvent-oil mixtures are useful in the design of solvent processing equipment. Prutton *et al.* (*Ind. Eng. Chem.* 37, 90, 917) reported that corrosion of lead or cadmium by fat acids did not take place appreciably in nonpolar solvent media. However, in the presence of fat acids, molecular oxygen or peroxides attacked lead. In absence of fat acids an oxide film accumulated and protected the metal. They suggested that hydroperoxides, although less reactive toward lead than either dihydroxyl, dialkyl, or acyl peroxides, are likely to be much more damaging from a corrosion standpoint since they possess greater stability toward heated oil. The boiling points and densities of mixtures of cottonseed and peanut oils in commercial hexane were measured by Pollard *et al.* (*Ibid.* 1022). The data by Magne and Skau (*Ibid.* 1097) contained the viscosities and densities of the same oils in commercial hexane, acetone, and 2-butanone.

Touchin (*J. Oil & Colour Chem. Assoc.* 28, No. 297, 49) found that the amount of "break" formed during a refining test formed a better basis than the acid number for determining the amount of lye necessary for refining an oil. The relationship: excess of lye

added to the oil multiplied by the time required to obtain a break-free oil raised to a constant power was found to be roughly constant and should be useful in planning refining processes. Clayton (*U. S. 2,374,924*) patented a special process of refining oil while in organic solvent solution. According to Buxton (*U. S. 2,380,411*) refining a marine oil by saponifying 10-30% of the glycerides, and removing the oil from soap with isopropanol containing at least 9% water, removed odor, taste, and pigments.

In the field of bleaching oils there were two reviews. One treated the general field briefly (Boyle—*Manufg. Chemist* 16, 133); the other listed and critically discussed all the chemicals suggested for the process (Hetzer—*Seifensieder-Ztg.* 1944, 2). In an investigation on the influence of pH on the adsorption properties of bleaching adsorbents for oils by Hassler (*Oil & Soap* 22, 60), the active clays and carbons were found to adsorb peroxide bodies; this effect did not necessarily reflect greater stability. Bergelund (*Actas y trabajos Congr. peruano quim.* 2, II, 197) recorded that coloring matter in cottonseed oil could be removed with negatively charged material such as chromium or aluminum sulfate. He reported that the coloring matter was in the form of a positively charged colloidal suspension. Lee and King (*U. S. 2,368,669*) designed equipment to deodorize oils continuously.

Loury (*Bull. mat. grasses inst. colonial Marseille* 27, 151) thoroughly investigated chromatographic methods for refining oils. They were considered impractical because the best adsorbents, alumina and silica gels, were required in amounts, respectively, 10 and 30 times the amount of free fat acids present. The use of a chromatographic method for regeneration of waste edible fats and oils was patented (J. Lyons & Co. Ltd.—*Brit.* 558,150).

In a comparison of production of medicinal fish livers by digesting the livers with steam and with pepsin, followed by separating the oils with centrifuges, the latter yielded oils of lower vitamin potency (Cunningham and Scott—*New Zealand J. Sci. Tech.* 26B, 21). All the oils were light in color, clear and free from objectionable odor. A patented preextraction treatment for fish livers (Kaufman—*U. S. 2,380,847*) comprised storage and digestion of the livers in 3-12% alcohol solution containing a small amount of acetic acid.

The patented processes for producing high potency vitamin oils dealt principally with concentrating the unsaponifiable constituents of the oil. Those assigned to National Oil Products Co. (*U. S. 2,380,408-10, 2,380,413-4, 2,389,955; Brit.* 555,447, 558,820) cover the use of antioxidants, sugar, sugar esters, ketones, or edible gums in the process of saponification and removal of the unsaponified. According to some of the patents, partial and selective saponification was induced, followed by extraction of the unsaponifiable with acetone or isopropanol. The soaps formed were predominantly from the most saturated glycerides; a high iodine number oil suitable for the paint industry was separated by cooling of the organic solvent solution, and the unsaponified material containing the fat soluble vitamins was recovered from the solvent. Binnington's (*U. S. 2,373,646*) equipment for production of vitamin concentrates was based on extracting the unsaponifiable material from oils. Swain and McKercher (*Fisheries Res. Board Can. Prog. Repts.*

*Pacific Stas. No. 65, 67*) and Swain (*Ibid. No. 63, 32*) investigated chromatographic methods of concentrating the vitamins. In the latter paper concentrations from dogfish liver oil of 25-250 times that of the original oil were obtained. An additional doubling of the concentration was said to be possible by crystallizing out the cholesterol. The adsorption on the alumina column was made from hydrocarbon solution, and benzene and methylene chloride proved to be good eluting agents for the vitamin A. In continuing the work with several other oils the selectivity of several solvents for elution of unsaponifiable constituents from alumina was partially characterized. The methylene chloride eluate contains all the cholesterol and the vitamin A of the unsaponifiable. This eluate from tests on soupfin shark liver oil was approximately 80% vitamin A. Three inventions dealt with preparation of fish liver oil vitamin products in dry form. Buxton (*U. S. 2,375,278*), and Buxton and Briod (*U. S. 2,375,279*) accomplished this by mixing the comminuted livers with oil meals and drying or by adding fish liver oils to a mixture of meal and gelatine solution, drying, and powdering the dried mass. Sokoloff (*U. S. 2,375,501*) prepared a dry carrier for the medicinal fish liver oil by extracting pork and beef livers with a 0.1% solution of lactic acid and drying the insoluble portion. This dried material preserved the vitamin A of the fish liver oil and suppressed the fishy flavor.

In the field of processing tall oil, several diverse methods were used to improve the crude material. Dressler *et al.* (*U. S. 2,369,446, 2,371,230*) and Turck and Ross (*U. S. 2,389,284*) hydrogenated it to remove odor and to improve its soap making qualities. Novelty in the Dressler patents was pretreatment with clay or nickel catalyst to render the tall oil capable of being hydrogenated. Turck and Ross selectively hydrogenated the fat acid constituents with hydrogen at, not less than, 50 pounds per square inch pressure and at temperatures below 135°. Several inventors converted the tall oil acids to glycerol or other alcohol esters. Borglin (*U. S. 2,366,589*) esterified the hydrogenated tall oil acids with glycerol in organic solvent solution. Esters of tall oil and polyhydric alcohols were improved in stability by a polymerization treatment (Rummelsburg—*U. S. 2,369,109*; Anderson—*U. S. 2,369,125*; Humphrey—*Brit.* 556,456; Pollak and Willingham—*U. S. 2,374,700*). Other methods of improving the crude tall oil were heating with stannic chloride (Mitchell—*U. S. 2,371,307*) or boron compounds (Borglin—*U. S. 2,374,975*), extraction with water at elevated temperature and pressure (Arnold—*U. S. 2,382,196*), and conversion into soap, followed by passing inert gas or steam through the soap mixture (Ross—*U. S. 2,369,409*).

Patented methods of separating tall oil into resin acids and fat acids continue to appear. According to patents issued to Hercules Powder Co. (*U. S. 2,372,446, 2,379,986*) the resin acids were condensed with phenols and the fat acids were recovered by vacuum distillation; or the resin acids were precipitated from acetone solution by ammonia as diacetone amine abietate. In the latter process evaporation of the liquid yielded ammonium salts of the fat acids, and heating the precipitate permitted recovery of ammonia, acetone, and mesityl oxide. By low temperature precipitation Segessemann (*U. S. 2,373,978-9*) accomplished the separation of the fat acids

from a solution of the tall oil in ethanol. Loughlin (*U. S. 2,382,890*) converted the fat acids into *n*-butyl esters and the rosin acids into their sodium salts and then extracted the former with hexane. Houpt (*U. S. 2,378,359*) neutralized the fat acids and extracted the resin acids with amyl alcohol. Methods by Hixson and Miller (*U. S. 2,388,412*) and Adams (*U. S. 2,363,925*) utilized the countercurrent liquid-liquid extraction principle. The former extracted the fat acids at 90° with propane; the latter preferentially dissolved the resin acids with methyl ether of ethylene glycol from a solution of the tall oil in naphtha. A review on the separation of components of tall oil and their uses was compiled by Jennings (*Paper Trade J. 120*, No. 19, 41).

The recovery of by-products during refining of oils was the subject of many inventions. Two patents assigned to Distillation Products, Inc. (*U. S. 2,375,078*, *2,379,420*) described methods of concentrating tocopherols from vegetable oil deodorizing scums; respectively, by a chromatographic process and by hydrogenating the crude material and removing the fatty constituents by crystallization from acetone. Two methods (Yoder *et al.*—*Ind. Eng. Chem. 37*, 374; Picard and Seymour—*J. Soc. Chem. Ind. 64*, 304) described for the production of cholesterol from wool fat were based on the formation of a cholesterol-oxalic acid complex by reaction of the wool alcohols with anhydrous oxalic acid in ethylene dichloride, ethyl acetate, or benzene.

The innovations in concentrating phosphatides were based on the preparation of solutions that resolved into at least two phases, one of which preferentially dissolved the phosphatides. Freeman (*U. S. 2,390,528*) used furfural saturated with water. Christiansen (*U. S. 2,356,382*) used alcohol to concentrate crude phosphatides containing water, using a centrifuge to assist the resolution into two liquid phases, one of which was high in phosphatides, was assisted by centrifuging. Siffert (*U. S. 2,371,476*) treated water emulsions of phosphatides with ethylene dichloride which dissolved the diluting lipids in crude products, thus allowing phosphatides of 95-98% purity to be recovered from the aqueous phase. Julian and Meyer (*U. S. 2,391,462*) reduced the viscosity of phosphatide concentrates in fatty carrier by special treatment with mineral acids. A brief review on the commercial uses of phosphatides was compiled by Schofield (*Manufg. Chemist 16*, 135). Pangborn (*J. Biol. Chem. 161*, 71) discussed the purification and standardization of phospholipids for serologic use.

Gueniot (*Bull. mat. grasses inst. colonial Marseille 27*, 167) encouraged the use of phosphoric in place of sulfuric acid for splitting fats; it was found to be quicker, the glycerol recovery was better and the acids obtained were clearer. The remainder of the information on splitting fats was on improvements in continuous systems. According to two patents (Stalman—*U. S. 2,356,628*; Lever Bros. & Unilever Ltd.—*Brit. 561,191*) the oil was steamed in successive containers overflowing successively to lower containers in a series; or hot water was passed countercurrently with the oil in successive stages. Improvements in like systems by Davey (*U. S. 2,389,246*) and Daniels (*U. S. 2,387,884*) were, respectively, the designing of the equipment to absorb steam pressure pulsations and adjustment of fat-to-water ratio at optimum levels. As a substitute for splitting and to obtain good

glycerol recovery, workers at the Colgate-Palmolive-Peet Co. (*U. S. 2,383,579-80*, *2,383,596*, *2,383,599*, *2,383,601-2*, *2,383,614*, *2,383,632-3*) devised innovations in the commercial application of ester interchange to produce lower monohydric alcohol fat acid esters and glycerol from the alcohols and the fats.

In tests on fractional crystallization of the fat acids of cottonseed oil from solvent solution, Singleton, Lambou, and Bailey (*Oil & Soap 22*, 168) found that polar solvents were superior to nonpolar solvents because the temperature of crystallization was higher with the polar solvents. By conducting crystallization at 5° F. or lower with acetone and at -5° F. or lower with petroleum naphtha, with a solvent:fat ratio of 4:1, the liquid fat acids from unhydrogenated cottonseed oil could be reduced to below -2° F. in titer and to below 3% in saturated acid content. With hydrogenated oils the bulk of the higher melting isoöleic acids was precipitated at about -5° F. in acetone and -15° F. in petroleum naphtha. Swern, Knight, Scanlan, and Ault (*Ibid.* 302) recorded data from tests on fractionally crystallizing tallow fat acids from acetone at temperatures ranging from 0° to -60°. The saturated acid fraction crystallizing at 0° to -20° amounted to 40-50% of the starting material and corresponded to the commercial double- or triple-pressed stearic acid. A good yield of purified oleic acid was produced by crystallization at -50 to -60° followed by fractional distillation. Brown's (*Brit. 555,570*) patented procedure of improving the drying properties of fish oils comprised fractional crystallization from petroleum solvents in two steps, one at -10 to -30 and the other at -40 to -80°. For the same purpose, Buxton (*U. S. 2,380,412*) selectively partially saponified the saturated glycerides of fish oils and separated the unsaponified higher iodine value oils from the soap mass. A modification in oils was accomplished by Eckey (*U. S. 2,378,005-7*) by selective ester interchanges. For example, the lower weight fat acids were removed from coconut oil by heating it with methyl esters of high molecular weight acids and removing the low boiling esters by distillation. New vacuum equipment designs for fat stills were assigned to Distillation Products, Inc. (*U. S. 2,379,151*, *2,379,436*).

A review on manufacture of glycerides and fat acid esters of other alcohols was compiled by Lindner (*Fette u. Seifen 50*, 396). The dietary and technical uses of the products were given. Tests on reesterification of fat acids with glycerol by Feuge, Kraemer, and Bailey (*Oil & Soap 22*, 202) showed that the reaction was bimolecular. Velocity constants and heats of activation for the initial and final stages of the reactions were recorded. Zinc and tin chlorides proved to be outstanding catalysts for the reaction. These catalysts were removed by alkali refining. Polymerization or conjugation of the oils did not occur during esterification. Work of a similar nature by Konen, Clocker, and Cox (*Ibid.* 57) was on production of pentaerythritol and other polyhydric alcohol esters for use in the protective coating industry. They recommended strong acids as catalysts, 5% more than the theoretical amount of alcohol, and temperatures at about 450° F. for the process. Bruun and Perrine (*U. S. 2,384,793*) patented a continuous system of esterification in which the reagents were flowed at 100-150° through a catalyst, countercurrently, to an inert gas.

Reactions occurring during hydrogenation of oils were the subject of three investigations. Mattill (*Oil & Soap* 22, 213) recorded the changes in composition and characteristics of soybean oil during the course of heating with nickel catalyst and during the course of hydrogenation. Spectrometric and iodometric analyses indicated that during hydrogenation there were formed isomers of polyunsaturated acids which do not react normally upon analysis. This suggested that the nickel treatment caused a change, isomerization, within the fat molecules which resulted in lowered iodine and thiocyanogen numbers, and in spectrometrically determined linoleic acid, but did not decrease the total unsaturation. In similar work Daubert and Filer (*Ibid.* 299) recorded evidence to indicate that a double bond which resisted isomerization was produced on partial hydrogenation of methyl linoleate. It was suggested that the iso-acid may be identical with that which arises from preferential hydrogenation of 9,12,15-linoleic acid. Natarajan and Godbole (*Indian Soap J.* 10, 35) plotted the changes occurring in the composition of oils during hydrogenation. They believed that formation of iso-acids resulted from partial hydrogenation. Patents issued to Lever Bros. and Unilever Ltd. (*Brit.* 557,618, 557,620-1) described a method of hydrogenation comprising two successive stages: in the first stage the temperature was 110-120° and the catalyst was nickel; in the second stage the treating temperatures were 130-250° and the catalyst was a mixture of metal oxides. Very porous, low density catalysts were prepared by Turck (*U. S.* 2,375,506) by reducing the metal hydroxides with isopropyl alcohol or other reducing organic compounds. Vahlteich and Neal (*U. S.* 2,365,125) prepared a hydrogenation catalyst by reducing nickel salts of organic acids in a mixture of white mineral oil and fatty oil.

#### Products (Except Detergents)

The desirability for culinary purposes of hydrogenating the soft lards from hogs fed a ration high in soybeans was studied by Jordan (*Purdue Univ. Agr. Exper. Sta. Bull.* 498, 30 pp.). Her data and observations indicated that hydrogenation made soft lard similar in properties to a commercial brand of hydrogenated lard and hydrogenated fat with respect to shortening value, flavor of pastry and of biscuits, and behavior in deep-frying of doughnuts. Tests on soybean flours by Gabel and Sunderlin (*Oil & Soap* 22, 271) resulted in the observation that fat contained in flour had approximately the same shortening value as equivalent amounts of plastic fat. Pratt (*Bakers Helper* 84, No. 1053, 38; No. 1054, 64) recorded that 0.3% lecithin plus 1% shortening seemed equivalent to 4% shortening alone in baking tests. Black (*Bakers Digest* 19, 22) gave a lecture on cooking fats in which he discussed shortening, margarine, lard, frying fats, flavor and stability problems, plastic range, and specialty fats.

Lard has been successfully used as a protective material for meats (Hiner—*Quick Frozen Foods* 8, No. 4, 126). The process reduced weight losses and the rate of decrease in palatability. However, at high storage temperatures or long storage time, the lard may impart a slightly rancid flavor to the meat.

The recent war fostered interest in the manufacture of butter oil, since this product was more conveniently stored and shipped and could be reconstituted to butter on demand. The process of producing butter

oil for export or storage without refrigeration as described by McDowall *et al.* (*New Zealand J. Sci. Tech.* 24, 54B) comprised systematic means of melting, settling, centrifuging, dehydrating, cooling, and packaging. Hamdi and Zollikofer (*Mitt. Lebensm. Hyg.* 35, 66) cautioned against slow cooling of butter oil for they demonstrated that very slow cooling in a container caused pronounced fractionation, giving portions with constants varying widely from normal butterfat. The improvement in keeping quality of butter stored in the form of butter oil was pointed out by Josephson and Dahle (*Food Industries* 17, 630). However, a cooked flavor in butter oil was undesirable for some uses, consequently commercial butter rendering processes should be controlled to impart maximum stability to the fat with a minimum of cooked flavor or odor. El-Rafey *et al.* (*J. Dairy Sci.* 27, 807) recommended processing at a temperature of 110°. They believed the improved keeping quality was the result of greater transfer of phospholipid material from the non-oil phase to the oil, presumably because of the denaturing action of heat on the protein and phospholipid-protein complex. At high temperatures the reducing substance became concentrated in the butter oil. A tropical butterfat spread prepared by Wiley (*Australian Dairy Rev.* 11, No. 9, 4) contained butter oil, hydrogenated butter oil, finely powdered salt, dried skim milk, and diacetyl flavoring.

Some of the steps in butter making were better elucidated by the newer work. Hoecker and Hammer (*Iowa State Coll. J. Sci.* 18, 267) pointed out that acid and flavor development in butter cultures was better on incubation at 21° than at 7°, but as acidity increased, the flavor compounds were destroyed. Additions of citric acid increased the flavor compounds, *i.e.*, acetylmethylcarbinol and diacetyl. White (*Sci. Agr.* 25, 137) found that when acidity of cream was increased from 0.11 to 0.31% a flavor loss occurred so that the butter scored 2-3 points lower. Metallic, sour, and fishy flavors were more evident in butters from high acid creams. The reports of Jenness and Palmer (*J. Dairy Sci.* 28, 611, 653) were in connection with the theoretical concept of the colloidal behavior of proteins and phospholipids in butter churning. An adsorption "membrane" containing proteins and phospholipids which surrounds fat surfaces in cream was said to be disrupted by churning. This disruption apparently breaks some of the linkages between proteins and phospholipids as well as between phospholipids and fat. During melting of the butter the phospholipids continued to cling to the higher melting fat molecules with the result that they were pulled into the serum.

Partial esters of polyhydroxy alcohols and fat acids were used as emulsifiers for several preparations. A composition for prevention of fogging of glass surfaces contained a 1:1 mixture of mono fat acid ester of nona ethylene glycol and fat acid ester of ethylene glycol (Bennett—*U. S.* 2,372,171). A dispersed wax for laundry purposes contained paraffin, hydrogenated fish oil, and partial fat acid esters of polyhydroxy alcohols (Griffin—*U. S.* 2,374,931). The latter were also used in lacquers for a hectograph blanket (Bour—*U. S.* 2,372,354). Mixtures of partial fat acid esters of sorbitol, mannitol, and hexane pentols and these same compounds treated with ethylene oxide were patented as emulsifiers for waxes (Griffin—

*U. S. 2,380,166*). A mixture of petrolatum and water emulsified with diethylene glycol monostearate and sulfated hydrogenated castor oil was considered a substitute for the official ointment base (Fiero and Loomis—*J. Am. Pharm. Assoc.* 34, 218). Partial polyglycerol fat acid ester was also an ingredient of a patented brushless shaving preparation (Thomas and Whitham—*U. S. 2,366,759*). Mechanical means of emulsification in the manufacture of mayonnaise and salad dressing were patented by Lindsey (*U. S. 2,369,744*) and McLean (*2,370,978*).

An advertisement requesting suggestion of the names of edible emulsifiers yielded the following list: corn sirup, dextrose, glycerol, glycol, oleic acid, sodium lactate, sodium malonate, sodium tartrate, sucrose, Duponol PC, Santomerse B, Solvereg, Vatsol K, and Vatsol OP (*Food Industries* 17, 1322). No advice as to the utility or legality of their use was given. Methods of employing lecithin as an emulsifier in many food products were published by Cook (*Ibid.* 740, 900). Methylated cephalin, a derivative of commercial lecithin, was used to reduce the viscosity of chocolate (Julian *et al.*—*U. S. 2,373,686-7*). A mixture of cholesterol and fat alcohols derived from lanolin was patented for emulsification purposes (Taylor—*U. S. 2,365,915*). Solvent extracted soybean flour was reported to be a good substitute for egg yolk as an emulsifier for salad dressings (Watts—*Proc. Pacific Sci. Congr. Pacific Sci. Assoc.* 6, 453). A new method of extracting emulsifier from Irish moss was patented (Stoyle—*U. S. 2,375,259*). A non-heat-coagulable proteinaceous fermentation residue was used as an emulsifier in a fat soluble vitamin preparation (Peters and Rupp—*U. S. 2,356,350*). Alkali treated starches (Gaver—*U. S. 2,347,678-80*) and special ether compounds containing alcohol, fat acid, and alkyloamine radicals (Katzman and Epstein—*U. S. 2,390,942*) were said to be good general purpose emulsifiers. A paste wax patented by Dolian (*U. S. 2,374,474*) contained fat acid derivatives of amino monohydric alcohols as the emulsifiers. The patented emulsifiers for asphalt were a sodium hydroxide-saponified product of wood rosin oil (Mayfield—*U. S. 2,370,911*), an amino alkylamide of a fat acid (Mikeska—*U. S. 2,389,680*), and a fat acid amidine (Mikeska—*U. S. 2,389,681*).

Fat derived demulsifier compounds were prepared for use in releasing oil from crude petroleum oil emulsions (Petrolite Corp.—*U. S. 2,364,118, 2,366,239-40, 2,366,498, 2,366,792, 2,369,817-18, 2,371,429, 2,372,254-9, 2,372,364-6, 2,372,623, 2,372,641, 2,373,228-30, 2,375,529-40, 2,375,606, 2,375,899, 2,381,115-18, 2,381,575-7, 2,382,612, 2,384,605-8, 2,385,969-70, 2,386,445-6, 2,386,936-7, 2,390,078-83*; Bishkin—*U. S. 2,374,917*). Most of the demulsifying compounds were derivatives of castor oil fat acids.

Because of the scarcity of drying oils the work in the protective coating industry reflected a strong interest in preparing substitute derivatives from the oils and materials at hand. Among the general publications on the protective coating industry Mattiello (*Chem. Eng. News* 23, 136) and Lilley (*Paint Tech.* 10, 133) reviewed recent progress in the field; alkyd resins, amine resins, interpolymers, new drying oils, and rosin were the main topics of the papers. In similar papers Catlow (*Oil & Soap* 22, 131) discussed the synthetic resins and Fonrobert (*Fette u. Seifen* 50, 514) reviewed the possible reactions of unsatu-

rated oils with phenol-aldehyde resins. Recent theories on the mechanism of heat polymerization of drying oils and mechanism of drier action were surveyed, respectively, by Bolley (*Am. Paint J.* 29, No. 37, 19) and Rudd (*Paint Manuf.* 14, 331). Procedures for processing oiticica oil in the paint industry were outlined by Huffman (*Am. Paint J.* 29, No. 50, 48).

A very small number of publications appeared on the theoretical aspects of changes occurring in drying oils. In work on oxidation of ethyl linoleate, Bolland and Koch (*J. Chem. Soc.* 1945, 445) reported that the primary product was a monohydroperoxide which according to spectrographic methods contained 70% conjugated diene isomers. One of the first decomposition products appeared to be a ketone. In a similar work Phalnikar and Bhide (*J. Indian Chem. Soc.* 21, 313) recorded some of the products developed on heat polymerization of safflower, niger seed, and olive oils. Lichtenwalner, Adams, and Powers (*J. Phys. Chem.* 49, 511) studied monolayers of linseed oil glycerides. The attraction of water for the polar group in the oil causes it to spread; with oxidation the molecules flatten further. A limiting area was reached with the addition of three atoms of oxygen per glyceride molecule.

Several innovations for bodying oils were patented. Harvey and Schaufelberger (*U. S. 2,366,525-6*) bodied soybean and cottonseed oils by distilling them under reduced pressure until 10-35% of the starting material was evaporated. Varlamov and Drinberg (*Russ.* 59,845) steamed marine oils in the presence of oxides of zinc, calcium, manganese, or lead; the saturated acids were distilled off during the process. Carleton (*U. S. 2,367,666*) designed equipment to polymerize oils, hydrolyze them, and remove saturated acids by distillation, all in a continuous process rather than by intermittent steps. Berger *et al.* (*U. S. 2,380,394*) polymerized oiticica oil in the presence of boron fluoride as a catalyst and after the desired body arrested the polymerization with quinoline. McNally and Dickey (*U. S. 2,386,250*) treated polymerized oils with phosphorus whereby a phosphato or a phosphito radical was attached through a carbon-oxygen-phosphorus linkage. Heating with mono- or di-isocyanates was also recorded as a method of improving bodied oils (Bunge and Bayer—*Ger. 742,519 Cl. 22h; Belg. 446,151*).

Three patents dealt with conjugating the unsaturated acids of drying oils. Saponification at 235-250° was said by two inventors to cause conjugation without polymerization (Kirschenbauer—*U. S. 2,389,260*; Stevens—*Brit. 558,881*). Another method of conjugation was to oxidize the oil and dehydroxylate the oxidized product in the presence of a dehydroxylating agent dissolved in water (Colbeth—*U. S. 2,388,122*).

A thorough investigation of manufacturing drying oils by dehydroxylation of castor oil was published by Grummitt and Fleming (*Ind. Eng. Chem.* 37, 485). The oil was acetylated in the presence of *p*-toluenesulfonic acid. The rates of decomposition of the acetylated product were measured at seven temperatures between 295 and 340°. The thermal polymerization which occurred during the reaction was minimized by the higher reaction temperatures with shorter reaction times. Best products were obtained with *p*-toluenesulfonyl chloride as the decomposition catalyst. The control conditions of using a 3:1 castor

oil:acetic acid ratio in acetylating and a temperature of 280° for decomposing were patented by Nessler and Schuelke (*Can. 428,728*). Fisher and Fein (*U. S. 2,374,428*) preferred to use no catalyst in acetylation of castor oil, thus avoiding the necessity of filtration. Urben and Price (*Can. 428,786*) prepared the phthalic esters of castor oil acids and decomposed these. Patented catalysts for dehydroxylating by heat were zinc (Distillers Co. Ltd. —*Brit. 558,780*), alkalis (Kirschenbauer — *U. S. 2,388,158*), and aluminum (Vigdorov — *Russ. 57,912*). A continuous process of dehydrating the oil comprised passing it over a calcined composite of phosphoric acid and a siliceous adsorbent at a dehydrating temperature (Bloch — *U. S. 2,380,720*). Rector and Cron (*U. S. 2,367,376*) prepared castor oil for use in cellulose preparations by the blowing procedures used in bodying oils.

The drying properties of many oils were improved by transforming them into esters of alcohols containing more hydroxyl groups than glycerol. In a comparison between natural linseed and tung oils with poly-pentaerythritol drying oils made from these oils, Burrell (*Ind. Eng. Chem. 37, 86*) developed data showing the superiority of the synthetic esters in regard to ability to body, to form water- and alkali-resistant varnish, and to withstand weathering. Brandner, Hunter, Brewster, and Bonner (*Ibid. 809*), in similar work on sorbitol esters, reported that these were better than the pentaerythritol esters, mannitol esters, or the natural linseed oil with respect to drying time and about equal to the best of the others in hardness and alkali resistance. Two papers gave directions for manufacturing poly-pentaerythritol-tall oil esters for use in low-cost, rapid-drying varnish of acceptable color and fair outdoor durability (Burrell and Valk — *Paint, Oil Chem. Rev. 107, No. 25, 14*; Golden Gate Paint and Varnish Production Club — *Ibid. No. 22, 84*). Burrell (*U. S. 2,360,393-4*) patented the use of several metal and alkali metal soaps as catalysts for preparing pentaerythritol esters of fat acids. Bradley's (*U. S. 2,378,827*) patent on esters of pentaerythritol and polyallyl alcohol of more than five hydroxyl groups stated that the fat acids used should have an iodine value of at least 100 and that at least five of the hydroxyl groups should be esterified. Burrell and Bowman (*U. S. 2,390,202*) patented a synthetic drying oil composed principally of di- and tri-pentaerythritol esters of unsaturated fat acids. Other synthetic drying oils were pentaerythritol or other polyhydric alcohol esters of fat acids and other compounds. The latter were organic acids with double bonds in the two and four positions (Cupery — *U. S. 2,381,880*),  $\beta$  furylacrylic acid (Rothrock — *U. S. 2,381,881*), cyano acids with double bonds in the two and four position (Cupery — *U. S. 2,381,882*), cinnamalacetic acid (Brubaker — *U. S. 2,381,883*),  $\beta$ -furylacrylic acid modified resin (Rothrock — *U. S. 2,381,884*),  $\alpha,\beta$ -ethylenic- $\alpha$ -(alken-1-yl) monocarboxylic acid (Sauer — *U. S. 2,381,885*), acylacrylic acid (Cupery — *U. S. 2,381,886*),  $\alpha,\beta$ -ethylenic- $\beta$ -aryl monocarboxylic acid (Sauer — *U. S. 2,381,887*),  $\alpha,\beta$ -unsaturated monocarboxylic acid (Agre — *U. S. 2,381,888*), and thienylacrylic acid (Brubaker — *U. S. 2,381,889*). Esters of unsaturated fat acids and amino hydroxy alkyl alkanes containing at least two hydroxy groups were also good artificial drying oils (Lycan and Eyre — *U. S. 2,373,250*).

Several factice materials were invented. Bencowitz's (*U. S. 2,382,284*) product was prepared by boiling soybean oil with levulinic acid in naphtha solvent. Three products suitable for floor covering were a reacted mixture of polyhydric alcohol, drying oil, and diene resin (Cohen *et al.* — *U. S. 2,381,486*), a copolymer of drying oil and vinyl compounds (Dunlap — *U. S. 2,382,212-3*) and a mixture of gelled polyhydric alcohol mixed ester of a hexadien-2,4-oic acid and the acids of drying oil, and a pigment filler (Cupery — *U. S. 2,382,297*). An oil cloth composition contained a special bodied linseed oil, pigment, filler, and solvent (Lent — *U. S. 2,381,915*). A leather-like coating for upholstery fabric comprised a mixture of nitrocellulose, plasticized resin of castor oil, maleic anhydride and glycol, and condensation product of castor oil, diethylene glycol and maleic anhydride (Hedges *et al.* — *U. S. 2,387,393-6*). A putty by Zolad (*U. S. 2,389,708*) contained granular material, ethyl cellulose, and a drying oil modified alkyd resin. Oxidized soybean oil was mixed with a rubbery gum to yield material suitable for manufacture of golf ball covers (Miller — *U. S. 2,374,692*).

The largest number of fat derived varnish resins was prepared by reacting oils, polybasic acids or their anhydrides, glycerol, and other compounds (Bent and Ryan — *Can. 423,559*; Gray — *U. S. 2,374,598*; Hubbuch and Robinson — *U. S. 2,370,962*; Luaces — *U. S. 2,389,794-5*; Moore — *U. S. 2,369,683, 2,384,846*; Root — *U. S. 2,374,381*; Scrutchfield — *U. S. 2,376,823*; Waldie — *U. S. 2,387,424*; Weide — *U. S. 2,378,886*). A resin prepared by Rummelsburg (*U. S. 2,370,688*) was a copolymer of terpene hydrocarbons and glycerol esters. A coating composition patented by Rostler and Bornstein (*U. S. 2,371,652*) comprised resin and drying oil dissolved in petroleum by-products. A similar preparation by Fain (*U. S. 2,368,126*) contained a reaction product of shellac and drying oil. Other resinous derivatives of fats were a condensation product of stearyl benzene and formaldehyde (Lieber — *U. S. 2,384,935*), polymers of castor oil and allyl acid carbonate (Muskat and Strain — *U. S. 2,385,934*), a heat treated mixture of dihydric alcohol polyesters of polymerized fat acid and rubber compounding agents (Cowan and Teeter — *U. S. 2,384,443*), and specially treated mixture of fatty oils and thermoplastic resins (Church — *U. S. 2,369,434*). In several patented resins, fatty oils, principally castor oil, were used as plasticizers (Bradley — *U. S. 2,379,413*; Gutkin — *U. S. 2,374,812-4*; Opp — *U. S. 2,385,377*; Rector and Cron — *U. S. 2,367,375*). Tall oil and special esters of tall oil were found to be good plasticizers for synthetic rubber. At the government regional laboratories, several derivatives such as the esters of polymeric fat acids with allyl alcohols (Teeter and Cowan — *Oil & Soap 22, 177*) or with dihydric alcohols (Cowan and Ault — *U. S. 2,373,015*), or with the amides of the acids (Falkenburg, Teeter, Skell, and Cowan — *Oil & Soap 22, 143*) were suggested for use in lacquers, adhesives, plastics, rubber, etc.

Several protective coatings containing oils or fatty oil derivatives were made in the form of water dispersions. Stamberger (*U. S. 2,391,041-2*) prepared such a water dispersed lacquer by bodying drying oils in water solution containing an emulsifier; hydrogen peroxide was used as the oxidizing agent in the bodying. Special methyl cellulose compounds were used as the dispersing agent for Auer's (*U. S. 2,382,532-3*)



dispersion of drying oils in water. Proportions of ingredients, a special blown oil, and use of the ball mill were featured in the patented water-emulsion paints of Balassa (*U. S. 2,384,270*). Quaternary ammonium salts were used to disperse methacrylic polymers (Neher and Conn—*U. S. 2,372,108*). A water dispersible coating was prepared by heating together urea, potassium carbonate, rosin, and a drying oil (Hirsch—*U. S. 2,372,577*). In casein, zein, and other protein water paints, castor oil (Scholz *et al.*—*U. S. 2,379,402*), soaps (Fales and Fales—*U. S. 2,367,108*), and nonsoap detergents (Atwood—*U. S. 2,389,605*; James—*U. S. 2,377,237*) were used as the dispersing agents.

Several types of alcohol derivatives were prepared from fats. Johnston (*U. S. 2,347,562*) polymerized unsaturated acids and subsequently hydrogenated to obtain glycols containing 36 carbon atoms and trihydric alcohols of 54 carbon atoms. The products were useful as plasticizers or as intermediates for the production of wetting agents. In the manufacture of fatty alcohols by hydrogenation of fat acids, catalysts of zinc-vanadium (Rittmeister—*U. S. 2,374,379*) and copper and cadmium soap (Richardson and Taylor—*U. S. 2,375,495*) were patented. Bag and Egupov (*Uspekhi Khim. 14*, No. 1, 56) described their experiences in the commercial production of the alcohols by hydrogenation in the presence of copper-aluminum alloy catalysts. Another method of preparing the alcohols was by treatment of the fat acid esters with metallic sodium in alcohol solution (Soc. anon. d'innovations chim. dite Sinnova ou Sadic—*Belg. 446,042*). A review on the cosmetic uses of wool wax alcohols, with representative formulas was prepared by Lower (*Soap, Perfumery, Cosmetics 18*, 125, 219). Another review (Stossel—*Soap Sanit. Chemicals 21*, No. 8, 38) dealt with the fatty alcohols prepared from cheap petroleum products. Details for the reaction of monounsaturated fat acids with hydrogen peroxide and formic acid to produce hydroxylated compounds were given by Swern *et al.* (*J. Am. Chem. Soc. 67*, 1786). Oleic and elaidic acids, respectively, yielded 93 and 97% of dihydroxystearic acid. Oleyl alcohol was converted to dihydroxyoctadecanol by the process. A patented process of manufacturing the hydroxy acids comprised subjecting sulfated fat acids to acid hydrolysis (Price and Griffith—*U. S. 2,367,050*).

A method of making pure stearic acid by Schuette and Roth (*Oil & Soap 22*, 294) involved separating the ethyl ester of 12-hydroxystearic acid from the ethyl esters of hydrogenated castor oil fat acids by solvent methods and dehydroxylating this via its halogen derivatives. A new class of compounds, epoxidized oils, was prepared for the first time by Findley, Swern, and Scanlan (*J. Am. Chem. Soc. 67*, 412) by reaction of the oils with peracetic acid in glacial acetic acid solution. Kirkpatrick (*U. S. 2,372,090*) prepared high molecular weight dicarboxylic acids from monounsaturated fat acids by heating in water and carbon monoxide in contact with boron fluoride. Myers *et al.* (*U. S. 2,369,036*, *2,369,108*, *2,389,191*) selectively oxidized the polyunsaturated acids of semidrying oils with dilute chromic acid. The process makes oleic acid available with dibasic acids as by-products.

In a search for development of plasticizers and waxes, Swern and Jordan (*J. Am. Chem. Soc. 67*, 902) prepared and recorded the properties of C<sub>3</sub> to C<sub>18</sub> esters of 9,10-dihydroxystearic acid. Snell and

Guiteras (*U. S. 2,385,849*) patented a synthetic wax comprising special esters of higher alcohols and fat acids. The wax modifiers of Lieber (*U. S. 2,389,293*) were Friedel-Crafts condensation products of halogenated tall oil and aromatic organic compounds. Patented special cellulose ester preparations invented by Salo and Vivian (*U. S. 2,387,773-4*) contained butyl stearate. Oleic acid esterified with glycerol and ozonized was said to be of therapeutic value (Johnson—*U. S. 2,356,062*). Buu-Hoi and Cagniant (*Bull. soc. chim. 10*, 477) prepared and recorded the properties of many aliphatic and aromatic  $\alpha$ -substituted fat acids.

Bradley (*U. S. 2,367,712*) prepared synthetic hard waxes by reacting  $\omega$ -hydroxydecanoic acid with fatty amines. Bersworth (*U. S. 2,374,915*) converted unsaturated fat acid amides into amino acid amides by reaction with amines in the presence of hydrogenating catalyst. In a continuation of work on fat derivatives, Pool, Harwood, and Ralston (*J. Am. Chem. Soc. 67*, 775) recorded physical data to indicate that fat amine acid salt formation may result in the production of more than one salt, *i.e.*, octadecylamine and acetic acid yielded a mono and a diacid product. Another paper from the same laboratory (Hoffman, Hoerr, and Ralston—*Ibid.* 1542) reported that stearonitrile-palmitonitrile mixtures exhibited dimorphism, although this behavior was not observed in the pure compounds.

Reviews on preparation and application of soluble oils in the textile industry were prepared by Neville (*Am. Dyestuff Repr. 34*, 534) and Treffler (*Chem. Industries 55*, 922). The patented emulsifiers of two textile oils were, respectively, petroleum sulfonates (Heintz and Zillessen—*U. S. 2,387,510*), and a mixture of petroleum sulfonate, oleic acid, and butyl alcohol (Donlan and Gathman—*U. S. 2,391,087*). Certain monofat acid saccharide derivatives were added to viscose spinning solutions to prevent fouling of the spinnerets (Bley—*U. S. 2,348,203*; Collins—*U. S. 2,359,750*). In the spinning of alginic yarns vegetable oils in emulsified form were used to prevent the freshly coagulated fiber from adhering (Speakman—*U. S. 2,371,717*). Among the patents on treating textiles to render them water repellent or moth proof, or to give them a special finish, three were based on the use of insoluble metallic soap preparations (Treacy—*U. S. 2,369,992*; Gardner—*U. S. 2,371,884*; Damison—*U. S. 2,374,447*) and the remainder were based on resinous derivatives of fat acids and methods of using them (Chappell—*U. S. 2,385,794*; Hood—*U. S. 2,371,892*; Kaase and Waltmann—*U. S. 2,370,405*; Pingree—*U. S. 2,386,631*; Rogers—*U. S. 2,386,140-3*; Thurston—*U. S. 2,385,765-6*; American Viscose Corp.—*Brit. 555,480*; Phrix-Arbeitsgemeinschaft—*Belg. 446,800*; I. G. Farbenind. A.-G.—*Belg. 446,073*, *446,102*). The introduction of polycarboxylic acid and fat acid radicals into cellulose acetate material was said to improve the heat stability and crease resistance of textiles made therefrom (Moncrieff and Bates—*U. S. 2,372,386*).

The fat derivatives prepared for insecticidal purposes were a di-allyl amide of a fat acid (Evans and Williams—*U. S. 2,379,223*), dilauryl sulfite Hechenbleikner—*U. S. 2,377,148*, and dispersed hydroxy copper soaps (Minich—*U. S. 2,368,560*). Certain monomeric bis quaternary ammonium salts containing a fat acid radical were made for use as disinfectants

(Kirby and Lontz—*U. S. 2,375,853*). Wyss *et al.* (*Arch Biochem.* 7, 415) and Kodicek and Worden (*Biochem. J.* 39, 78) recorded data on bactericidal and fungicidal action of fat acids. The former found that long chain saturated and unsaturated fat acids were superior to other acids and related derivatives. The latter recorded that the methyl esters were not bactericidal and that lecithin, cholesterol, and other sterols reverse the inhibiting effect of the fat acids on lactic acid bacteria.

Several fat derivatives were used in flotation with different ores. A mixture of sodium oleate and oleic acid was the flotation reagent for iron ore (Clemmer and Clemmons—*U. S. 2,383,467*). Fat acid amines were used in concentrating the tin ores, siderite, and cassiterite (Gaudin—*U. S. 2,381,662*). For barite ores, a mixture of tall oil, lauric acid-ester-diethylene glycol-ammonium sulfate, and an alcohol was used (Hoag—*U. S. 2,371,292*). Mahogany sulfonates (Keck—*U. S. 2,373,688*) and a mixture of polyethylene polyamines and coconut oil (Christmann *et al.*—*U. S. 2,356,821*) were utilized on phosphate ores. The C<sub>12</sub> fat acids and  $\alpha$ -hydroxy fat acids proved superior to the lower homologs as reagents for collectors of iron oxides (Erlenmeyer *et al.*—*Helv. Chim. Acta* 27, 1429).

Some fat materials were used as anticorrosives. Those for use in lubricating oils were mixtures of fat and esters of dicarboxylic acid having at least 16 carbon atoms (Shell Development Co.—*U. S. 2,369,640-1*), succinic acid di thio ester of a fat acid (Shell Development Co.—*U. S. 2,349,044*, *U. S. 2,371,143*), a mixture of isoamyl octyl acid phosphate, and "coco" fat acid amines or other amines (Gulf Oil Corp.—*U. S. 2,371,851-4*), and mono-fat acid amides of phthalic acid (Gulf Oil Co.—*U. S. 2,378,442-3*). Glycol antifreeze was rendered less corrosive by addition of glycerol monoricinoleate (Balcar—*U. S. 2,386,182-3*).

Several uses for fat and fat derivatives were difficult to classify. Fatty alcohols, esters, ethers, and oximes were added to the chlorinated hydrocarbon solvents used in degreasing metals in order to inhibit a metal induced decomposition (Petering and Aitchison—*U. S. 2,371,644-7*). A paste of ground roasted coffee beans and cacao butter was patented for use in shoe polishing compositions (Brown—*U. S. 2,376,956*). Special fat acid quaternary ammonium compounds (Gunderson—*U. S. 2,366,727*), a mixture of insoluble metal soaps, glycol polymers, and fat acid esters (Fritz—*U. S. 2,390,212*), and reaction products of oils and diethylene triamines (Fritz and Robinson—*U. S. 2,347,178*) were new patented defoamers. Two patented printing ink compositions contained tall oil (Davis—*U. S. 2,385,613*; Carman and Reil—*U. S. 2,385,793*). The life of carbon electrodes was extended by impregnating them with drying oil (Kiefer and Krellner—*U. S. 2,368,306*). Metallic soaps of hydroxy fat acids were added to urea-formaldehyde resins to improve the moisture resistance of the resin (Corwin and Moffitt—*U. S. 2,372,178*). Solutions of aluminum stearate containing naphtha, low molecular weight alcohols, acetic acid, or other acids, and cumar resins were prepared for coating freshly laid concrete to prevent moisture loss (Madison—*U. S. 2,374,446-7*).

A comprehensive review on preparation, properties, and uses of insoluble metallic soaps was published by Lesser (*Soap Sanit. Chemicals* 21, No. 7, 36; No. 8,

40). These types of soaps appeared most frequently in the patent literature in connection with preparation of lubricants. The patented methods for their preparation indicated that their principal use was as lubricant constituents. Färber (*U. S. 2,367,462*) prepared a metallic soap product from tall oil using less than one-third of the metal hydroxide necessary for neutralization and evaporated the mass until the residue became neutral. Schiller (*U. S. 2,389,873*) prepared heavy metal soaps from water suspensions of insoluble metal hydroxides and alkali soap solutions; dilute strong acid was added to neutralize the excess alkali and to liberate one molecule of fat acid from the soap; and the remainder of the procedure dealt with separating the products. Hodges (*U. S. 2,381,822*) used the "floating soap" collected from black liquor in the manufacture of cellulose material for the sulfate or soda process for the raw material for metal soap manufacture. Tin soap lubricant ingredients patented by Elliott (*U. S. 2,373,387*) contained 30-45% tin.

Morgan *et al.* invented many new special lubricant greases. Among those which were especially characterized as having comparatively constant viscosity were a mixture of lithium and aluminum stearates, and hexyl ether (*U. S. 2,366,042*), a mixture of the above soaps, polymerized castor oil, tributyl phosphate, latex, and sulfurized tin salts of an alkylphenol carboxylic acid (*U. S. 2,376,312*), a composition of alkyl acetylricinoleate, lithium stearate, and sulfurized tritoyl phosphite (*U. S. 2,379,850*), and a mixture of diethylene glycol, methyl, ethyl, or butyl ether, and a sodium soap (*U. S. 2,383,915*). Morgan's low temperature grease inventions were cumene or isocumene, small amount of "Polane," and soap (*U. S. 2,355,993*), a mixture of mineral oil alkyl acetyl ricinoleate and aluminum and lithium stearates (*U. S. 2,383,147*), ethyl, butyl, or isobutyl lactate with a small amount of sodium stearate (*U. S. 2,383,916-17*), and certain mixtures of lithium and aluminum soaps and petroleum products (*U. S. 2,390,450*). A blended mixture of lithium, aluminum, and lead soaps, and petroleum oil by the same inventor (*U. S. 2,375,485*) was made for gun-turret lubrication. Special lubricating grease blends of alkali metal and heavy metal soaps with mineral oils were prepared by Zimmer *et al.* (*U. S. 2,360,631*, *2,374,966*, *2,383,904-5*, *2,391,113*). The mixtures varied considerably to give the individual greases such special characteristics as low pour point, high adhesiveness, water-resistance, etc. A lubricant suitable for machinery for manufacturing butyl rubber at temperatures as low as  $-100^{\circ}$  F. contained low pour point naphtha, zinc stearate, and a fat acid soap of a metal of group II of the periodic table (Gerlicher and Bannon—*U. S. 2,356,313*). A grease invented by Leyda (*U. S. 2,389,523*) contained special proportions of barium, calcium, and magnesium soaps and mineral oil. The grease patented by Woodward and Arkis (*U. S. 2,369,705*) contained metal soap, di-*p*-methoxydiphenylamine, diphenyl-*p*-phenylene diamine, and phenyl- $\beta$ -naphthylamine. A continuous process for manufacturing lubricating greases was designed by Zimmer and Morway (*U. S. 2,383,906*).

Fat and fat derivatives improved mineral oil lubricants in many ways. A reaction product of castor oil and tributyl phosphite improved the lubricant properties of mineral oils (Gilbert—*U. S. 2,361,022*). The

addition of phosphatides and a tin soap to Diesel engine lubricant oil reduced ring sticking, bearing corrosion, and sludge formation (Towne—*U. S. 2,366,817*). Phosphatides and detergent mixtures were also recommended for addition to internal combustion engine lubricants to reduce "varnish" formation (Julian and Meyer—*U. S. 2,374,681-2*); Bell—*U. S. 2,365,377*). A mixture of fat alcohols, heavy metal soaps, oil soluble sulfur, and methyl salicylate was also a sludge reducer (Nill—*U. S. 2,349,224*). Ethylxanthylchlorostearate was said to improve film strength and stability and reduce corrosiveness of lubricants (Lincoln and Byrkit—*U. S. 2,368,670*). The presence of small amounts of fat acid amides of ethylphosphoric acid in Diesel engine lubricant had a scrubbing action on impurities accumulated in engine parts (Hurn—*U. S. 2,366,190*). Special alkali salts of phthalic acid mono esters containing a fat acid radical (Johnston—*U. S. 2,372,955*) and fat acid esters of tri- and tetrahydric alcohols having neo-carbon atoms (Johnston—*U. S. 2,371,333*) conferred good detergent properties on lubricating oils. Foaming was prevented with a small amount of aniline reaction product of sulfonated castor oil (Zimmer—*U. S. 2,355,255*). Two household lubricant oils contained mineral oil, castor oil, sperm oil, antioxidants, and anticorrosive agents (Smith and Cantrell—*U. S. 2,371,655-6*). A steam cylinder lubricant comprised a major portion of mineral oil and minor portions of fatty oil and phosphatides (Adams and MacLaren—*U. S. 2,373,733*). Several inventors prepared special sulfur-treated fats or fat derivatives for addition to lubricating oils

(Lincoln and Byrkit—*U. S. 2,371,631*; Kaufman and Philson—*U. S. 2,367,355*; McCoy and Towne—*U. S. 2,367,362*; Williams and Backoff—*U. S. 2,375,060-1*; Smith—*U. S. 2,360,905*; Dietrich—*U. S. 2,373,879*; Davis and Barth—*U. S. 2,385,912*).

Bowden *et al.* (*Nature* 156, 97) published a communication on lubrication by fat acids. Metals which were reactive enough to form soap, *e.g.*, zinc, cadmium, copper, etc., were efficiently lubricated by 1% lauric acid in paraffin oil, while unreactive material, *e.g.*, platinum, nickel, chromium, glass, etc., were poorly lubricated. This was regarded as evidence that soap formation by reaction with metallic oxides did occur with the reactive metals.

Patented lubricants for cold-rolling of metal strips were a mixture of mineral oil with minor proportions of sulfonated castor oil (Kingerley—*U. S. 2,391,631*) and a mixture of mineral oils, fat acids, and fish oils (Reswick—*U. S. 2,377,106*). A patented cutting oil was a vegetable oil-water emulsion (Alsmark—*U. S. 2,359,503*). A comprehensive survey on cutting oils was published by Cady (*Metals and Alloys* 22, 432).

Cracked vegetable oils were replacing mineral oils during the blockade in China (Cheng and Teng—*J. Chinese Chem. Soc.* 11, 79; Cheng—*Chem. & Met. Eng.* 52, No. 1, 99). McCorkle (*U. S. 2,355,314*) prepared  $C_{12}$  to  $C_{18}$  hydrocarbons by heating the corresponding primary amines with a nonoxidizing inorganic acid. The above mentioned amines were derivatives of fat acids.

(Part II to follow in May)

## The Pigment Glands of Cottonseed

### I. Behavior of the Glands Toward Organic Solvents

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THE current expansion of the oilseed processing industry has led to an increased use of solvent extraction methods. In view of the recent development of many improvements in solvent extraction processes (10), it might be expected that their extension to the processing of cottonseed would not be difficult and would involve primarily an engineering problem. Examination of the literature on the subject (7,11,12,13) indicates, however, that solvent extraction of cottonseed presents many problems, chief among which is that involving the complex pigment system which is present in cottonseed.

Cottonseed is very much more highly pigmented than most other oilseeds. Moreover, the amount of pigmented material extracted from the seed is a function of the type of solvent used. The behavior of the cottonseed pigments during solvent extraction of cottonseed as well as their stability in the seed is not readily explained on the basis of the solubilities of the isolated pigments. Petroleum ether extracts very little of the yellow cottonseed pigment, gossypol,

despite the fact that gossypol is readily soluble in mixtures of hydrocarbons and cottonseed oil (15). Gossyfulvin, the recently isolated orange-colored isomer of gossypol, is soluble in pure hydrocarbon solvents but occurs in only relatively small amounts in petroleum ether extracts of cottonseed (2). Even the solvents which do extract the pigments effect complete extraction only after prolonged contact with the seed. For example, 24 hours' contact with diethyl ether or chloroform is the shortest time required for complete extraction of gossypol from finely ground cottonseed or cottonseed flakes (2).

The cottonseed pigments differ markedly from other plant pigments not only in their chemical nature but in their distribution in the seed (14,16,8). Whereas most plant pigments occur as discrete particles on the outside surface of the plants, dissolved in the cell sap, or concentrated in small cell inclusions known as plastids, the cottonseed pigments occur in walled-off cavities or glands many times larger than the surrounding parenchyma cells. It seemed not improbable that the segregation of the pigments in these specialized glands might account for their anomalous behavior in the seed, *i.e.*, the phenomenon of chemically

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