Oils, Detergents and Maintenance Specialties ŋ .

OILS, DETERGENTS and MAINTENANCE SPECIALTIES

Volume 1 MATERIALS and PROCESSES

by

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Preface

Presented in this book are quantities of data, gathered during many years in my practice of chemistry, either as resident chemist in manufacturing plants, or as a consultant to the soap and related industries.

As in my previous volume, *Oil, Fat, and Soap*, published in 1951, the reader will find the subject matter presented in a clear and concise manner, so that he may readily satisfy his interest without extensive reading.

The style is didactic and such that it may readily be understood by non-technical personnel. Involved theoretical and technical discussions have been avoided. As far as possible, references have been included at the end of each chapter.

Although much of the information contained in this work is well within my own experience, much of it has been gleaned also from manufacturers' technical bulletins or through private correspondence.

Many patents have been cited, merely as examples of products discussed; this is not to be construed as recommending the infringement of any such patents. The various formulations are presented in good faith, but no warranty is given, nor is freedom from any patent to be inferred. With a little ingenuity on the part of the reader, many useful and efficient products may be made along the lines discussed, without in any way infringing on patented products.

Because of numerous factors affecting results, all the formulations cited herein, although believed to be reliable (most of them having emanated from the greatest laboratories in the world) should be tested thoroughly. It is especially recommended that manufacturers make their own tests to determine the suitability of the formulations, for the specific applications intended.

I am indebted to the manufacturers of the many chemicals named in the book, for information which I gathered either from direct correspondence or from their technical bulletins; also for their many samples with which I compounded some of the formulas. Special mention should be made of those companies that supplied photographs of equipment and installations depicting various processes.

I have tried to include all information pertinent to each formula, and credit has been given to all identified suppliers, so that additional information, if needed, may be obtained from the manufacturers of the basic materials used.

Finally, I am grateful to the publishers for valuable assistance in the organization and presentation of my quantities of material which now comes out as not merely a second edition of my *Oil*, *Fat*, *and Soap*, but as a much more comprehensive new book.

September, 1966

Benjamin Levitt

Contents

1	INTRODUCTION	1
2	Animal Fats and Oils	8
3	VEGETABLE FATS AND OILS	26
4	FATTY ACIDS—FATTY ALCOHOLS—GLYCEROL	44
5	SURFACTANTS AND SURFACE ACTIVITY	54
6	PRODUCTION OF FATS AND OILS	75
7	Soap Manufacture	129
8	Synthetic Detergents	205
9	Analysis of Oils and Detergents	225
	Index	271

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chapter 1

INTRODUCTION

Early History of Soap

The aphorism that "cleanliness is indeed next to godliness" preached by the English cleric, John Wesley, may truly have some basis in fact. It is thought by some that soap had its beginnings on the sacrificial altar of primitive peoples, when fat from slain animals dripped over the wood ashes, thereby combining with the potash. Although soap is mentioned in the Bible,¹ it is quite certain that the product bore slight resemblance to the products of the present day. It is claimed that the Phoenicians, who engaged in commerce on the Mediterranean about 600 B.C., were the first people to produce soap on a commercial scale.

Pliny² refers to it as an emollient and remedy for external use. He calls it *savinum caprinum cum calce*, and gives an account of soap being first made by the Gauls and being used as a cosmetic. It was made of goats' suet and beechwood ashes, and used in both solid and liquid forms.

Galen (131–200 A.D.), the Greek physician to the Roman emperor Marcus Aurelius, wrote that Gallic soap was best, because of its emollient effect and that it was useful for removing dirt from the body and clothes.

The Romans under the leadership of Julius Caesar, who later conquered Gaul, were quick to learn the Gallic method of soapmaking and introduced this useful cleansing agent for their personal comfort.

As early as the 7th century, soapmakers of Italy were organized as a craft guild. Under Charlemagne (768–814) soapmakers were recognized as craftsmen. Boissonade³ wrote that in Venice, in the 15th century, bourgois capitalists speculated in the raw materials necessary to industry, and manufactured goods. He named among other

commodities lard, potash, and soap. Italian and Flemish merchants sold tallow and lard daily at markets and at fairs. In the 14th and 15th centuries, soap was manufactured at Savona, Italy. The words savon (French), jabon (Spanish), seife (German), and soap are derivations from the name of that city.

Soon afterwards, Marseilles became a rival in the manufacture of soap. The natives had learned to make soap of olive oil and even perfumed it with floral odors, of which they had a plentiful supply. Marseilles soapmakers dominated the European market for four centuries.

Another center of manufacture was at Castile in Spain, which has given its name to a product made of olive oil. The name is still retained, but the composition of the soap has been modified to include other oils and fats.

American Developments

In colonial America, a "Mr. Brown, soapmaker" was granted admittance to Salem, Massachusetts in 1637. In 1716, John Lucena was granted the sole right to make Castile soap in the Rhode Island Colony. In 1735, *The Pennsylvania Gazette* carried an advertisement for "Super Crown Soap", describing its sweetness of flavor and immediate fine lather as rendering it pleasant for use by barbers.

Soap was also imported from Europe in colonial times. In the biography of Stephan Girard,⁴ a colonial merchant of Philadelphia, a cargo from Marseilles is mentioned as comprising among other commodities, 500 cases of blue mottled soap.

About 1757, Bernard Gratz,⁵ a Philadelphian, was in partnership with Michael Moses, a professional tallow chandler, for whom he supplied the capital. These kindred lines of business were often carried on under the same roof; for example, the partnership of Procter, a candle-maker, and Gamble, a soapmaker.

Benjamin Franklin, in his autobiography, mentions that his father who was a tallow chandler, tried to make a soapmaker of him, much to the disgust of the younger Franklin, who chose to become a printer instead.

Abraham Riviera, an uncle of Aaron Lopez, a leading businessman of the Revolutionary period, produced candles of sperm oil. Aaron's half brother, Moses Lopez obtained a license for the manufacture of potash.

Before and after the American Revolution, Solomon Simon and

INTRODUCTION

his brother Samson were engaged in supplying the army. Samson became founder of the New York Chamber of Commerce. He was a partner in a spermaceti factory and one of the proprietors of the United Whaling Co.

J. L. Bishop,⁵ stated that soap was manufactured in Boston in 1794. John Slidell & Co., at 50 Broadway in New York, was among the early soapmakers in the U.S.A. It was in this establishment that William Colgate learned the business. He started his own company on Dutch Street, in New York, in 1806. Colgate was the first soapmaker to render fats in his own plant.

In 1830 Jesse Oakley, of Newburgh, New York, introduced wrapped soap in cake form. Prior to that time, the grocer received soap in large blocks, from which he cut smaller bars and cakes for sale.

Philadelphia was established early as a center for soap making. Joseph Elkinton started his soap and candle factory in Philadelphia in 1831. Twenty-six years later, his son Thomas began making silicate of soda for use in the firm's soap. In 1861, silicate of soda was first offered for sale to others but the market for silicate expanded only slowly and it was not until 1904 that it was great enough to justify the discontinuance of soapmaking. This enterprise later became the Philadelphia Quartz Company.

The Glenn Perfumery and Toilet Soaps were known in Philadelphia in 1832. In 1848, Maas and Trebouillet obtained the first patent for the distillation of fatty acids, under vacuum.

Vroom and Fowler's Walnut Oil Military Shaving Soap, in tablet form, is said to have been invented in 1840. Thomson's Soap Foam, "the purest soap in concentrated powder form" is also an early product of Philadelphia. The labels for these soaps were reprinted recently in *The Philadelphia Inquirer* and may now be seen in the Atwater Kent Museum.

The Thomas Worsely Soap Works, in Combes Alley, Philadelphia,⁶ was established in 1846 and sold in 1876 to Fels and Company, which had been founded in 1866. The latter became a part of the Purex Corp. in 1964.

In 1848, Alexander McConnell commenced the manufacture of fulling soap, tallow candles, and sal soda. J. Eavenson began to manufacture soap at 731 Hubble Street, Camden, N. J.

James Pyle and Sons were the originators of soap powder in the U.S.A. Prior to 1856, Pyle had sold washing soda crystals and bluing. In 1857, he started to make soap under the trade-mark "O.K"

and a soap powder known as "Pearline." This business was later sold to Procter & Gamble.

The Los Angeles Soap Company is the oldest soapmaking firm west of the Mississippi and now the fifth largest in the U.S.A. It was started in 1860, in the Mexican village of Los Angeles.

B. T. Babbitt is credited with the production of pressed laundry soap in New York, in 1865.

The Pennsylvania Soap Works, of McKeone, Van Haagen and Company, established in 1854 on Callowhill Street, Philadelphia, was the largest soap plant in Pennsylvania. The use of rosin in soapmaking was begun shortly before the Civil War. A. Van Haagen developed a means of hardening rosin soap by using sal soda.

The recovery of glycerol from waste lye was an English invention which was improved in a U. S. patent granted in 1870. The world, however, is no longer dependent on the soap kettle for glycerol.

The first floating soap came into being when a workman stirred his batch of soap too long, thus aerating it sufficiently to make it buoyant. Ivory was its name.

The Industries of Philadelphia, published 1884, by Scharf and Wescott, lists thirty-one soap plants seven of which made perfumed soap. At that time the Dallet family of three generations, were makers of common and fancy soap and of moulded and dipped candles.

Besides the names listed, there were such names as Enoch Morgan and Sons, Hay, Brown, J. C. Hull's Sons, and Fay, all of whom started in the early years of our country. As in many other industries, there has been a great number of mergers, so that most of the early companies have lost their identity.

Scientific Study of Oils, Soap, and Lye

The first scientific study of soap was made in 1741 by Geoffroy, a French chemist, who pointed out that the fat recovered from soap by treatment with an acid was not of the same composition as the original fat. He showed that the fat derived from the soap dissolved in alcohol, whereas the original fat was insoluble in alcohol. It is to be noted that with the exception of castor oil (*ricinolein*), none of the neutral fats or oils is soluble in alcohol.

Scheele (Swedish chemist) in 1783, while boiling lead oxide with olive oil in making lead plaster, discovered a sweet substance as a by-product, which he called *Oelsuss* (sweet oil), or *principium dulce oleorum* (sweet principle of oils). The substance is the glycerol of today. Chevreul (another French chemist), in 1815, based his work

INTRODUCTION

on these discoveries. He disclosed the true nature of oils, glycerol, and soap. He showed that soap is the result of the interaction of the acids in the fats, with an alkali.

Up to the time of the French revolution, the lye necessary for soapmaking was obtained by lixiviation of wood ashes or the ashes from kelp. It is worth noting that the first patent granted by the U. S. Patent Office—to Samuel Hopkins on July 31, 1790—covers an apparatus and process for making pot-ash and pearl ash. This historical document, written on sheepskin, was signed by President George Washington, in New York, which was then the national capital.

During the French revolution, when the supply of kelp was cut off by an embargo, a prize was offered by the French Academy of Science for a method of manufacturing soda ash from salt. LeBlanc won the prize in 1790 by using sulfuric acid, limestone, and coal, in the following three-step process:

1. Common salt is warmed with sulfuric acid, forming sodium sulfate (salt cake) and hydrochloric acid:

 $2 \operatorname{NaCl} + \operatorname{H}_2 \operatorname{SO}_4 = \operatorname{Na}_2 \operatorname{SO}_4 + 2 \operatorname{HCl}$

2. Sodium sulfate is heated with coal and limestone:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2;$$

 $Na_2S + CaCO_3 = Na_2CO_3 + CaS$

3. Black ash is lixiviated with water to dissolve out, and then crystallize, the sodium carbonate.

Although this process was used for many years, it was cumbersome and it produced impure soda ash. It was superseded in 1863 by the Solvay process, which is based on the reaction of salt with ammonium bicarbonate. Ammonia and carbon dioxide are led alternately into a cold concentrated solution of salt under pressure:

 $NaCl + (NH_4)HCO_3 = NaHCO_3 + NH_4Cl$

The sodium bicarbonate settles out of the cold concentrated ammonium chloride solution. It is then calcined to yield soda ash and carbon dioxide.

Caustic soda was produced by causticizing soda ash with lime. At present, practically all caustic soda is produced by the electrolysis of brine.

Synthetic alkali was first used in soapmaking in 1823. It was manufactured in England by James Muspratt by means of the LeBlanc

TABLE 1:1

PRODUCTION AND CONSUMPTION OF OILS, FATS, AND DERIVATIVES* (Millions of Pounds)

	1961	1963	1964
Baking and Frying Fats	2,456.1	2,584.3	2,664.1
Butter	1,536.0	1,453.0	1,468.0
Castor, consumption	115.7	124.5	136.6
Coconut {crude refined	498.0	348.3	327.6
refined	463.0	554.5	506.0
Cooking and Salad Oils	2,123.7		
Corn (crude	335.8	390.5	413.9
refined	321.7	363.3	393.1
Corn {crude refined Cottonseed {crude refined	1,793.8 1,506.0	1,917.0 1,577.3	1,932.4 1,600.0
Fatty Acids	706.0	835.6	936.0
Fish, including Mammal oil, except Sperm	258.1	185.8	180.2
Glycerol, crude	270.2	302.1	328.1
Crude used in refining	269.1	295.6	313.2
Imports	18.4	2.9	11.8
Refined	269.4	303.2	320.1
Lard	2,384.0	2,373.0	2,388.0
Linseed, raw and boiled	426.3	399.1	443.6
Margarine	1,723.7	1,793.6	1,857.4
	1,72017	0.7	0.2
Olive Oil {sulfured imports edible		32.9	66.9
Palm Kernel	53.6	52.3	63.8
Palm Oil, consumption	65.8	44.2	37.5
n (crude	96.8	99.1	123.3
Peanut { refined	94.6	79.2	60.5
Sofferer (crude		116.1	withheld
Peanut {crude refined Safflower {crude refined		76.9	75.4
Sperm, consumption			
Selected products	46.6	36.1	33.6
Imports		65.9	58.9
Soybean { crude refined	4,442.3	5,053.2	4,943.8
	3,592.7	4,033.7	4,591.8
Edible Tallow	443.7	527.9	553.2
Inedible Tallow and Grease		11565	
Production	3,554.3	4,156.5	4,565.7
Consumption: Soap		684.0	
Fatty Acids		448.8	
Feeds Lybricente etc		754.5 80.2	
Lubricants, etc.		166.3	
Other products	826.3	991.3	1,104.0
Tall {crude refined	139.2	150.4	1,104.0
Tung, production crude	16.0	11.8	24.5
Consumption, selected products	37.8	11.0	4--- , <i>J</i>
Vegetable Foots	278.9	284.0	261.1
	21019	201.0	201.1

* From U. S. Dept. of Commerce.

INTRODUCTION

process. Commercial production of caustic soda dates from 1854, when William Gossage, in England, produced an improved product for the use of soapmakers and papermakers. Although Solvay took out the first patent in Belgium in 1863, it was not until 1881 that a plant for the Solvay process was established at Syracuse, New York.

Important contributions to the study of oils were made by such men as Mercer (sulfonated olive oil), Twitchell (fat-splitting), Wesson (refining and deodorizing), Sabatier and Normann (hydrogenation), Lewkowitsch (technology), and many others. These authors and their work will be discussed in other chapters under the appropriate headings.

CLASSIFICATION OF FATS AND OILS

Fats and oils are complex mixtures of glycerides. They are esters of fatty acids and the trihydric alcohol, glycerol.

Cottonseed oil, for example, consists of the glyceryl esters of linoleic, oleic, palmitic, myristic, and stearic acids, mentioned here in order of their decreasing percentages.

The distinction between fats and oils is a purely arbitrary one, based on their physical state at ordinary temperatures, the oils being liquid and the fats, pasty or solid. There are, however, many exceptions, such as coconut, babassu, palm, and palm kernel oils, which range from pasty solids to hard waxlike solids in a temperate climate. The latter have received the designation "oil" only by convention.

Another classification of oils is based on their origin, such as animal (terrestrial or marine), vegetable, and mineral. As the members of the last class consist almost entirely of hydrocarbons and have their origin in petroleum, the scope of this book does not permit discussion of mineral oils.

The number of products available as aerosols seems to be unlimited and increasing. Many practical suggestions for this form of application will be discussed in Chapter 1 of Volume 2.

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Index

Α

ABS detergents, 60, 219 Absorption bases, 22 Acetin method for crude glycerol, 266 Acetyl number or value, 235 Acid number, test for, 234 Acidless tallow oil, 10, 12 Actamer, 155 Activated Sludge Method for biodegradability, 263 Additives for soap and detergents, 170-176 Aerosol OT, 56 Aerosol shaving cream, specification for, 203 Alcohol-soluble matter in soap, test for, 259 Alfols, 52 Alkali refining of oils, 77 Alkylbenzene, sulfonation of, 215 Almond oil, 41, 42 Aluminum soaps, 159 Amine cationic compounds, 61 Amine soaps, 165 2-Amino-2-methyl-1,3-propanediol, 168

2-Amino-2-methyl-1-propanol, 168 Ammonia soaps, 164-169 Amphoteric surfactants, 65 Analysis, of fats, 225–242 glycerol, 264-268 oils, 225–242 potash soaps, 251–253 soaps, 243-253 soap powders, 253-258 synthetic detergents, 258-264 Anhydrous, salt-free soap, 260 Animal fats, bleach test, 239 Animal oils in mixtures, test for, 240 Anionic surfactants, 55-61 test for presence of, 259 Antibacterial soap, specification for, 195 Antaron FC, 34, 66 Antioxidants, 119, 173 Anti-pollution Law, 72 ASTM Specification, combination bar soap, 223 Autoclave, fat-splitting, by, 101 saponification in, 145 Automobile soap, specification for, 183

В

Babassu oil, 29, 42 Bactericides in soap, 181 Bacteriostats in soap, 155, 181 Bar, detergent, specifications for, 220 Bar soap, specifications for, 192 combination, specifications for, 223 Baudoin's Test for sesame oil, 241 Bellier's Test for peanut oil, 241 Bentonite, 175 Benzenesulfonates, 59 BHA, 34, 119 BHT, 34, 119 Biochemical Oxygen Demand, 72 Biodegradability, importance of, 68 test for, 263 Biodegradable detergents, 217-219 sulfonic acids, properties of, 218 surfactants, 69-71 Bleach test for animal fats, 239 Bleaching of oils, 87, 89 Blown or bodied oils, 90 Blue, mottled soap, 158, 177 ultramarine, 158, 157 BOD, 72 Boiled soaps, 135-145 Borax, 174 soap for dispensers, 200 tests for, 246 British Standards for Glycerol, 268 Buffers, use of, 121 Builders for soaps and detergents, 170-176

Built soap, specifications for, 185, 190 Bunching, 136 Butter, 19, 42, 95 Butylated hydroxyanisole, 34, 119 Butylated hydroxytoluene, 34, 119

С

Cacao butter, 27, 42 Cake soap, specifications for, 196 Calgon, 172 Carbonate(s). in soap, test for, 245 in water, 124 Castile soap, 156 Castor oil, 6, 26, 41, 42, 91 dehydration of, 92 Castor seed, press cake, 39 Catalyst for hydrogenation of oils, 97 Cationic surfactants, 61 test for presence of, 259 Centrifugal oil refining, 80 Cerium stearate soap, 160 Cetyl alcohol, 50 Characteristics of fatty acids, 48 Chelating agents, 125-127 Chemical bleaching methods, 89 Chemical classification of surfactants, 55 Chemithon process of sulfonation, 216 China-wood oil, see Tung oil Chinese vegetable tallow, 36, 42 Chlorides, test for, 262 Chlorinated trisodium phosphate, 171 Chips (soap), specifications for, 190, 191 Cholesterol, 24

Chromium soaps, 160 Cobalt soaps, 160 Cocoa butter, see Cacao butter Coconut fatty acid, content of, 27 Coconut oil, 6, 27, 42, 135 refining of, 81 Coconut soap base, 156 Cod liver oil, 18, 42 Cold fractionation refining, 85 Color, tests for, 228 Coloring soaps and detergents, 158, 176-179 Combination soap-surfactant, 222 - 224ASTM specification for, 223 Constants of oils and fats, 42-43 Continuous process, distillation of fatty acids, 106 fat splitting, 101 refining of oils, 85 soap-making, 147 Corn oil, 6, 29, 41, 42 Copper soaps, 160 Cottons, soap for, 162 Cottonseed meal, 39 Cottonseed oil, 6, 30, 41, 42 extraction of, 76 hydrogenation of, 96 Halphen test for, 240 Coupling agents, 60 Crambe seed oil, 36 Cream, shaving, specification for 201

D

DDBSA, 205–207 Dégras, 22 Moellon, 23 Dehydration of castor oil, 92 DeNora Hydrogenation Process, 111 Deodorizing of oils, 89 Deriphats, 65 Detergent(s), bar, specifications for, 220 biodegradable, 217-219 coloring of, 176 compounding of, 206 dry, 211 hard, 60, 69 homogeneity of, 209 LAS, 218 liquid, 209 perfuming of, 180 powdered, 208 protein, 56 soft, 51, 69 specifications for, 220-224 surgical, 220 tablets, 213 Diethylaminoethanol, 169 Diethylene triamine, 168 Dimethylbenzylammonium chloride, 61 Dimethylethanolamine, 167 Distillation of fatty acids, 104-109 Dodecylbenzenesulfonates, 60, 205-207, 211 Dodecylbenzenesulfonic acid, composition of, 205 Duzon-Hydrozon refining process, 80 Dry neutralization, 212 Drying oils, 41 Dyes, fluorescent, for soaps and detergents, 178

E

Edible tallow, 6, 8, 12

Effect of surfactants on alkaline cleaners, 68 Efficient surfactants, 68 Emersol process for fatty acids, 109 Emulsification by Votator, 95 Emulsifying agents, evaluation of, 169 Ester gum, use of, 38 Equipment for soap plant, 129-134 Ethylenediamine, 167 Ethylene oxide condensates, 63 Examination of fatty acids, 249 Expeller process for vegetable oils, 75 Extraction of fats and oils, 75-77 F

Fats and oils, constants of, 42 production and consumption of. 6 Fats, splitting of, 100-111 by autoclave, 101 by distillation, 104-109 by Emersol process, 109 by Twitchell process, 103 Fatty acids, 44-50 alkanolamides of, 60 characteristics of, 48 comparison of, 45, 109 distillation of, 104-109 examination of, 249 fractionated, 45, 109 (free), test for, 225 hydrogenation of, 111 occurrence of, 44 pressing of, 104 saturation in, 46 splitting of, 100-111

Fatty acids, synthetic, 47 unsaturated, 45 volatile, test, for, 237 Fatty alcohols, 50-52 derivatives of, 51 hydrogenation of, 111 new uses for, 51 production of, 50 Fatty matter, test for, 262 Federal specifications, for soaps, 181-204 for synthetic detergents, 219-223 Federal Trade Commission decision on castile soap, 156 Filtration-extraction of oil, 76 Fish oils, 17 constants of, 42 Fish liver oils, 18 Fire test for fats and oils, 236 Fitelson Test for teaseed oil, 241 Fitting, in boiled soap, 138 Flake soap, 151 Flash test for fats and oils, 236 Floating soap, 139 specifications for, 196 Fluorescent dyes, 178 Foots, nature of, 38 Free caustic alkali, test for, 245 Free fatty acids, test for, 225 Full-boiled soap, 135-145 Fulling soap, for wool, 3, 163 Furfural process of refining, 86

G

Glass-cleaning, soap for, 182 Glycerol, analysis of, 264–268 applications of, 53 British Standards for, 268 occurrence of, 52

Glycerol, production of, 6, 111, 116 properties of, 52, 115 recovery of, 4, 113 saponification crude, 116 sources of, 52 synthetic, 53, 116 Gossypol, 30 Greases, miscellaneous, 12, 13 standard grades of, 14 Green soap, tincture of, 181 Grit soaps, specifications for, 186-190 Guanidine carbonate in soaps, 169 Gum guaiac, as antioxidant, 119

Η

Hairdressers' shampoo, 156 Half-boiled soap, 145 Halphen Test for cottonseed oil, 240 Hand soaps, grit, 186–189 Hard detergents, 60, 69 Hardness of water, 123 test for, 243 Hexachlorophene, in soap, 155, 181 High-titer soap, specifications for, 185 House grease, 14 Hydrogenation, catalyst for, 97 DeNora process, 111 of fatty acids, 111 of oils, 96-98 Hydrogen ion concentration, 120-123 Hydrophilic group, 55 Hydrophobic group, 63 Hydrotropes, 59

Hydroxychromans, 119

I

Igepons, 56 Impurities in oil, test for, 226 Industrial alkalies, composition of, 173 Invert soaps, 61 Iodine number, Wijs test for, 229 Isoelectric point, 66 Isopropanolamines, mixed, 166

K

Kettles, types of, 129 Killing change, in soap making, 136 Kreis test for rancidity, 118, 242 Kritchevsky patents, 64, 73

L

Lamepons, 56 Lanolin, 20 modified, 21 Lard, 10, 12, 42 Lard oil, 12, 13 LAS detergents, 218 Laundry soap, 4, 140-142 perfuming of, 179 specifications for, 190-193 Lead compounds in soap, 161 Lecithin, 39, 43 commercial distribution of, 40 Liebermann-Storch test for rosin, 249 Linear alkylate benzenesulfonate (LAS), 69 Linseed meal, 39 Linseed oil, 30, 42 refining of, 93

Lipophilic group, 55

Liquid detergents, 209 Liquid soap, coloring of, 178 specification for, 197 Lithium soap, 161 Low-titer soda soap, 163, 190

Μ

Magnesium compounds in soap, 123, 161 Manganese soap, 161 Mannitol triacetate, 119 Marble floors, soap for, 181 Marine oils in vegetable oil, test for, 240 Maypons, 56 McNicoll test for rosin, 230 Medical uses of soap, 180 Melting point of fats, determination of, 234 Metallic soap, 159-162 Milled soap, 152-156 specification for, 196 Mineral soap stock, 175 Miranols, 66 MIU tests, 227 Moellon dégras, 23 Moisture, tests for, 225, 244 Monoamylene amine, 168 Morpholine, 167 Mottled soap, 158, 177

N

Nalkylene compounds (LAS), 219 Naphtha, in soap, 175 Naphthalenesulfonate(alkyl), 55 Naphthenate, sodium butyl, 55 Naphthol hydroquinone, 119 Neatsfoot oil, 12, 15 Neutralization, dry, 212 Nickel (Raney) catalyst, 97 Nickel soap, 161 Nigre, 139 Non-drying oils, 41 Nonionic surfactants, 62–65 test for, 259 Nordihydroguaiaretic acid (NDGA), 119

0

Oatmeal, in soap, 155 Oil(s), Almond, 41, 42 and Fats, constants of, 42-43 production and consumption of, 6 babassu, 29, 42 bleaching of, 87, 89 blown or bodied, 90 castor, 6, 26, 42, 91-93 coconut, 6, 27, 42, 81, 135, 156 cod liver, 18, 42 corn, 6, 29, 41, 42 cottonseed, 6, 30, 41, 42, 76, 96, 240 crambe seed, 36 deodorizing of, 89 drying, 41 filtration-extraction of, 76 fish, 6, 17–19, 42 hydrogenation of, 96-98 lard, 6, 13 linseed, 30, 43, 93 neatsfoot, 12, 15 non-drying, 41 oleo. 8 olive, 6, 31, 156 oxidation of, 117 palm, 6, 32 palm kernel, 6, 29 polymerization of, 91 refining of, 77-87

Oil(s), safflower, 6, 32 sardine, 17, 86 salmon, 17 scientific study of, 4 soluble sulfonates, 57 soybean, 6, 34, 85 sperm, 6, 23 sulfated, see sulfonated sulfonated, 58 sulfonation of, 98 tall, 6, 34, 35 whale, 15, 43, 98 winterizing of, 89 Oleo oil, 8 Oleomargarine, 19 manufacture of, 93 Olive fig soap, 163 Olive oil, 6, 31, 156 Ottasept, 155 Oxo process, 50

Ρ

Packing house products, tests on. 12 Palm oil, 6, 32 Palm kernel oil, 6, 29 Perfuming soaps and detergents, 179 pH, of chemical solutions, 120 color indicators for, 122 measurement of, 121 sets for, 122 uses of, 121 Phosphates, 171–173 tests for, 253-258 Phosphonols, 57 Phytosterol, 41 Pitching, in boiled soap, 138 Poisoned stock, 136

Podbielniac (Duzon-Hydrozon) oil refining, 80 Polenske number, 239 Polymerization of oils, 91 Polypeptides, 56 Polyphosphates, threshold effect, 125 Potash, first U.S. patent, 5 tests for, 252 Potash soap, 146 analysis of, 251-253 Production, fats and oils, 6 glycerol, 111 synthetic detergents, 206-214 synthetic glycerol, 116 soap, 135-147 soap powder, 3, 147-152 Propyl gallate, 119 Protein detergents, 56 Puffed borax, 174 Pumice, 176

Q

Quaternary ammonium compounds, 61

R

Rancidity, Kreis Test for, 118, 242 Raney Nickel catalyst, 97 Rapid saponification, 143 Refining of oils, 77–87 Reichert-Meissl value, 237 River Die-away Test for biodegradability, 263 Rosin, 37 in laundry soap, 140–142 specifications for, 190–193 tests for, 249–251

S Safflower oil, 6, 32 Sapo durus, -mollis, 181 Saponification, crude glycerol, 116 number, 42, 134, 233, 235 process of, 134 rapid, 143 Salmon oil, 17 Sarcosinates, 57 Sardine oil, 17 Solexol treatment of, 86 Semi-boiled soap; see Half-boiled soap Semi-drying oils, 125 Sequestering agents, 125-127 Sewage-treatment plants, 72 Shake-flask Test for biodegradability, 264 Shampoo, hairdressers', 156 Shaving soap, 3, 201-204 Silicates in soap, 170 analyses, 171 tests for, 245 Smoke test, 236 Soap(s), abrasive, 189 additives for, 170 ammonia, amine, 164-169 anti-bacterial, 195 anhydrous, salt-free, 260 for automobile and floor, specification for, 183 bactericides in, 181 bacteriostats in, 155, 181 bar, specifications for, 192, 196 borax, for dispensers, 200 builders for, 170 built high-titer, powdered, 185 built, low-titer, powdered, 190

Soap(s), Castile, 156 cerium stearate, 160 chips, 190 chromium, 160 cobalt, 160 cold process, 146 coloring of, 176-179 continuous process, 147 copper, 160 for cottons, 162 cresylic acid in, 155 Federal specifications for, 181-204 flakes, industrial, 151 floating, 139, 196 full-boiled, 135–145 fulling, for wool, 163 glass-cleaning, 182 granular, 192 green, tincture of, 181 grit, 181-189 guanidine carbonate in, 169 half-boiled process for, 145 Hexachlorophene in, 155, 181 history of, 1–5 invert, 61 laundry, 4, 140-142, 179, 190-193 liniments, 181 liquid, 178, 197 lithium, 161 low-titer, 163 magnesium compounds, in, 123, 161 manganese, 161 for marble floors, 181 medical uses of, 180 medicated, 181 metallic, 159-162 milled toilet, 152-156, 195, 196-199

Soap(s), mottled, 158, 177 naphtha in, 175 nickel, 161 olive fig, 163 pine-tar, 155 plant equipment for, 129, 134 potash, 146, 251-253 powder, 3, 147, 181-182, 185, 188–190, 192, 253, 258 rapid saponification of, 143 saddle, 193 scouring, specifications for, 182, 186 scrap, 143 for shaving, 201-204 silicates in, 170, 245 for silks, 164 stability of, 248 stock, 38 -surfactant combinations, 222-224 surgical, 194 textile, 162-164 toilet, 152-156 specifications for, 195, 196-199 variegated, 158 vegetable oil, for system drums, 157 veterinary, 181 for wool, 162 wrapped, 3 Sodium, lauryl sulfate, 55 naphthalenesulfonate, 55 phosphates, 171-173, 253-258 silicates, 170, 245 thiosulfate, 231 Soft detergents, 69 Solexol process of refining oil, 85 Solvent extraction of oils, 75

Sopanox, 153 Soybean oil, 6, 34, 85 Solexol treatment of, 86 Specifications for soap products, 181-204 for synthetic products, 219-224 for tallows and greases, 14 Specific gravity of oils, test for, 239 Spermaceti, 23 Sperm oil, 6, 23 Standard grades, tallow and grease, 14 Stark and Dean Test for moisture, 243 Sterols, 24 Stigmasterol, 41 Strengthening change, in soapmaking, 138 Strontium soaps, 161 Sugar ester surfactants, 64 Sulfonated dodecyl diphenyloxide, 60 Sulfonated oils, 58 Sulfonates, benzene, 59 oil-soluble, 57 Sulfation, see sulfonation Sulfonation, alkylbenzene, 216 of oils, 98 Sulfonic acid, uses of, 215 Surface activity, 54 Surfactants, amphoteric, 65 anionic, 55-61 biodegradable, 69 cationic, 61 classification, 55 differentiation of types, 259 efficiency of, 68 history of, 55 nonionic, 62-65

Surfactants, -soap combination, 222 specifications for, 219–222 tests for, 258–264 Swedish oil refining process, 83 Synthetic detergents, 205 *see also* Surfactants biodegradable, 217–219 composition of, 54–68 compounding of, 206 specifications for, 219–224 tests for, 258–262

Т

Tallow, edible, 6, 8, 12 Tallow oil, 6, 35 Test, animal oils in vegetable oil, 240 Baudoin's, for sesame oil, 241 Bellier's for peanut oil, 241 bleaching, of animal fats, 239 for borax, 246 carbonate, 245 chlorides, 262 differentiating surfactants, 259 fatty acids in soap, 249 free caustic, 244 Halphen, for cottonseed oil, 240 hardness of water, 243 iodine number (Wijs), 229 Kreis, for rancidity, 118, 242 MIU, 227 packing house products, 12 potash, 252 rosin, 249 silicate, 245 synthetic detergent, 258-262 tetrapotassium pyrophosphate, 253 total alkali and total fat, 247 trisodium phosphate, 255

248 Tin soaps, 161 Tri(hydroxymethyl)aminomethane, 168 Trisodium phosphate, chlorinated, 171 Tung oil, 6, 41, 43 U Ucuhuba butter, 36, 43 Ultramarine blue, in soaps, 158, 177 Uniterge, 67 Unsaponifiable matter, test for, 226, 248 Unsaturated fatty acids, 45 Uses of pH determination, 121 sulfonic acids, 215 v

Test, unsaponifiable matter, 226,

Vegetable tallow, 36 Vermilion, coloring, 158, 177 Vitamins, daily allowance, 19 in oleomargarine, 94 Volcanic ash, 175 Votator, emulsification in, 95

W

Water, hardness in, 123 test for, 244 Wax emulsions, physical properties, 170 Wax-resin for emulsifying agents, 169 Whale oil, 15, 43, 98 Winterizing of oils, 89 Wool, soaps for, 162 X Xylene sulfonate, 59

Ζ

Zinc soaps, 162