# Oils, Detergents and Maintenance Specialties

# OILS, DETERGENTS and MAINTENANCE SPECIALTIES

Volume 1

MATERIALS and PROCESSES

*by*

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# Oils, Detergents and Maintenance Specialties, Volume 1, Materials and Processes



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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

# 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.

Pliny [2] 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. Boissonade [3] 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

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

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:

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl$$

2. Sodium sulfate is heated with coal and limestone:

$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2;$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

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 | 498.0 | 348.3 | 327.6 |
| Coconut { refined | 463.0 | 554.5 | 506.0 |
| Cooking and Salad Oils | 2,123.7 | | |
| Corn { crude | 335.8 | 390.5 | 413.9 |
| Corn { refined | 321.7 | 363.3 | 393.1 |
| Cottonseed { crude | 1,793.8 | 1,917.0 | 1,932.4 |
| Cottonseed { refined | 1,506.0 | 1,577.3 | 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 |
| Olive Oil { sulfured imports | | 0.7 | 0.2 |
| Olive Oil { edible | | 32.9 | 66.9 |
| Palm Kernel | 53.6 | 52.3 | 63.8 |
| Palm Oil, consumption | 65.8 | 44.2 | 37.5 |
| Peanut { crude | 96.8 | 99.1 | 123.3 |
| Peanut { refined | 94.6 | 79.2 | 60.5 |
| Safflower { crude | | 116.1 | withheld |
| Safflower { refined | | 76.9 | 75.4 |
| Sperm, consumption | | | |
| Selected products | 46.6 | 36.1 | 33.6 |
| Imports | | 65.9 | 58.9 |
| Soybean { crude | 4,442.3 | 5,053.2 | 4,943.8 |
| Soybean { refined | 3,592.7 | 4,033.7 | 4,591.8 |
| Edible Tallow | 443.7 | 527.9 | 553.2 |
| Inedible Tallow and Grease | | | |
| Production | 3,554.3 | 4,156.5 | 4,565.7 |
| Consumption: Soap | | 684.0 | |
| Fatty Acids | | 448.8 | |
| Feeds | | 754.5 | |
| Lubricants, etc. | | 80.2 | |
| Other products | | 166.3 | |
| Tall { crude | 826.3 | 991.3 | 1,104.0 |
| Tall { refined | 139.2 | 150.4 | 143.6 |
| Tung, production crude | 16.0 | 11.8 | 24.5 |
| Consumption, selected products | 37.8 | | |
| Vegetable Foots | 278.9 | 284.0 | 261.1 |

* From U. S. Dept. of Commerce.

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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