HISTORICAL REVIEW OF SOAP MANUFACTURING.*

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This paper is partially a compilation taken from various books, journals, and other sources, together with results of the author's experience in the manufacture of soaps covering a period of forty years.

Soap is mentioned in the Old Testament, and the Hebrew words used in the passages Jeremiah ii: 22, and Malachi iii: 2 are stated by authorities to refer to vegetable and mineral lyes; *i.e.*, potash and soda in some form.

In Homer's time the cleansing of clothes seems to have been effected by simply rubbing or pounding in water without any addition, for he tells how Nausicaa and her attendants washed clothes by stamping them with their feet in pits filled with water.

Later on the juices of certain plants were employed as detergents, also natural soda and wood ashes. The fact that the strength of alkalies can be increased by lime was already known to Palus Egina. Fuller's earth was, however, the principal agent used for washing in ancient times, the fuller's art being due, it appears, to one Nicias, the son of Hermais. The Roman fullers (*fullones*), who washed dirty garments, were persons of no little importance. Their trade and manner of carrying it on were regulated by laws. At one time fuller's earth, found of a superior quality in Staffordshire and other counties of England, was considered so indispensable for the dressing of fabrics that it was made a contraband commodity, and its exportation made equally criminal with the heinous and wicked export of wool.

The elder Pliny gives us the earliest account of soap as having been first manufactured by the Gauls, and used by them as a cosmetic and for dyeing the hair red.[1] Dyeing the hair red shows the presence of free alkali.

He also states that it was made from tallow and ashes, the best being prepared from goat's suet and beechwood ashes, and that the Gauls employed it both in a solid and liquid form.

From this statement by Pliny it has been generally concluded that the invention of soap was due either to the Gauls or the Germans.

E. Moride is of the opinion that Pliny's statement simply refers to the application of soap as a cosmetic and hair-dye, and believes the Phœnicians, who settled in Gaul 600 B.C., to have been the actual inventors of soap.

It cannot, however, be supposed that the first soap was an artificial product like that of the present day. It was very likely a mixture of oil and wood ashes, which was used as a salve in eruptions of the skin and similar diseases. Later on it may have been accidentally discovered that more effective salve was obtained by mixing the wood ash with water and burnt lime before combining it with the oil. Thus, no doubt, products were gradually obtained which resembled the

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[1] When Praxiteles was asked which of his works in marble he valued most, he is said to have answered: "Those on which Nicias has set his mark." Pliny explains this expression by the comment, "So much importance did Praxiteles attach to the circumlition (covering of color) applied by Nicias." This passage was for a long time the principal foundation for the theory that the Greeks painted their statues, which is now confirmed by the works themselves. The hair of the Hermes of Praxiteles had a red color when discovered.

present soaps of Algiers, of which Leon Droux writes: "In the interior of Algiers the Kabyles bring to market a mass which serves the double purpose of a remedy and for household use. It is a soap prepared almost in the cold way, of a slightly yellowish color, somewhat transparent, and of a jelly-like consistency, but with a very small content of water. It is made from olive oil and lye, the latter being prepared by allowing water to percolate through a mixture of wood ashes and burnt lime. The Arabs used the salve-like product thus obtained for affections of the skin, as well as for household purposes, and for washing wool to be worked into tissues."

As a detergent, soap is first mentioned by the authors of the second century after Christ. The celebrated physician, Galenus, speaks of it as a detergent as well as a medicament, and considers the German soap as the best, and the Gallic as the next in quality.

But little is known of the further gradual development of the soap industry. Marseilles, it is said, carried on a considerable trade in soap as far back as the ninth century. In the fifteenth century Venice was the principal market, but was outstripped in the seventeenth century by Savona (whence the French name for soap, "*savon*"), Genoa, and Marseilles.

It is somewhat uncertain when soap-making was first introduced into England, but it was probably in the fourteenth century. The first patent for improvements in the manufacture of soap was obtained in 1622 by Messrs. Jones and Palmer, of London. At the same time a company obtained a monopoly for the manufacture of soap, paying annually a tax of $10,000 for 3000 tons of soap.

In France the monopoly system was also in force in the seventeenth century. In 1660, Pierre Rigat, a merchant of Lyons, made a proposition to the king to manufacture by special methods sufficient soap for the needs of France without importing any of the materials required in the manufacture. Louis XIV accepted the proposition and granted him the sole privilege for twenty years of erecting factories for the manufacture of white, mottled, and all other kinds of soap in any location it suited him. The six or seven factories then in existence were allowed to remain, but under the condition that they should not increase their capacity and would sell their products to Rigat at a fixed price. This patent, being the cause of many disputes, was revoked in 1669.

But little is known about the soap industry in Germany during the early centuries.

The business was carried on on a small scale, and this could not well be otherwise, since, with the impure raw material, principally crude tallow and wood ashes, one boiling frequently required as many days as hours at present. The industry was further hindered by the general practice of every household preparing its own soap, which continued up to the introduction of artificial soda and tropical vegetable fats. But since then many large factories have been established, and, as the German soap-boilers applied to the trade its true chemical character, they produced superior goods. The soft soap of Germany is still much used for household purposes as well as for manufacturing, and it has acquired a reputation for excelling in quality that of other countries.

Not much advance was made in the manufacture of soap until at the beginning of the present century it commenced to attract the attention of scientific men, and Leblanc gave to the world his splendid process for the production of soda from common salt.

The next great discovery, and not second in importance, was due to Chevreul, who, by describing the exact constituents of the fatty bodies and making known

the processes for their separation, raised soap-making from empiricism and guesswork to its present position as a truly scientific art. By establishing the practical and scientific basis upon which the soap industry is now carried on, Chevreul and Leblanc may be considered as its founders.

The introduction of new fats and oils, especially of palm oil, palm-kernel oil, and coconut oil, added an important variety to the list of soaps, particularly of toilet soaps. The employment of caustic soda, which enables the soap-boiler to prepare with great ease caustic lyes of a high degree, was also of great importance, as well as the production of potassium chloride, and that of caustic soda in the electrolytic way.

A considerable change in the mode of boiling appears to have been brought about by the use of fatty acids for the manufacture of soap, and the saponification by alkaline carbonates connected therewith. When, about fifty years ago, the price of glycerin rose enormously, many factories engaged in the business of abstracting the glycerin from the fats and selling the fatty acids to the soap manufacturers. Some larger soap plants also installed at that time autoclaves for the saponification of fats, and the question has recently been again agitated, particularly by the introduction of fermentative splitting of fat, chiefly because the latter requires a less expensive plant than autoclave saponification.

Material changes and improvements have been made in the machinery used in the manufacture of soap. In this country there has been a steady progress in the improvements constantly making in this important branch of industry, until now we are producing goods which for quality compare favorably with any made elsewhere; moreover, we have invented much new and improved machinery and apparatus that greatly facilitate the processes, saving labor and time and improving the quality. Thus the United States is at this time but little behind any other country, either in the amount made or in the quality of the article; while in the economy and facility of their manufacture this industry is fully abreast, if not in advance, of that of nearly all other countries, and is steadily progressing, so that it cannot be long before we shall equal in quality and excel in quantity.

The primitive system of slabbing by hand and drawing a wire, in parallel lines uniform distances apart, through the frame of soap, has been almost entirely replaced by mechanical slabbing devices. Mechanical crutchers have been largely substituted for hand crutchers, thus doing away with the laborious work connected with the latter. Great improvements have also been made in presses, this being of importance not only for toilet soaps, but also for cosmetic soaps, as more value is now attached to the external appearance of the latter than was formerly the case. Iron frames are now largely used in place of wooden ones. To prevent the soap from cooling too rapidly, the frame is sometimes enveloped in a poor conductor of heat in the form of a mattress stuffed with tow.

In modern times it has been endeavored to shorten the time for production of soap by avoiding long cooling in the frames. Pioneers in this respect were A. and E. des Cressonieres, of Brussels, with their "*broyeuse secheuse continue.*" While only dried soap could formerly be used in the milling machine, the above-mentioned apparatus allows of the working of the hot liquid soap as it comes from the kettle, and soap finished in the kettle yesterday can, perfumed and colored, be brought the next day into commerce. This invention was originally intended only for the preparation of milled toilet soaps, but it was soon found to be of use also for the manufacture of various kinds of domestic soap, and the idea has been utilized in the construction of soap-cooling machines.

The manufacture of soap in the closed boiler under pressure has been fre-

quently tried. Thus Arthur Dunn, a number of years ago, patented in England a process the object of which was to accelerate the process of saponification by effecting it in a pressure boiler at a temperature of from 302° to 320° F. Moveau later on proposed to effect the manufacture of soap in a pressure boiler provided with a safety valve. The boiler was furnished with a stirrer and was surrounded by a jacket into which steam for heating the boiler or water for cooling could be introduced. A temperature of 302° to 320° F. was produced in the boiler. Previous to boiling, the fat and lye were introduced through a manhole, which was then closed; after the air had been expelled the safety valve was also closed. Additions of fat or lye required after the commencement of boiling were forced into the boiler by means of a pump. The spent lye and finished soap were discharged through a pipe provided with a stopcock which passed from the bottom of the boiler through the jacket.

However, all these methods for the preparation of soap in pressure boilers have been abandoned because they did not prove satisfactory, and there is no probability that the desired result will be attained by such experiments. Saponification is, to be sure, rapidly effected in a closed boiler under pressure, but the saponified fat is not soap such as is demanded by commerce. Besides the saponification of the fats, there are other operations in the production of the artificial product known as soap, and in order to be quite sure these operations can only be carried on when the soap-boiler has the soap before him in the open kettle.

Manufacture of soap is at the present time connected with greater difficulties than it was thirty or forty years ago. The frequent changes in the prices of raw materials, while the prices of the soaps themselves have become very low, allow no longer of work by rule of thumb, and force the soap-boiler to adapt his manufacturing processes to prevailing conditions in order to enable him to compete with others.

RAW GOODS USED IN THE MANUFACTURE OF TOILET SOAPS.

Raw goods used in the manufacture of the better grade of toilet soaps are as follows:

Coconut oil (Cochin), coconut oil (Ceylon), palm-kernel oil, bleached white tallow, unbleached tallow, olive oil, etc.

Cochin coconut oil, at ordinary temperature, is a solid white fat possessing a bland taste, and, when fresh, a peculiar, although not unpleasant, odor of the coconut. This oil is chiefly used in soap-making, but during recent years vegetable butter has been manufactured by the Schlicks process from Cochin coconut oil by treatment with alcohol and animal charcoal whereby the free acids are removed. This product is sold under various names, such as coconut butter, vegetable butter, lactine, vegetaline, neucoline. The color of this product is perfectly white; same consistency as butter, with a sweet, agreeable flavor and free from any tendency to turn rancid. Cochin coconut oil is obtained, as the name conveys, from Cochin, China, Siam, and the Malabar Coast.

Ceylon is the second-quality oil manufactured from coconuts. This is obtained from nuts which have fallen from the tree and are collected by the natives and the oil extracted by either expressing or boiling. It is then filled into large barrels and sold to the middleman, who accumulates sufficient for shipment and then exports same to America and Europe.

Coprah coconut oil is fat obtained from the dried-out kernel which has been exposed to the sun or kiln-dried, filled into bags, exported to Marseilles, in France, Hamburg, in Germany, or Hull, in Great Britain, where it is treated and the oil extracted and then in turn exported to America.

Palm-nut oil is obtained from the kernels of the palm-tree fruit. The kernels are imported from Europe, and the fat is obtained from them either by expression or by extraction with solvents. The color of the palm-nut is white; the darker oils, formerly met with owing to faulty manufacture, have disappeared from the market. It possesses a pleasant smell and an agreeable nutty taste. When fresh, the oil is neutral, but on keeping it easily turns rancid with liberation of free fatty acids. Palm-nut oil is chiefly used for soap-making.

Tallow is the fat extracted from the carcasses of beef, mutton, or goats. The quality used for perfectly white soaps is bleached, but for other soaps unbleached tallow answers all requirements.

Olive oil is extracted from the fruit of the olive tree by expression or by extraction. The quality of the olive oil depends upon many circumstances, such as the variety of the olive itself (there are 300 or more varieties of olive trees), the degree of ripeness of the fruit, the manner of gathering, the mode of expressing, etc. The finest oils prepared from the picked fruit, under the names of Virgin, Provence, Aix oil, are edible. The next quality ranks and is sold in this country as finest Tuscan cream. This is used as salad oil. The next lower grade is used for soap-making, which latter is the one with which we are now dealing. Olives in this case, after the fine oil has been expressed, are subjected to further high pressure, equivalent to 4000 pounds to the square inch, which yields a pale-green olive oil which finds extensive use in toilet soaps.

Caustic soda such as is used in soap-making is manufactured by the direct process of liberating chlorine from a solution of common salt by electrolysis. This splits up the salt solution, chlorine being collected over lime which makes bleaching powder, the sodium being taken up by the mercury which is in the bottom of the tanks used in this process and the sodium extracted from the amalgam with water. This liquid is then evaporated to a solid mass, in which form it is delivered to us. To enable us to use the caustic soda, we dissolve this with water to the various degrees of strength necessary.

Caustic potash is mostly manufactured from potassium sulphate which is derived from the so-called Stassfurt salts found in enormous quantities about twenty-five miles southwest of Magdeburg. This mineral is treated by the Leblanc process by roasting in a furnace equal quantities of potassium sulphate, limestone, and small coal. The fused mass is taken from the furnace and allowed to cool, when it is dissolved in water until the potassium carbonate which it contains is dissolved out. This solution is treated by boiling with lime, which converts the carbonate into potassium hydroxide. The solution is then concentrated until it becomes solid, and is then filled in drums.

PROCESS OF MANUFACTURING TOILET SOAPS.

The tallow, coconut and olive oils, or other fats are first of all melted, each one by itself, in square iron tanks and pumped from them into the soap kettle. When the full quantity necessary for the boiling of soap is pumped into the kettle the process of boiling begins.

Steam is turned into the kettle through open coils, and caustic soda slowly pumped into the melted fats until there is sufficient added, a matter that is left to the judgment of the man in charge of the process. This mixture is boiled until saponification is complete. When this point is reached, salt is added to the kettle to separate the soap from the lye. When this is accomplished, the steam is shut off and the kettle allowed to stand at rest until the following morning. The waste lye in the bottom of the kettle is then drained off through a valve and pipe at the

bottom of the kettle. When all the lye is removed, steam is turned into the kettle and caustic soda added slowly as in the previous operation. This is again salted out and the kettle allowed to rest until the following morning. This ends the second operation.

The third operation, or washing change, is the repetition of the previous operations, only after the lye is drained off it requires a much smaller amount of caustic soda to perfectly saponify the whole of the remaining fats that may have escaped in the two previous operations. When satisfied that saponification is complete, salt is added, and when separation is nicely balanced the kettle is allowed to remain until the following morning.

Fourth and last change: the lye is drained off the kettle as in previous operations, and steam turned into the kettle and boiled vigorously. This is the last and most important operation. This is the point where skill and judgment are required such as cannot be obtained from any text-books on the subject. It entirely remains with the soap-maker to finish the product in the most satisfactory manner, such as experience only can teach. The operation of boiling has now been completed. The kettle of soap is now allowed to stand for three, four, or five days, or more if necessary, until the temperature of the soap drops to about 140° to 160° F. The soap is then ready to pump out into frames of a capacity of about 1300 pounds. These frames are so built that the sides and ends can be taken off when the soap becomes solid (which takes three to five days), when it is cut up by wires into slabs, bars, and chips. These chips are then placed in a dry room to take out all the excess of moisture and put same in condition for milling. The soap as it is pumped from the kettle contains about 62 percent of fats, but after it leaves the soap mills it contains 80 to 82 percent fats. When the chips are sufficiently dried they are taken to the soap mill and crushed over the rollers several times until a perfect ribbon rolls off on the opposite side of the machine. During this milling process perfume, colors, or medicinal substances are added. These ribbons are transferred to the plodder and are there compressed by a large screw eight inches in diameter and forced through the orifice in front of the machine in a long bar, the necessary size for the tablet of soap required. The long bars are placed on a cutting table, cut into sections, and then placed in the stamping machine and there subjected to further pressure of eight tons, which gives the bars of soap the necessary shape and lettering.

This covers the whole process of soap manufacturing in general. There are many specialties which are made by different processes which do not concern us.

Soap powder is made in the same manner as the soap mentioned above, only in this case coconut oil and tallow only are used. This soap, after being dried in chips, is subjected to further treatment by grinding it into an impalpable powder. This powder must be absolutely dry, and, as all soaps are slightly deliquescent, it is necessary to keep same in a dry place, as it absorbs moisture from the atmosphere, especially if stored in a humid or damp place.

Soft soap or shampoo is made of a mixture of tallow, coconut oil, and in many cases a little castor oil. In this case caustic potash is used. This makes the soap soft, clear, and transparent and easily soluble in water, as should be the case for the purpose for which it is required.

Liquid soaps are made of coconut oil, tallow, and castor oil. These also are made with caustic potash at the lowest possible temperature, and, to facilitate the free lathering qualities of liquid soap, a quantity of alcohol is used. The coloring matter and perfume are added when quite cold. It is filtered and bottled ready for the trade.

USES OF SOAP.

The various functions desired in the use of soaps are that they should be good detergents both for the removal of dirt and any natural secretion or fat from the skin. To do this without injury to the epidermis it is necessary that the soap should have a very slight amount of free alkali. The free alkali removes a small portion of the natural fats of the skin, leaving the pores clean and open so that they can perform their natural duties. Superfatted soap, or, as it is commonly known, soap with an excess of free fat, will not answer this purpose.

Most persons have long believed that a liberal use of soap and water insures bodily cleanliness. It will be a shock to learn, therefore, that some persons have skins that soap only makes dirty. This is on the high authority of the London Lancet.

The active principle of all soaps is alkali, the action of which ordinarily is to separate dirt from the oil of the skin and enable it to be washed away.

But it seems that certain skins are not proof against the action of alkali, and soap acts as a detergent because it forms an emulsion with dirt and the liberated alkali removes the fat which causes dirt to cling. Any inquiry, therefore, turned to the question of the effects of soaps upon the skin amounts to the determination of the sensitiveness of the skin to the action of alkali.

Owing to hydrolysis, soaps when dissolved in water exhibit a marked alkaline reaction, and this is true also of the so-called superfatted soaps, though these are generally made with superior materials, and for that reason may be preferred. An interesting contribution on the subject appears in the reports recently issued from the laboratory of the Royal College of Physicians of Edinburgh. In an article entitled "Soaps and Their Effects on the Skin," Dr. Gardiner points out that among the more expensive toilet and superfatted soaps the proportions of mineral ash and alkali are at least as high as in the coarser types.

When an alkaline solution such as that of soap touches the skin there is induced, he says, both an excessive secretion of the acid sebum and sweat, and a solvent effect on the protective epithelium. Reviewing the different ingredients found in soaps, he concludes that all soaps from their chemical constitution must be irritant to the normal skin. The effect varies, he states, with the individual skin, and is more pronounced in senile and diseased skins. Cotton-seed oil and rancid fats, according to his observations, are probably largely responsible for the irritant effects in cheaper soaps.

Castor-oil soap, he finds, is least irritating, but it has the disadvantage of being too freely soluble and therefore wasteful, while it is apt to become rancid. Cocoanut-oil soap is decidedly irritating, while palm-oil soap, though still an irritating variety, is less so, and tallow soap shows a low irritating value.

If these deductions are correct, Dr. Gardiner thinks they supply a reason for the bad effects of modern domestic soaps of the cheaper and clothes-washing kinds, as they are made mostly from cheaper fats and the cheap oils, coconut and cotton-seed. Formerly tallow and olive oil were more used, and the evil effects of soaps were not so pronounced at that time.

No one can be in touch, he says, with the out-patient department of a large hospital and not observe the economic loss, not to speak of physical damage, due to soaps and soap powders. If hands were considered as well as the clothes, and more of the old-fashioned joint oil pressed into service, the results, he considers, would tend to lessen this serious and increasing occupational dermatitis.

Another of the uses to which soap is of the very largest benefit is that of a germ destroyer, and Dr. H. W. Hill, of the State Board of Health of Minnesota,

declares that the frequent washing of the hands with good soap would prevent the spread of many contagious diseases. It has lately become known that soap possesses disinfectant and deodorizing properties in a high degree. According to an experiment carried out by the Berlin Health Commission, a solution of one part of potash soap in 10,000 parts of water completely prevented the development of the bacilli of a permanent cattle disease, and the said commission has recommended a solution of potash soap, 15 to 10,000, as a first-rate disinfecting medium.

In a recent test on soap solution on various bacilli the following result has been compiled:

In a one percent soap solution on cholera bacillus in one minute there was no growth. The same applies to diphtheria, typhoid, plague, tuberculosis.

It is also found that potash soft soap is eight times as powerful as potash solution, which goes to prove that any good soap is a powerful antiseptic and that the purer the soap the stronger are its antiseptic properties.

In a paper presented before the International Congress of Zoologists in 1907, the writer stated: "We have confirmed the fact that the insecticidal value of soap is very considerable."

There are two classes of insecticides—those which act as poisons on the food of the insect, such as sprinkling the place they infest with soap powder, or the external kind which kills the insect by simple contact. This latter system is the one which interests us mostly.

In order to wet a given body in the best way a liquid must be chosen which has a low surface tension. This can be obtained by making a solution of sodium oleate (soap). The same wetting effect can be produced by the addition of 5 percent of a solution of 0.1 percent. Solutions of one in a thousand are as efficient as those of 50 percent. For hard water a little carbonate of soda should be added. This solution is taken through the vineyard, the hop plantations, or through trees, and is sprayed over the leaves and branches early in the season. This solution instantly wets the insects, dries on them, and causes their death.

As you are probably aware, there is no other article which is used in so many different ways as soap. A few of those who utilize soap largely are silk dyers, wool scourers, toilet supply companies, dry cleaners, carpet cleaners, disinfecting companies, auto garages, wire spinners, wire drawers, veterinarians, gardeners, farmers, etc.

In 1909 the soap manufactured in the United States was valued at $111,357,777, and 18,000 persons were engaged in the manufacture of it. It is peculiar that, though the number of soap factories has been decreasing since 1859, the production has, of course, enormously increased. This is accounted for by the elimination of the small makers, those who in the days of our fathers and grandfathers used to peddle the soap of their own making.

In this progressive age soap manufacturing requires a high degree of scientific knowledge and skill such as cannot be retained by the small factory. The excessive cost of small productions also militates against the small man's survival. He is under a great disadvantage in the purchase of raw goods on account of purchasing small quantities.

The cost of production for fifty tons of soap is only little more than for producing five tons, so that without a large amount of capital it is very difficult in these days for a small manufacturer to exist.

The civilization of a country can also be estimated by the quantity of soap which is produced or, in other words, used per capita of population. The consumption of soap in the United States and Great Britain is about equal, namely, fourteen pounds, while the consumption in Russia is one and one-half pounds per

capita. The same amount is approximately consumed in South America, India, and China. This is not because the people will not use soap, but it is on account of the poor wages they are earning and the distance from the place of importation, which places a prohibitive price upon this commodity. In the interior of China, ten years ago, it was the writer's experience, when travelling four hundred miles from Shanghai, to see in the native market small pieces of soap used as money. This evidences that there are markets open in these countries for an enormous amount of goods when we shall be in a position to deliver to them.

The world improves with each passing year
Because each man in his little sphere
Takes off his jacket, grins and sings,
And keeps on doing the same old things.

LABORATORY, FREDERICK STEARNS & COMPANY.

IDENTIFICATION OF CASCARA ADULTERANT.

The adulterant of Cascara bark noted by F. A. Miller (Jour. Am. Pharm. Asso., 1912, p. 1207), but which he did not identify, and again mentioned by Gathercoal (Jour. Am. Pharm. Asso., 1915, p. 70) and there pronounced to be the bark of a *Prunus,* has been definitely identified as the bark of *Prunus padus.* This bark is a commercial article in Germany, according to Prof. E. M. Holmes, and has been received in England as a substitute for wild cherry bark.

The adulterating bark closely corresponds in internal structure to a specimen of fresh *Prunus padus* bark recently received from Kew Gardens, London.

No further report has been received of any of this false Cascara since the shipment to Chicago in 1914. Probably the attempt of some unscrupulous European exporter or American importer to depreciate the standard of American cascara was frustrated by the publicity given to the matter by Mr. Miller in 1912. —*E. N. Gathercoal,* University of Illinois School of Pharmacy.