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SOAPS

A PRACTICAL MANUAL OF THE MANUFACTURE OF DOMESTIC, TOILET AND OTHER SOAPS

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PREFACE.

THE substance of this book has already appeared in the form of articles in the pages of *The Oil and Colour Trades Journal.* These articles were received with so much favour by the readers of that Journal that it has been thought desirable to collect them together and reprint them in book form. For this purpose the articles have been thoroughly revised and new matter added to bring the subject up to date. The author has not attempted to write a complete treatise on Soap Manufacture, but has aimed at presenting in a brief but, it is hoped, clear manner the principal processes of soap manufacture, with an account of the raw materials used and the scientific principles which underlie the various operations.

The author here acknowledges his indebtedness to several engineering firms for the loan of machinery blocks wherewith to illustrate the chapter on Soap Machinery.

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CHAPTER I.

INTRODUCTORY.

SOAP has been known from very early times, it is several times referred to in the Bible, and is also referred to by some of the ancient Greek writers: Aristophanes, who lived about B.C. 434, and by Plato, who lived about B.C. 348. Pliny, who died in A.D. 79, states that soap was first invented by the Gauls, and gives an account of its manufacture from alkali and fat, the caustic alkali being produced from the ashes of wood, and, he states, natural earths, by which it is presumed lime is meant. The best soap was made from the fat of goats and the ashes of beechwood, but it was also made from other forms of fat and wood ashes. Pliny also gave an account of the manufacture of lead soap and its use in medicine. The remains of a soap factory have been found among the ruins of Pompeii. The earlier Arabian alchemists in their writings speak of soaps being used for detergent purposes, and for personal application. It may be added that prior to the invention of soap, and even up to the present time, the ashes of wood, together with such earthy matters as fuller's earth, which appear to have detergent properties, were largely used for washing and cleansing.

Up to about the fourteenth century the Spaniards and Italians were the largest makers of soap. About the thirteenth or fourteenth century soap-making was introduced into France by the Phoceans, people of Egyptian origin who established themselves at Marseilles, which from that time has remained the seat of a very extensive soap trade, for it has very many natural conveniences, the forests of Southern France giving the needful wood ash, while the seaweed of the sea yielded the barilla needful for the manufacture of hard soap, lime for the causticising was readily obtained, while the climate of Southern France favoured the growth of the olive trees, from which the main ingredient, olive oil, of the Marseilles soap was obtained. Being situated on the sea-coast, Marseilles was able to import large supplies of olive oil from Italy, and barilla from Spain.

It is somewhat uncertain when soap-making was first introduced into England, but it would probably be about the fourteenth century, and came to us from France, and the French method was long practised. The earliest English patent relating to soap-making was granted in 1622, since which time many have been issued. Until about the end of the last century no improvements either in the process or the materials were made, then Leblanc introduced his process of making soda from salt, and gradually the Leblanc soda replaced the barilla soda in soap-making. The foundation of modern invention in soap-making is largely based upon the work of Chevreul on the chemistry of fats, and upon this work, together with that of Leblanc, the practical basis upon which soap-making is to-day conducted has been based.

NATURE OF SOAP.

As ordinarily understood soap is the product obtained by boiling the various animal and vegetable fatty matters with one or other of the caustic alkalies in a variety of ways, the product being used for cleansing purposes of all kind. The alkali reacts with the fatty matter and liberates from it the substance known as glycerine, while the alkali combines with certain fatty bodies of an acid nature to form the familiar article with which every one is acquainted, and the appearance of which must be known to all persons. The alkali soda is the one most commonly used, and yields what are known as the hard soaps, while the alkali potash yields another kind of soap which is known as soft soap. As the chemistry of soap-making is dealt with in detail in another chapter, it is not needful to discuss it more fully here. It may be pointed out that compounds of the fatty acids with other bases than the alkalies, such as, for instance, lime, lead, alumina, etc., are known, and some of them are of service in various directions, but in common usage the term soap is restricted to the soda and potash compounds already alluded to.

ACTION OF SOAP.

That soap is of very material assistance in the removal of dirt and grease from clothes and the bodies of persons has long been known, but the manner in which it acts is not equally well known, and probably depends upon a variety of causes, some of which are of a physical nature, while others are of a chemical nature. Many investigations have been made by various persons as to the cleansing property. Probably the simplest explanation would be that the soap exerts an emulsifying action upon the greasy matters which always accompany the dirt in clothes, etc., and enables it to become diffused through the water with which the soap is accompanied.

The alkali no doubt plays an important part in the detergent action of soap, but that it is not all-important is proved by the fact the pure alkali by itself has not the same cleansing action, nor has the alkali which is present in the form of silicate of soda or aluminate of soda the same action as the alkali of soap.

There is no doubt that water has some action upon soap: when soap is boiled with a large quantity of water it dissolves to a perfectly clear solution, but on cooling this becomes more or less turbid. Another feature which must be noticed is that there is an increase in the alkalinity of the soap when it is dissolved in cold water; this can be shown by dissolving a piece of soap in alcohol, adding a few drops of phenolphthalein solution and allowing the alkali solution to set into a jar; on pouring water into the jar the soap gradually becomes dissolved, and the solution acquires a reddish tint showing the production of the free alkali.

Messrs. Wright and Thompson have conducted a series of experiments upon this subject, the action of water upon soap, and they have determined the amount of hydrolysis by using various quantities of water; their results are given in the following table:—

Soap made from	Mean Molecular Weight.	Hydrolysis brought about by x Molecules of Water.				
		x = 150	x = 250	x = 500	x = 1000	x = 2000
Pure stearic acid. .	284	0·7	1·0	1·7	2·6	3·55
Nearly pure palmitic acid . . .	256	1·45	1·9	2·6	3·15	3·75
Crude lauric acid (coconut oil) . .	195	3·75	4·5	5·4	6·45	7·1
Pure oleic acid . .	282	1·85	2·6	3·8	5·2	6·65
Crude ricinoleic acid	294	1·55	2·2	3·0	3·8	4·5
Chiefly stearic, palmitic and oleic acids (palm-oil tallow soap) . . .	271	1·1	1·55	2·6	4·1	5·3
Chiefly tallow and rosin (primrose) . .	280	1·5	2·2	3·1	4·2	5·3
Cotton seed . .	250	2·25	3·0	5·0	7·5	9·5

The figures in this table are the quantities in per cent. of the alkali in the soap. It is to be noted that a tallow soap is less hydrated than a palm-oil soap and much less than a coconut-oil soap, while a cotton-oil soap is more hydrolysed than any other kind. The reaction which takes place may perhaps be expressed in the following equations:—

$$\begin{array}{ccccccc} \text{Sodium Stearate.} & & \text{Water.} & & \text{Caustic Soda.} & & \text{Sodium Acid Stearate.} \\ 2\,NaC_{18}H_{35}O_2 & + & H_2O & = & NaOH & + & \begin{matrix} NaC_{18}H_{35}O_2 \\ HC_{18}H_{35}O_2 \end{matrix} \end{array}$$

Now it is evident that if this be the action of water upon soap the alkali that is thus set free will have an action in saponifying and emulsifying the grease with which it is brought into contact, when used for washing purposes, and therefore to enable it to be removed and washed away. In some cases the small percentage of fatty acid which is set free may assist the cleansing operation.

The relative hardness of a soap, with which may be combined its solubility in water, is of very material importance as regards its cleansing effects; there is a considerable variation in regard to the hardness of a soap, and naturally the harder the soap the smaller the quantity that will be rubbed off it when it is used. A soap made from tallow is very much harder than a soap made from olive or from coconut oil, and it takes therefore more rubbing. Again the proportion of water which may be left in a soap influences its hardness; the average quantity of water in a well-made sample of soap may be taken at 20 per cent., in a toilet soap it may be as low as 13 to 15 per cent. In low-grade soaps it may reach from 30 to 35 per cent.; the more water there is present the softer they are and the more easily are they rubbed away. Again soaps vary in their solubility in water; thus, for instance, while the oleate of soda is soluble in 10 parts of water, the stearate of soda requires about 100 parts of water for solution. This has a material influence on the washing and lathering properties of a soap, also upon the lasting properties; soaps from olive oil and cotton-seed oil lather better but are rather more wasteful than soaps made from tallow and palm oil.

CHAPTER II.

SOAP-MAKERS ALKALIES.

In the manufacture of soap two materials are required: (1) the fat, (2) the alkali. The fat or fats which are used in the preparation of soap will be described in the next chapter in some detail. In this chapter will be discussed the alkalies, for there is more than one that can be used, and the alkaline salts used in soap-making.

Whenever a highly basic body like sodium hydroxide, caustic soda $NaOH$, or potassium hydroxide, caustic potash KOH, or calcium hydroxide, slaked lime CaH_2O_2, or even lead oxide PbO, is boiled with a fat, the latter undergoes what is called saponification; that is, there is produced a body which is known as soap, an article of great domestic and commercial use, together with another body known as glycerine. In the chapter dealing with the soap fats it is shown that they are combinations of sundry acid bodies, which are generally known as the fatty acids with the base, glyceryl, or glycerine, or, as chemists prefer to call it, glycerol, to show that as far as its chemical relations are concerned it is allied to the alcohols. Taking, for instance, a typical oil, olive oil, this is composed almost entirely of olein, which is a combination of oleic acid, $HC_{18}H_{33}O_2$, with glyceryl, C_3H_5. The latter body is a tribasic compound, while oleic acid is only a monobasic body, so that one chemical equivalent of glyceryl requires three chemical equivalents to form olein; the latter, therefore, has the formula:—

$$C_3H_5 \left\{ \begin{array}{l} C_{18}H_{33}O_2 \\ C_{18}H_{33}O_2 \\ C_{18}H_{33}O_2 \end{array} \right.$$

Similarly stearin, the characteristic constituent of tallow, is a compound of stearic acid, $HC_{18}H_{35}O_2$, and glyceryl. Palmitin, the characteristic body in palm oil, contains palmitic acid, $HC_{16}H_{31}O_2$, combined with glyceryl in like proportions to those present in olein.

When these fats are boiled with the alkaline bodies named above the glyceryl splits off and forms glycerol, while the alkali combines with the fatty acid to form soap, as is shown in the following chemical equations:—

$$\begin{array}{ccccccccc}
\underset{\text{Olein}}{C_3H_5 3C_{18}H_{33}O_2} & + & \underset{\substack{\text{Sodium}\\ \text{hydroxide}}}{3NaOH} & = & \underset{\substack{\text{Sodium oleate}\\ \text{(soap)}}}{3NaC_{18}H_{33}O_2} & + & \underset{\text{Glycerine}}{C_3H_5(OH)_3} \\
\underset{\text{Stearin}}{C_3H_5 3C_{18}H_{35}O_2} & + & \underset{\substack{\text{Potassium}\\ \text{hydroxide}}}{3KOH} & = & \underset{\substack{\text{Potassium}\\ \text{stearate}}}{3KC_{18}H_{35}O_2} & + & \underset{\text{Glycerine}}{C_3H_5(OH)_3} \\
\underset{\text{Primitin}}{2C_3H_5 3C_{16}H_{31}O_2} & + & \underset{\substack{\text{Calcium}\\ \text{hydroxide}}}{3Ca(OH)_2} & = & \underset{\substack{\text{Calcium}\\ \text{palmitate}}}{3Ca2C_{16}H_{31}O_2} & + & \underset{\text{Glycerine}}{2C_3H_5(OH)_3}
\end{array}$$

The soaps which are formed by the alkaline earths (calcium, barium, strontium, and magnesium), lead, iron, copper, and the metals generally, are insoluble in water; those formed by the alkali metals (potassium, sodium, lithium) are soluble in water, hence these only are used in domestic and industrial work, although the fact that lime and other metals will form insoluble soaps has been taken advantage of for various useful purposes. The alkalies sodium and potassium will therefore be dealt with here, although a word or two will be said concerning lime and magnesia.

The term alkali comes down to us from Arabic times; its meaning is really *al kali*, the salt, and it was used to denominate a saline body often found in the hot Eastern climes as an efflorescence on the soil, and more especially in the neighbourhood of stables and the drainage of rubbish heaps. This alkali was of a very crude composition and varied somewhat in its composition according to its source; the property which gave it value was that of forming an emulsion with oil, and this emulsion had stronger cleansing powers than either the oil or the alkali. There is no doubt that this property was due to the alkali containing appreciable quantities of the carbonate and caustic forms of the alkali proper. As course of time went on it was found out that a similar body was obtained by the combustion of wood, which was found to leave a white ash on burning, this ash possessing stronger alkaline properties than the original alkali.

These gradually usurped the name to themselves. Then it was ascertained that seaweeds also left ashes of an alkaline character on combustion, which are found to be different in their actions on oils than the ashes from wood, the soap they made being harder in character than that made by wood ashes, consequently two kinds of alkali came to be recognised—marine alkali from seaweeds, vegetable alkali from trees; and, moreover, the soap-makers began to produce two kinds of soap—hard soap from the first-mentioned alkali, soft soap from the vegetable alkali. Then the fact that by treatment with burnt lime these alkaline bodies could be converted into stronger bodies, the caustic alkalies, came to be found out, and that these had more action on the fats was also recognised and made use of in soap-making. Then finally came the discovery by Sir Humphrey Davy that the alkalies were compounds of two peculiar metallic bodies, one of which he named sodium, the other potassium. Of these metals it will be sufficient to say that sodium has since become of some industrial importance; they are soft metals, considerably lighter than water, on which they float. When fresh they have a silver-white appearance, but soon become oxidised on exposure to the air, becoming coated with a film of oxide; on water they have an energetic action. Sodium floats with a hissing sound, and causes the evolution of hydrogen, while caustic soda, sodium hydroxide, remains in solution. Potassium has rather more energetic action, and the hydrogen which is liberated is set on fire, and burns owing to the great amount of energy which is developed, while caustic potash remains in solution. The following equations represent the action of these two metals on water:—

$$\underset{\text{sodium}}{Na} + \underset{\text{water}}{H_2O} = \underset{\substack{\text{sodium}\\\text{hydroxide}}}{NaOH} + \underset{\text{hydrogen}}{H}$$

$$\underset{\text{potassium}}{K} + H_2O = \underset{\substack{\text{potassium}\\\text{hydroxide}}}{KOH} + H$$

The alkaline compounds which are of most interest to the soap-maker are the two named above as the result of the action of the metals on water, *viz.*, sodium hydroxide or caustic soda, which has the chemical formula $NaOH$, and potassium hydroxide, or caustic potash, the chemical forumla of which is KOH, as these alone are capable of acting upon and forming with fats the various commercial forms of soap. Besides these the carbonates of the same metals, sodium carbonate, or as it is better known soda, Na_2CO_3, and potassium carbonate, or potash, K_2CO_3, also merit attention as being the original forms of the alkali from which the caustic forms are manufactured.

While it is only the caustic alkalies which have the property of saponifying fats, as has been pointed out above, yet both the caustic and carbonate alkalies will act upon and combine with the fatty acids to form soaps; in the former case soap and water are the only products formed, while in the latter carbonic-acid gas is evolved at the same time. The manufacture of soda is now one of the greatest chemical industries known, many millions of money being invested in the alkali manufacture which is carried on with great energy and skill in Great Britain.

SODA.

Of the two alkalies used in soap-making, soda occupies the first place, the two forms, carbonate Na_2CO_3 and caustic

NaOH, being those used in soap-making, and these will now be considered.

The compound which is universally understood whenever the term "soda" is used, is the carbonate of the metal sodium, whose chemical formula has just been given. It is virtually a compound of the dioxide of carbon or carbonic acid gas with the oxide of metal sodium. It comes into commerce in five forms:—

Soda ash, a more or less pure anhydrous carbonate.

Refined alkali, almost, if not quite, pure anhydrous carbonate; this form is that generally known on the continent as calcined soda.

Soda crystals, known as sal soda in America; this is in the form of large crystals, and contains 10 molecules of water of crystallisation; it has the formula $Na_2CO_310H_2O$.

Crystal carbonate or crystal soda; this is in the form of small crystals, and contains one molecule of water of crystallisation; it has the formula $Na_2CO_3H_2O$.

The bicarbonate, the form mostly used in ordinary culinary work and medicine; it has the formula $NaHCO_3$.

The raw material for the manufacture of the different forms of carbonate of soda is salt, the chloride of sodium having the formula NaCl, although before the time of Leblanc seaweeds constituted the source from whence it was made.

There are two chief processes whereby soda is made from salt, that known as the Leblanc process, and that known as the ammonia-soda process, the latter being the one which bids fair to be the chief process of the future. It is not intended here to enter into a minute account of the details of the manufacture, because, as a rule, soap-makers do not make their own alkali, and are not thereby interested in the details. A brief account of the various processes of manufacture will be given.

The Leblanc soda process was invented by Nicholas Leblanc in the latter part of the last century, during the time of the first French Revolution, which if it did nothing else, gave the Leblanc soda process to the world. It is due to English enterprise and chemical skill that the process has attained the perfection it has, although in the main principles it is just the same as when Leblanc first described it.

The process of making soda by this method takes place in several stages. In the first place, salt is mixed with sulphuric acid in iron pans, when there is evolved large quantities of hydrochloric-acid gas. In the early days of alkali-making this gas was sent into the atmosphere, much to the detriment of the vegetation of the surrounding districts; but now it is absorbed by passing the gasses up large towers, down which a current of water is continually passing. The acid gas is very soluble in water, and almost if not quite all of it is taken up by the water to form what is commonly known as "tower salts," the commercial form of hydrochloric acid. Besides the hydrochloric acid, there is formed sodium sulphate, or as it is known "salt cake". The equation representing the change is :—

$$\begin{array}{ccccccc} 2NaCl & + & H_2SO_4 & = & Na_2SO_4 & + & 2HCl \\ \text{Sodium} & & \text{Sulphuric} & & \text{Sodium} & & \text{Hydrochloric} \\ \text{chloride} & & \text{acid} & & \text{sulphate} & & \text{acid} \end{array}$$

This stage of the process is known as the "salt cake" process.

The next stage of the process is a more complicated one. The salt cake from the last operation is now mixed with a certain proportion of ground coal and limestone, and heated to a red heat in what is known as the black-ash furnace; here it is well worked about by rabbling until all chemical action has ceased, the product forming what are called balls of black ash. It owes its name, "black ash," to the fact that in the early days of the industry it was black, but now as a rule it is of a brownish-grey colour; nevertheless the name is retained. The form of furnace formerly used is that known as the reverberatory furnace, the working being done by hand, and is a very laborious piece of work, but now revolving furnaces are used, worked mechanically, thus doing away with hand labour.

The chemical reactions which go on in the black-ash furnace are probably of rather a complicated description, but briefly they may be considered to proceed upon the following lines: the sodium sulphate and the carbon of the coal react with one another resulting in the formation of sodium sulphide and carbon monoxide. The sodium sulphide thus formed reacts with the calcium carbonate with the formation of sodium carbonate and calcium sulphide. Although these are the main reactions which occur, yet there are some subsidiary reactions going on, so that black ash is a complex mixture of compounds.

The process is shown in the form of an equation as:—

$$\underset{\substack{\text{Sodium}\\\text{sulphate}}}{NaSO_4} + \underset{\text{Carbon}}{4C} + \underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{4CO} + \underset{\substack{\text{Calcium}\\\text{sulphide}}}{CaS}$$

as well as a simple equation can do.

Black ash contains both soluble and insoluble constituents, and the following is a complete analysis of a sample:—

ANALYSIS OF BLACK ASH.

Soluble constituents		
Sodium carbonate, Na_2CO_3	28·144	per cent.
Sodium oxide, Na_2O	5·860	,,
Sodium chloride, $NaCl$	2·808	,,
Sodium sulphate, Na_2SO_4	·192	,,
Sodium sulphite, Na_2SO_3	·151	,,
Sodium thiosulphate, $Na_2S_2O_3$	·189	,,
Sodium sulphide, Na_2S	·358	,,
Sodium aluminate, $Na_2Al_2O_4$	·344	,,
Sodium silicate, Na_2SiO_3	1·026	,,
Sodium cyanide, $NaCN$	.186	,,
Sodium sulphocyanide, $NaSCN$	0·74	,,

Insoluble constituents.

Calcium sulphide, CaS	29·504	per cent.
Calcium carbonate, $CaCO_3$	12·657	„
Calcium oxide, CaO	10·048	„
Ferrous sulphide, FeS	·554	„
Alumina, Al_2O_3	·172	„
Silica, SiO_2	1·095	„
Magnesia, MgO	·266	„
Sodium oxide, Na_2O	·344	„
Carbon	4·263	„
Sand	1·237	„

The next operation consists in the extraction by a process of lixiviation with water of the soluble constituents. This is done by an ingenious arrangement of vats whereby all the soluble portion is completely extracted without much difficulty, weak liquors from previous batches being used at first and fresh water for final treatments. The insoluble portion goes to form what is called vat waste, which used to be at one time the *bête noir* of the alkali-maker, but comparatively recently a process has been invented whereby the sulphur it contains, and this is the valuable constituent of it, is recovered and used for making sulphuric acid.

As might be expected from the analysis of black ash which is given, the liquor which is known as black-ash liquor has a complex composition. It usually has a specific gravity of 1·26 to 1·29 (52° to 58° Tw.), and contains:—

Sodium carbonate, Na_2CO_3	68·91	per cent.
Sodium hydroxide, NaOH	14·43	„
Sodium sulphide, Na_2S	1·31	„
Sodium sulphite, Na_2SO_3	2·23	„
Sodium thiosulphate, $Na_2S_2O_3$	trace	
Sodium sulphate, Na_2SO_4	7·02	„
Sodium chloride, NaCl	3·97	„
Sodium silicate, Na_2SiO_3	1·03	„
Sodium aluminate, $Na_2Al_2O_4$	1·02	„

with traces of sodium cyanide, sodium ferrocyanide, sodium sulphocyanide, alumina, silica, ferrous sulphide.

The weak tank liquors have a similar composition, and usually contain about 14 parts per 1000 of solid matter.

The tank liquor is run into settling tanks to allow any alumina, silica, etc., to settle out. It is then run down a tower through which carbonic-acid gas and air are passing. This brings about certain changes, resulting in the increase of the amount of carbonate the liquor contains. This it does by the carbonic acid acting on the caustic soda, sodium sulphite and thiosulphate, and converting them into carbonate. Then, at the same time, a certain amount of oxidation occurs; the iron, sulphur, sulphocyanides, cyanides, sulphites and similar salts are oxidised. Some of them are then able to form insoluble bodies which settle out on the liquor being subsequently allowed to settle in tanks.

The next operation is called salting down. The liquor is placed in shallow tanks, usually in the flue of the furnaces, so as to make use of the waste heat which passes away from them. The water gradually evaporates away; the salts it contains crystallise, and are fished out by means of perforated iron ladles. Next the salts are mixed with a small amount of sawdust and furnaced when they are more completely converted into carbonate. The product is soda ash. Of this there are two forms, one known as caustic-soda ash, because it contains a small quantity of caustic soda. The other is known as carbonate ash; it is not quite pure sodium carbonate, but contains variable quantities of caustic, sodium chloride, sodium sulphate, etc. It is sold of varying degrees of strength known as 48 per cent., 50 per cent., 52 per cent., up to 58 per cent., which is the strongest made. These figures refer to the proportion of sodium oxide the ash may contain in the form of either caustic or carbonate. It is sometimes known as the available alkali, to distinguish it from that which is also present in the form of sulphate, chloride, etc., which is not available or useful for any of the purposes to which soda ash is put.

The following analyses are of a 48 per cent ash and of a 58 per cent. ash :—

	48 p.c. ash.	58 p.c. ash.
Sodium carbonate, Na_2CO_3	60·64 p.c.	98·72 p.c.
Sodium sulphate, Na_2SO_4	4·35 „	·20 „
Sodium hydroxide, NaOH	1·29 „	
Sodium chloride, NaCl	28·34 „	·54 „
Calcium carbonate, $CaCO_3$	traces	·13 „
Magnesium carbonate, $MgCO_3$		·04 „
Iron oxide, Fe_2O_3		·04 „
Alumina, Al_2O_3	1·12 „	·01 „
Silica, SiO_2		·09 „
Moisture, H_2O	43·6 „	·19 „

The great difference in the relative purity of the two samples of ash is seen from these two analyses, for while there is a fairly large number of impurities in the 58 per cent. ash, yet they are only present in very small amounts which can have no practical influence on the using of the ash; whereas in the 48 per cent. ash these impurities being in much larger amount·cannot fail to exert some influence.

What is know as refined alkali is made from soda ash of good quality by dissolving in water, allowing any insoluble matter to settle out, then boiling down, fishing out the crystal, which come out first, as these consist chiefly of the sulphate and chloride, then boiling down quite dry.

Soda crystals are the crystallised form, containing 10 molecules of water of crystallisation in it. This is therefore sometimes known as the decacarbonate or decahydrate to distinguish it from the other crystalline form, which is described below. Soda crystals are made by dissolving soda ash in water, allowing any insoluble impurities to settle out, then evaporating the solution down until it has a strength of 56° Tw., when it is placed in tanks to crystallise out, which it does in large, transparent, prismatic crystals.

These are drained from the mother liquor, dried or packed into bags or kegs for sale. These crystals keep very well, but are slightly efflorescent, that is, they tend to lose their water of crystallisation and become dry and powdery.

This is the most familiar form of soda, as it is in this form that it makes its appearance in our households for washing and domestic scouring.

It is this form of soda which is used in making dry soaps, for which purpose advantage is often taken of the fact that when heated soda crystals will melt into a liquid which when it cools will set into a brittle crystalline solid mass. Generally soda crystals, or sal soda as the Americans call it, is fairly pure, but it contains traces of other sodium compounds, as will be seen from the following analysis of a sample :—

ANALYSIS OF SODA CRYSTALS.

Sodium carbonate, Na_2CO_3	34·22 per cent.
Sodium hydroxide, NaOH	·10 ,,
Sodium sulphate, Na_2SO_4	2·54 ,,
Sodium chloride, NaCl	·27 ,,
Water, H_2O	62·84 ,,
Insoluble matter	·03 ,,

From which it will be seen that water is the principal constituent of soda crystals. The impurities which are present are usually accidental and cannot always be avoided, but it is not an uncommon circumstance to crystallise some sodium sulphate along with the crystals, as these tend to make the crystals harder, and, therefore, better able to resist handling without breaking.

The other process of making carbonate of soda from salt is that known as the ammonia-soda process, and which is worked in this country on an extensive scale by Brunner, Mond & Co., Ltd., of Northwich, the United Alkali Co., Ltd., at Middlewich, and by other firms.

The principle of this process has long been known. It consists in that when carbonic-acid gas is passed into a strong salt solution made alkaline with ammonia, carbonate of soda is formed and precipitates out, being insoluble in the alkaline liquors, while ammonia chloride remains in solution. Although so well known, many difficulties are met with in working the process on a large scale, and there are but few of the many plants devised to take advantage of the principle involved that have been at all successful. The most so is that of Solvay, which is the one in operation at all the principal ammonia-soda works in this country.

The product obtained at first is the bicarbonate of soda, as is indicated in the equation:—

$$H_2O + NH_3 + CO_2 + NaCl = NaHCO_3 + NH_4Cl$$

This bicarbonate is precipitated out, then heated in a furnace, when it is converted into the normal carbonate, which is then sent into commerce as soda ash. The product obtained by the ammonia-soda process is remarkable for its purity, as the following analysis will show:—

Carbonate of soda	99·0	per cent.
Sodium chloride	0·13	„
Silica	0·10	„
Lime	0·13	„
Magnesia	0·06	„
Alumina and iron	0·03	„
Moisture	0·15	„

From this raw material refined alkali is made by dissolving in water, clarifying the solution and evaporating down, while the other forms of carbonate, monohydrate and decahydrate crystals, are obtained by solution and crystallising in the usual way.

The ammonia soda has the advantage over the Leblanc soda of being purer and therefore stronger.

As regards the properties of the carbonate of soda, some idea will have been gathered from what has been said above. It will be sufficient to say that it is fairly easily soluble in water, the solubility increasing with increase of temperature; thus water at 0° C. will dissolve at 6·97 per cent. of the anhydrous carbonate, or 21·33 per cent. of the crystallised carbonate, and at 30° C. 37·24 per cent. of dry carbonate and 273·64 per cent. of soda crystals will be dissolved.

Sodium carbonate possesses slightly alkaline properties; it will react with all acids, producing the corresponding sodium salt with the evolution of carbonic-acid gas: thus it may be used in the preparation of soaps from the free fatty acids, although the evolution of gaseous carbonic-acid gas is a disadvantage, because it causes the soap to fob badly in the process. It cannot be used to make soap from the oils and fats, because carbonic acid, being weaker than the fatty acid in the oils, has no power to liberate those acids from their combinations with glycerine, with which they are combined in the various oils and fats.

CAUSTIC SODA.

Caustic soda, or sodium hydroxide, NaOH, is the soap-maker's alkali *par excellence*. In the early days of the alkali manufacture caustic soda was not an article of commerce, and every soap-maker had to causticise his own alkali, making it from the soda ash of that time; but the alkali-maker soon began to make caustic soda as an article of commerce, and the process has now become so perfected that caustic soda can be bought as a commercial article almost chemically pure, at all events containing something like 99·5 per cent. of the pure chemical.

On the large scale caustic soda is obtained either from the finished soda ash—this is not often done by the caustic-maker, but it is what the soap-maker does if he makes his own caustic—or from the liquor obtained in lixiviation of the black-ash balls, or from the red liquors. The latter yields what is known as "cream caustic," because it has a pale cream colour; it contains a good many impurities. Whatever may be the source of the alkali, the causticising operation is the same in each case. A liquor is made, if from the refined soda ash, by simply dissolving in water to a strength of from 20° to 22° Tw.; some makers use the liquor weaker than this, from 14° to 15° Tw., but there is no material advantage in so doing; the operation can be done with as much ease with 22° Tw. liquors as with 14° Tw. liquors, and it is much cheaper to boil down the strong liquors than it is the weak liquors; on the other hand it is not advisable to use liquors much if any stronger than 22° Tw., as then the causticising does not go on so well.

The liquors made from the black-ash balls are allowed to settle to get all insoluble matter out of them, and this must be done thoroughly; it is best to blow air through them first so as to oxidise some of the impurities contained in the mass whereby they are thrown out in an insoluble form.

The red liquors are used in the form in which they are obtained in the first instance.

The causticising can be carried out in almost any kind of convenient apparatus; some makers use old boilers set on end for the operation. The liquors are heated by steam to nearly the boil, then an iron cage filled with quick-lime of good quality is lowered in, the steaming is carred on until a portion of the liquor taken out, filtered and treated with a little dilute hydrochloric acid shows no trace of effervescence. The reaction which goes on is shown in the following equation:—

$$\underset{\substack{\text{Calcium}\\\text{hydroxide}}}{CaH_2O_2} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH} + \underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3}$$

It takes about an hour and a half to causticise a batch of soda liquor.

During the process of causticising many impurities in the soda liquors become altered and are thrown out in an insoluble form, thus any sulphide of sodium is oxidised to sulphate and this reacting with the lime forms sulphate of lime, which passes into the insoluble residue which is formed; any aluminate and silicate is similarly decomposed and insoluble alumina and silica thrown down.

When the causticising operation is completed, the calcium carbonate and insoluble impurities are allowed to settle out, and the clear caustic liquors are run into boiling pots to be boiled down to the solidifying point. The lime mud is not thrown away, but some fresh tank liquor is run in, and a new causticising operation carried out. The lime mud from this is treated with water and allowed to settle out. The liquors contain some alkali, and are used for dissolving some fresh balls, finally the lime is filtered from any liquor, and used in the black-ash furnaces.

The caustic liquors are first boiled down in wrought-iron pans or pots to a strength of about 34° Tw., then they are run into cast-iron pans, where the concentration is continued until a strength of from 70° to 80° Tw. is obtained. From these, after allowing any insoluble matter to settle out, the liquor is run into a cast-iron pot, in which it is concentrated down. When nearly finished, some nitre is added to oxidise any impurities, and so ensure their removal from the caustic. When nearly finished, the contents of the pot are tested for their alkalinity, and the working so arranged as to make the finished caustic of the required degree of strength.

The finished caustic is then run into wrought-iron drums in which it is allowed to solidify, and in which it is sold.

Commercial caustic soda is a creamy or white mass, having a slightly fibrous structure. It is very hygroscopic, readily absorbing water from the air and passing into a highly caustic liquor. It also readily absorbs carbonic acid from the air, passing into carbonate, so that it is not desirable that caustic soda should be exposed too much to the air.

It is sold as cream 60 per cent. caustic, white 60 per cent., 64 per cent., 74 per cent., and 77 per cent. These figures refer to the proportion of sodium oxide, Na_2O, contained in the caustic, irrespective of it being in the form of caustic or carbonate. The actual composition of various brands of caustic is shown in the following analyses:—

	Cream 60 per cent.	White 60 per cent.	White 70 per cent.	White 74 per cent.	77 per cent.
Sodium hydroxide	75·0	73·0	84·0	96·0	99·34
Sodium carbonate	3·1	1·5	4·2	0·2	—
Sodium chloride	6·8	19·0	6·0	1·3	·21
Sodium sulphate	1·5	5·5	5·1	1·5	·10
Sodium silicate	2·1	0·3	0·3	0·1	·05
Sodium aluminate	0·8	trace	trace	3·2	·30
Sodium sulphite	1·5				
Insoluble	0·2				
Water	9·0				

These may be taken to be fairly representative analyses of the various grades of caustic, from which it will be seen that the lower grades contain a large proportion of impurities. These have a material effect in soap-making. They pass into the lyes, being all soluble in water, and act by retarding the saponification of the oils and fats. This they do in virtue of soap being insoluble in solutions of alkaline salts, and so they tend to throw the soap out of solution as fast as it is formed, and this is just the opposite of what the soap-maker requires. To ensure perfect and rapid saponification, it is necessary that the soap as it is formed by the combination of the fat and alkali should pass into solution. It is therefore desirable to use as good a caustic soda as possible, and consequently better to purchase a 74 per cent. caustic than a 70 per cent., while in no case should a weaker caustic than 70 per cent. be used, although the writer knows that such is done by some soap-makers. The 77 per cent. caustic is not considered to make good soap by some soap-makers. The weaker caustics contain a variable proportion of carbonate, due to imperfect causticising. This carbonate has very little action, if any, in saponifying fats and oils, but it helps the other impurities in retarding the formation of soap. This effect of alkaline carbonates and salts will be discussed in full in another place in these pages.

It used to be the custom at one time for soap-makers to make their own caustic from soda ash, and many do so now, arguing that it is more economical for them to make their own than to buy it in the solid form, while the soap-maker has also to bear the expense of the labour attending its being dissolved into lye again. There can scarcely be any doubt that for a soap-maker to make his own caustic is cheaper than to buy it ready-made; on the other hand, and this is a consideration which weighs with some soap-makers, home-made caustic liquors are apt to be defective, either by containing undecomposed carbonate or by containing traces of lime which has been used in excess; then the residual lime carbonate sludge which is obtained is a source of anxiety and trouble to the soap-maker, who would often be at a loss how to get rid of it, while the caustic-maker can use it up again in some other branch of his business. It may, however, be worth while to describe the method somewhat in detail by means of which the soap-maker may, if he chooses, make his own caustic, and this description will apply equally well for either caustic soda or caustic potash.

First Method: Cold Process.—An iron tank is provided which may be made out of an old steam-boiler. On the bottom of this is placed a layer of 5 cwt. of fresh quicklime, and on this is poured sufficient water to slake it. Six cwt. of good soda ash are then evenly spread over the layer of lime. Above the soda is placed another layer of quicklime, and above this again another layer of soda. Water is now poured on, or weak lye from a previous treatment may be used, and the mass is allowed to stand for fifteen to sixteen hours, when all the lye which has been formed is run off from the bottom; this is generally known as first runnings. More water is now run on to the materials in the tank and again allowed to work for fifteen to sixteen hours, after which the lye is again run off, constituting second runnings; these will be weaker than the first. Afterwards a quantity of fresh water is run in, and after allowing it to stand the liquor is run off. This liquor is too weak to use for soap-making, and is used in place of water in making a new batch of lye. The residue in the tank is now thrown away. This method is rather faulty in many respects: the lye is apt to contain either unchanged carbonate of soda or some lime, and it is difficult to remedy these defects. The next process is preferable.

Second Method: Boiling Process.—As before, an iron tank is provided, which in this case is fitted with an open steam-pipe which is used to supply the necessary heat. Besides this, tanks are required for slaking the quick-lime and dissolving the alkali. Five cwt. of good soda ash are dissolved in 50 cwt. of water; 2½ cwt. of good quick-lime are slaked by adding sufficient water. When these materials are ready they are transferred to the boiling tank and heated by a current of steam for some hours, say from four to five. To see whether the operation has been properly done a small portion is taken out of the boiler, and the lime it contains allowed to settle out; to the clear liquor is added a little litmus, or better, methyl orange, and then sufficient hydrochloric acid to turn the colour red. Should no effervescence take place the operation has been properly done, and there is no carbonate present. Should there be effervescence, then sufficient lime has not been added in the first instance, and more should now be put in and the mixture again boiled for two hours, after which the settled lye can be again tested to see that no carbonate remains unchanged. The lye should also be tested for lime, which is done by taking a small portion of the clear lye and adding a solution of soda ash, when, if any lime be present, a white precipitate will fall down. In this event happening more soda ash should be added to the contents of the boiler, and the mass again boiled up. When the tests have shown that the lye does not contain either undecomposed carbonate of soda or lime, the mass is allowed to stand for the carbonate of lime which has been formed in the process to settle out. The clear liquor is drawn off into the lye tanks. The lime residue is then stirred up with clean water, and again allowed to settle. The clear liquor is drawn off and used for dissolving up fresh soda ash, while the lime mud is thrown away.

Third Method: Strunz Lye Apparatus.—Mr. S. M. Strunz has invented a very convenient form of apparatus for making caustic lye, which is shown in the accompanying drawing (fig. 1). Strunz's lye apparatus consists of two portions, one for making the caustic lye, the other for filtering the lime from the lye. In the top vessel, which is made boiler shape and provided with an open steam-pipe, are placed 800 lb. of soda ash. In the upper portion is a perforated iron plate on which lumps of quick-lime are placed. The boiler is now filled with water and steam turned on. The lime gradually slakes and dissolves, and passing downwards causticises the soda lye in the lower portion of the boiler. About 650 lb. of lime are stated to be required. After a few hours' boiling, the mass in the boiler is allowed

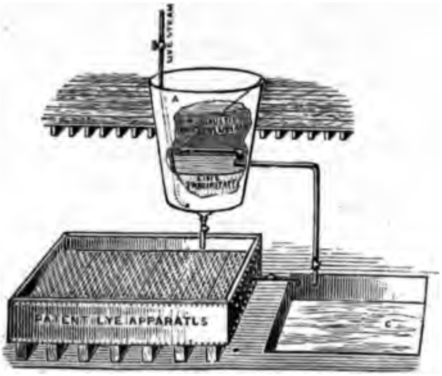


Fig. 1.—Caustic Lye Apparatus.

to settle; the clear solution of caustic soda is allowed to run out of the pipe, which is arranged at the side of the boiler for that purpose, into the lye store-tank. The residual lime, still containing some unseparated lye, is run into the lye apparatus below. This consists of a filtering material placed between perforated iron plates; the lye drains through them into the lye store-tank. The lime mud or refuse is thrown away. From the quantities of material given above it is possible to produce a solution of caustic-soda lye 25° Tw. strong, such as would be made from 600 lb. of 77 per cent. caustic soda.

It is not possible to make lyes of greater strength than 25° Tw., because the lime will not properly causticise such strong soda-ash liquors as must be used to make strong caustic lyes.

It should be borne in mind that the quality of caustic lyes made by any one of these processes is not only dependent upon the care with which the operation is carried out in the directions of ensuring perfect causticisation of the alkali used, but in preventing any excess of lime finding its way into the alkali lye which is made, but also on the quality of the soda ash used; the better the quality of this the purer will be the caustic made, inasmuch as the soluble impurities, salt, sulphate of soda, which are present in the low grades of soda ash, will find their way to a greater or less extent into the caustic lye which is made, although some of the sulphate which may be present in low-grade soda ashes will be causticised to some extent, but any chloride will not be affected in any way.

The commercial caustic soda is usually supplied in large drums, which require to be broken open before the caustic they contain can be dissolved. This caustic is dissolved in iron tanks with a suitable quantity of water; although there is not much difficulty in doing so, still there are a right and a wrong way of doing even this simple operation. The wrong way is to open the drums and throw the caustic to the bottom of the lye tank. Here it will become slightly acted upon by the water, and a strong lye will be formed, which will remain in contact with the solid caustic, and, becoming saturated, will prevent further solution; then again, the caustic will tend to set into a solid mass, which is difficult to deal with when at the bottom of a tank. The right way is to suspend the solid caustic at the top of the tank just underneath the surface of the water used to dissolve it; then the lye as it is formed, being heavier than the surrounding water, sinks to the bottom, so that the solid caustic is by reason of the currents thus set up always coming in contact with fresh water or unsaturated lye, and consequently soon becomes dissolved. This is carried out in some works by opening the drums at both ends and suspending them in the tanks by means of chains. A better method is, however, to have a perforated iron plate placed just under the surface of the water or liquor in the tanks. On this the drums may be placed, or the solid caustic may be broken out of the drums and thrown on to it (see fig. 2).

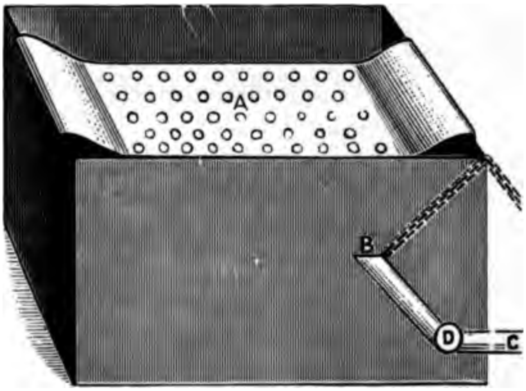


FIG. 2.—Lye Tank.

A tank is placed in a room or place above the soap-boiling kettles; part of this tank may be placed below the floor, but at least 18 in. should be above the floor; a swing syphon tube should be placed in the tank for the purpose of running off the lye. For this purpose a syphon tube has some advantages over a simple or fixed tap placed in the side of the tank. A grating should be fixed in the top of the tank just below the surface of the liquor contained in the tank; this grating may be placed on supports which extend from side to side of the tank. On this grating the drums of caustic which have had the ends knocked out are placed. The water penetrating into the drum gradually dissolves out the caustic, the solution, being heavier than the water, sinks to the bottom of the tank, a constant circulation of fresh water or weak liquor passing through the drum becoming stronger in so doing, which then goes down to the bottom of the tank. This goes on until all the caustic in the tank is dissolved. This method of working means less labour in the handling of the caustic, which is of some advantage; there is no undissolved caustic formed at the bottom of the tank, while the operation is done somewhat quicker.

From the solid caustic, soda lyes of any strength may be made. It should be remembered that the solution of solid-caustic soda in water is attended by the evolution of some considerable amount of heat, which may be utilised by running the fresh and still warm caustic lyes into the soap-boilers.

Caustic-soda lyes should not be kept too long exposed to the atmosphere, as they tend to absorb carbonic acid and pass into carbonate of soda, the alkaline or soap-making strength being thereby reduced. Should it be necessary at any time to keep lyes a considerable time before using they may be preserved by pouring on their surface some melted paraffin wax, which setting on cooling prevents any air from getting to the lyes. In this manner they may be kept for some time. The paraffin wax can be used many times.

The following table of the specific gravities of solutions of caustic soda will be of service to soap-makers:—

Degrees Twaddell.	Specific gravity.	Per cent. by weight of		Lb. of actual $NaOH$ contained in 1 gallon of lye made from commercial caustic of		
		Na_2O.	$NaOH$.	77 per cent.	74 per cent.	70 per cent.
1	1·005	0·368	0·474	0·048	0·046	0·043
2	1·010	0·742	0·957	0·097	0·092	0·087
3	1·015	1·114	1·436	0·146	0·131	0·129
4	1·020	1·480	1·909	0·194	0·185	0·180
5	1·025	1·834	2·365	0·243	0·231	0·219
6	1·030	2·194	2·830	0·291	0·278	0·262
7	1·035	2·521	3·252	0·335	0·320	0·303
8	1·040	2·964	3·746	0·389	0·371	0·350
9	1·045	3·244	4·184	0·438	0·417	0·393
10	1·050	3·590	4·631	0·486	0·461	0·438
11	1·055	3·943	5·086	0·536	0·510	0·483
12	1·060	4·292	5·536	0·586	0·558	0·528
13	1·065	4·638	5·982	0·636	0·607	0·573
14	1·070	4·972	6·413	0·680	0·653	0·617
15	1·075	5·311	6·911	0·742	0·707	0·668
16	1·080	5·648	7·285	0·786	0·749	0·709
17	1·085	5·981	7·715	0·836	0·798	0·755
18	1·090	6·311	8·140	0·886	0·845	0·800
19	1·095	6·639	8·564	0·937	0·894	0·846
20	1·100	6·954	8·970	0·986	0·941	0·890
21	1·105	7·276	9·386	1·037	0·989	0·938
22	1·110	7·594	9·796	1·087	1·037	0·981
23	1·115	7·910	10·203	1·137	1·123	1·026
24	1·120	8·223	10·607	1·187	1·175	1·071
25	1·125	8·533	11·107	1·238	1·181	1·117
26	1·130	8·893	11·471	1·296	1·237	1·170
27	1·135	9·251	11·933	1·354	1·292	1·222
28	1·140	9·614	12·401	1·413	1·350	1·277
29	1·145	9·965	12·844	1·470	1·413	1·337
30	1·150	10·313	13·303	1·529	1·460	1·381
31	1·155	10·666	13·859	1·600	1·528	1·445
32	1·160	11·008	14·190	1·646	1·541	1·456
33	1·165	11·347	14·637	1·705	1·627	1·539
34	1·170	11·691	15·081	1·764	1·684	1·593
35	1·175	12·025	15·512	1·822	1·739	1·645
36	1·180	12·356	16·139	1·904	1·817	1·719
37	1·185	12·692	16·372	1·942	1·853	1·753
38	1·190	13·016	16·794	1·998	1·887	1·804
39	1·195	13·339	17·203	2·055	1·962	1·856
40	1·200	13·660	17·629	2·122	2·026	1·916
41	1·205	14·058	18·133	2·185	2·085	1·973
42	1·210	14·438	18·618	2·252	2·147	2·033
43	1·215	14·823	19·121	2·323	2·221	2·097
44	1·220	15·124	19·613	2·392	2·280	2·161
45	1·225	15·502	19·997	2·444	2·338	2·206
46	1·230	15·959	20·586	2·562	2·417	2·285
47	1·235	16·299	20·996	2·593	2·475	2·341
48	1·240	16·692	21·532	2·669	2·548	2·410

Degrees Twaddell.	Specific gravity.	Per cent. by weight of		Lb. of actual NaOH contained in 1 gallon of lye made from commercial caustic of		
		Na_2O.	NaOH.	77 per cent.	74 per cent.	70 per cent.
49	1·245	17·060	22·008	2·739	2·615	2·474
50	1·250	17·424	22·476	2·809	2·681	2·536
51	1·255	17·800	22·962	2·881	2·750	2·602
52	1·260	18·166	23·433	2·952	2·818	2·666
53	1·265	18·529	23·901	3·020	2·886	2·730
54	1·270	18·897	24·376	3·095	2·955	2·795
55	1·275	19·255	24·858	3·171	3·027	2·863
56	1·280	19·609	25·295	3·237	3·090	2·932
57	1·285	19·961	25·750	3·308	3·158	2·988
58	1·290	20·318	26·210	3·381	3·227	3·053
59	1·295	20·655	26·658	3·452	3·364	3·117
60	1·300	21·156	27·110	3·524	3·394	3·182
61	1·305	21·405	27·611	3·603	3·439	3·253
62	1·310	21·785	28·105	3·682	3·514	3·224
63	1·315	22·168	28·595	3·760	3·593	3·395
64	1·320	22·556	29·161	3·849	3·674	4·475
65	1·325	22·926	29·574	3·919	3·742	3·539
66	1·330	23·310	30·058	3·997	3·816	3·610
67	1·335	23·670	30·535	4·072	3·891	3·681
68	1·340	24·046	31·018	4·156	3·967	3·754
69	1·345	24·410	31·490	4·232	4·042	3·824
70	1·350	24·765	31·948	4·312	4·116	3·894
71	1·355	25·152	32·446	4·396	4·196	3·970
72	1·360	25·526	32·930	4·478	4·274	4·043
73	1·365	25·901	33·415	4·561	4·354	4·109
74	1·370	26·285	33·905	4·645	4·434	4·194
75	1·375	26·650	34·382	4·728	4·513	4·269
76	1·380	27·021	34·855	4·810	4·592	4·344
77	1·385	27·385	35·328	4·893	4·670	4·418
78	1·390	27·745	35·795	4·975	4·794	4·493
79	1·395	28·110	36·258	5·058	4·828	4·567
80	1·400	28·465	36·720	5·141	4·907	4·642
81	1·405	28·836	37·203	5·227	4·989	4·720
82	1·410	29·203	37·674	5·312	5·071	4·797
83	1·415	29·570	38·146	5·397	5·135	4·873
84	1·420	29·930	38·610	5·482	5·233	4·950
85	1·425	30·285	39·071	5·567	5·314	5·027
86	1·430	30·645	39·530	5·653	5·396	5·104
87	1·435	30·995	39·986	5·738	5·467	5·181
88	1·440	31·349	40·435	5·823	5·558	5·258
89	1·445	31·700	40·882	5·908	5·640	5·335
90	1·450	32·043	41·335	5·923	5·721	5·412
91	1·455	32·460	41·875	6·093	5·816	5·502
92	1·460	32·870	42·400	6·191	5·909	5·680
93	1·465	33·283	42·935	6·290	6·004	5·679
94	1·470	33·695	43·467	6·389	6·009	5·769
95	1·475	34·092	43·980	6·487	6·193	5·856
96	1·480	34·500	44·505	6·586	6·287	5·948
97	1·485	34·899	45·013	6·685	6·381	6·035
98	1·490	35·245	45·530	6·784	6·476	6·126
99	1·495	35·691	46·041	6·884	6·571	6·216
100	1·500	36·081	46·545	6·982	6·665	6·303

The figures in this table have been most carefully calculated, and it is believed that they are accurate, at all events sufficiently so for all technical purposes. The figures in the last three columns giving the quantities of actual caustic in one gallon of lye are new; those for 74 per cent. and 70 per cent. caustics are based on the assumption that the impurities in such caustic have as much influence in raising the specific gravity of the lye as the actual caustic itself has, whereas, as a matter of fact, they have sometimes less influence, and sometimes more so; that the actual strength of the lye in contents of actual caustic depends upon the character of the impurities present, which will vary from time to time, still the figures given may be accepted as sufficiently correct for technical work. By knowing the strength of the commercial caustic he is using and the gravity of his lyes, the soap-maker from this table will be able to calculate the weight of actual caustic he may have in any given quantity of lye, and thus having a given quantity of fat, and knowing how much caustic this will require, he will be able to add just the right amount of lye to saponify the fat.

Solutions of caustic soda have a somewhat soapy feel; they react very strongly on the skin, dissolving it. They dissolve wool and animal tissues rapidly, and react upon cotton, making it become more transparent and causing it to swell. They are powerfully basic, and capable of neutralising the strongest acids, the sodium salts which are formed being characterised by their solubility in water; with oils and fats it reacts very strongly.

The following table gives the proportion of caustic soda required to saponify the various oils and fats commonly used in soap-making:—

Oil.	Per cent. of NaOH to saponify
Olive Oil	13·56 to 13·91.
Almond Oil	13·82 to 13·92.
Ground-nut Oil	13·56 to 13·93.
Sesame Oil	13·49 to 13·66.
Cotton Oil	13·56 to 13·92.
Linseed Oil	13·30 to 13·85.
Whale Oil	13·38 to 15·92.
Coco-nut Oil	17·48 to 19·05.
Palm-nut Oil	15·62 to 17·51.
Tallow	13·70 to 14·05.
Palm Oil	13·92 to 14·44.
Castor Oil	12·49 to 12·88.
Rosin	12·07 to 13·66.

POTASSIUM.

The second alkali metal much used in soap-making is potassium. This resembles sodium in many respects. It is a silver-white metal, very soft, lighter than water, having a specific gravity of 0·865. It melts at 62·5° C., and at a red heat can be volatilised, its vapour having a green colour. Exposed to the air it rapidly oxidises to the monoxide; thrown on water it rapidly decomposes it with the evolution of hydrogen and the formation of potassium hydroxide (caustic potash); the energy evolved in the reaction being sufficiently great to cause the hydrogen to burn. It is more energetic in its action than sodium. With one or two exceptions, *e.g.*, the platino-chloride, acid tartrate, all its salts are readily soluble in water, while none are absolutely insoluble. It was discovered by Sir Humphrey Davy in 1807 by the action of a powerful electric currrent on fused potassium hydroxide.

Potassium occurs very abundantly and very widely distributed in nature. It is found in sea-water, in marine plants, in plants of all kinds, from whose ashes potassium in the form of carbonate is largely obtained; it occurs combined with alumina and silicate in various natural silicates, and in the form of chloride associated with common salt, magnesium chloride, in various localities; it is also found as nitrate as an efflorescence on the soil in hot countries.

To potassium is assigned the symbol K, that being the first letter of the Latin name kalium, the Arabic term being kali. Its atomic weight is 39·1.

Two of its compounds are of special interest to the soapmaker, *viz.*, the carbonate and the hydroxide or caustic potash.

Potash, potassium carbonate.—This very important compound has the composition shown by the formula K_2CO_3. Its original source was the ashes of plants, but it is made also from the various deposits of potassium chloride found at Stassfurt and Stanislaus by a process analogous to that of the Leblanc soda process.

Trees and other vegetables have the property of absorbing potassium compounds from the soil in fairly large proportion, and as this is left behind in the ash when the trees, etc., are burnt, the ashes of wood have for a long period been used as a source of potash. The following table compiled from several sources shows the percentage of ash and that of potash yielded by various woods:—

Tree.	Ash per cent.	Potash per cent.
Ash	1·22	0·074
Beech	0·58	0·127
Box	—	0·226
Bean Stalks	—	2·000
Elm	2·55	0·390
Ferns	3·64	0·425
Oak	1·35	0·150
Pine	0·34	0·045
Vine	3·40	0·550
Willow	2·80	0·285

The manufacture of potash from wood is a considerable industry in Canada and America, from which countries Great Britain derives its principal supply.

The method of manufacture is comparatively simple.

The trees are split or cut up into logs of convenient size and burnt, the ashes are collected and thrown into a tank fitted with a false bottom, and a little water containing a little slaked lime is put into the tank. The carbonate and hydroxide in the ashes are freely soluble in the water and are dissolved out, while any sulphate, chloride, or other neutral salt is partially converted into hydroxide by the lime and partially left insoluble in the residue of the ashes, insufficient water being used to dissolve them along with the two products desired. The liquors when saturated are drawn off, run into iron pots, and then evaporated to dryness, when greyish-pink masses are left behind; these constitute "pot ashes". It is owing to this method of manufacture that this body owes its name of potash.

In this article, whenever potash is named it will have reference to the carbonate of potassium, while the hydroxide may be referred to as caustic potash, but never as "potash". The potashes are graded by inspectors into "firsts," "seconds," "thirds," and "unbrandables".

From the potashes "pearlash" is made by calcining in a reverberatory furnace; the small amount of carbonaceous matter in the potashes is burnt off, the hydroxide converted into carbonate, any sulphide, sulphite, thiosulphate present being converted into sulphate. The calcined mass is then lixiviated with a small quantity of water, the solution is then evaporated down to dryness, and by agitation during solidification the product is obtained in granular masses of a white colour and forms the pearlash of commerce. The process of manufacture thus briefly sketched is the one followed in most localities.

The composition of "potashes" and "pearlash" is very variable. Although the main constituent is the carbonate, yet there are also present hydroxide, sulphate, chloride, silicate, aluminate, small quantities of insoluble matter, sodium salts, etc. Potash is also obtained from beetroot molasses, the ashes from which contain 45 to 50 per cent. of potash. A small quantity is made from suint, the natural grease of wool. A large quantity is made from the sulphate and chloride of potassium by a modification of the Leblanc soda process. The sulphate is first prepared, then this is furnaced with limestone and coal, the resulting ash is lixiviated with water, the liquors are then evaporated down to obtain the potash. This process gives potash of a high degree of purity, and such potash is likely to supersede that from wood ashes owing to its greater purity and lower cost.

The following table shows the composition of various commercial qualities of potash, compiled from the published analyses of Tatlock and other chemists :—

	Montreal.	Firsts.	Seconds.	Thirds.	Pearlash.
Potassium carbonate . .	43·87	26·16	38·53	46·31	77·50
Potassium hydroxide . .	36·50	50·03	30·63	6·14	—
Potassium sulphate . .	10·40	15·32	18·92	20·53	11·65
Potassium chloride . .	2·43	3·38	6·13	7·63	2·65
Sodium carbonate . .	—	—	—	—	2·86
Sodium hydroxide . .	2·02	2·44	5·01	10·48	—
Soluble silica, alumina .	—	—	—	—	—
Insoluble	1·00	0·92	0·54	8·77	0·26
Water	3·75	1·83	trace	—	4·88

	French.	Beetroot.	Potash.	Suint Potash.	Leblanc	Potash.
Potassium carbonate	38·63	92·68	90·25	89·41	92·19	78·24
Potassium hydroxide	—	—	—	—	—	—
Potassium sulphate	38·84	·43	3·81	·17	3·94	·30
Potassium chloride	9·16	2·45	2·92	1·67	1·49	2·06
Sodium carbonate	4·17	3·98	2·52	3·83	1·43	3·44
Sodium hydroxide	—	—	—	—	—	—
Soluble silica, alumina	1·20	—	—	—	·13	—
Insoluble	2·66	·06	·21	·06	·15	·03
Water	5·34	·50	·45	4·70	·80	15·85

The above analyses will suffice to show the average composition of commercial potashes. They are sold on a basis of containing so much per cent. of actual carbonate, the standard being 90 per cent. of carbonate, a standard which is only obtainable in the best pearlashes.

Carbonate of potassium is freely soluble in water, 100 parts of which at 0° C. dissolve 83·12 parts; at 10° C. 88·72 parts; at 30° C. 109 parts; at 50° C. 112·9 parts; at 80° C· 134·25 parts, and at 100° C. 153·6 parts.

CAUSTIC POTASH.

This important potassium compound has the formula KOH. As far as its main properties are concerned, it closely resembles the corresponding sodium compound; it is, however, slightly more hygroscopic and shows greater affinity for the carbonic acid of the atmosphere. It is rather stronger or more caustic in its action on various bodies, a property due chiefly to the greater affinity of potassium for acids and other bodies.

It is a white, solid body, of an amorphous character, and having a specific gravity of 2·10. At a little below red heat it melts to an oily-looking liquid, which has a most powerful action on all animal and vegetable tissues. It dissolves easily in water, the solution being accompanied with the evolution of considerable heat, and it absorbs water on exposure to the atmosphere. The aqueous solution possesses strongly alkaline and caustic properties, and when of a moderate degree of concentration such solution has a solvent action on animal tissues. It is also capable of neutralising the strongest acids known, forming the potassium salts, all of which are soluble in water; a few may be obtained in the form of precipitates from very strong solutions of potash, owing to their slight solubility.

Exposed to the air caustic potash solutions rapidly absorb carbonic acid, passing first into the carbonate, ultimately into the bicarbonate; on this account it is desirable to expose potash lyes as little as possible to the air. Aqueous solutions precipitate the metal as hydroxide from solutions of some metallic salts such as ferrous and ferric chlorides, copper chloride, magnesium sulphate, aluminium sulphate, etc.

Potassium hydroxide is also soluble in alcohol, methyl alcohol, glycerine, and some other solvents.

Caustic potash is made by processes similar to those employed in preparing caustic soda, and although it may be purchased from the alkali-maker, soap-makers are still in the habit of preparing it themselves. The same methods of working as described under caustic soda may be used and need no further description here. Weight for weight potash takes less lime to causticise it than soda, the proportions being as 69 to 53. It is best to allow from 50 to 53 lb. of quick-lime to every hundredweight of potash.

Care should be taken in making that all the potash has been causticised, as will be shown by the acid test, and also that no excess of lime be used. These defects may be cured by using more lime, or the addition of more potash, as the case may be.

Convenient strengths of caustic potash lyes to make are 15°, 22°, 30°, or 40° Tw., which contain approximately 1 lb., 1¼ lb., 1¾ lb., and 2 lb. actual caustic potash per gallon. See table.

When caustic potash lyes are boiled down until they are in a state of quiet fusion, and then allowed to cool, solid caustic potash is obtained. Usually three qualities are made. The best contains from 80 to 85 per cent. of actual potassium hydroxide, the medium from 75 to 80 per cent., and the lowest from 70 to 75 per cent. The following analyses show the constituents usually found in commercial caustic potash :—

	No. 1.	No. 2.
Potassium hydroxide	77·64	75·64
Potassium carbonate	4·62	2·54
Potassium sulphate	·38	.21
Potassium chloride	2·29	·93
Potassium nitrite	·87	—
Sodium hydroxide	4·67	2·59
Soluble silica and alumina	·30	·20
Insoluble matter	·02	·22
Water	8·84	17·80

from which it will be seen that commercial caustic potashes are not of so pure a character as the commercial caustic sodas.

Several tables have been published by Dalton, Lunnerman and Richter, of the strength of aqueous caustic potash lyes. These tables are not very concordant, and good service would be rendered to technical chemistry by some college professor of chemistry setting his students to work to solve this problem. The following table is based on the one given by Dalton, which is probably as accurate as any of them :—

TABLE OF STRENGTH OF CAUSTIC POTASH SOLUTIONS AT 60° F.

Specific gravity.	Degrees Twaddell	Per cent. KOH.	Pounds of KOH per gal.
1·060	12	5·59	0·59
1·110	22	11·31	1·25
1·150	30	15·48	1·77
1·190	38	19·29	2·21
1·230	46	23·22	2·84
1·280	56	27·87	3·56
1·330	66	31·32	4·16
1·360	72	35·01	4·76
1·390	78	38·59	5·36
1·420	84	40·97	5·81
1·440	88	43·83	6·31
1·470	94	47·16	6·93
1·520	104	51·09	7·76
1·600	112	55·62	8·89
1·680	136	60·98	10·24
1·780	156	67·65	12·04
1·880	176	75·74	14·23
2·000	200	86·22	17·24

Caustic potash is used in soap-making only for making soft soaps. It acts upon and saponifies oils and fats much more readily than does caustic soda, and the soaps so produced are more freely soluble in water and have hygroscopic properties. One hundred parts of dry potassium oleate will absorb 162 parts of water from the air; the same quantity of potassium palmitate will take up 35 parts of water, while sodium stearate only absorbs 7½ per cent. of water.

Hard potash soaps are not manufactured in practice, although they can be made, as will be described farther on.

The combining equivalent of potassium hydroxide, KOH, being higher (56) than is that of sodium hydroxide, NaOH (40), oils require a larger proportion by weight of caustic potash than they do of caustic soda to saponify them ; on the other hand a proportionately greater weight of soap is yielded. Generally oils take from 18·5 to 20 per cent. of pure caustic potash to saponify them; some take a little more, others a little less. The following table gives the percentage of actual KOH required to saponify the oils commonly used with caustic potash to make soft soaps, although a few others have been added to make the table complete. These percentages correspond with the Koettstorfer numbers obtained in the testing of oils :—

Oil.	Per cent. of KOH.
Olive oil	19·1 to 19·6
Almond oil	19·47 to 19·61
Ground-nut oil	19·13 to 19·66
Sesame oil	19 to 19·24
Cotton oil	19·1 to 19·66
Linseed oil	18·74 to 19·52
Whale oil	18·85 to 22·44
Coco-nut oil	24·62 to 26·84
Palm-nut oil	22 to 24·76
Tallow	19·32 to 19·8
Palm oil	19·63 to 20·35
Castor oil	17·6 to 18·15
Rosin	17 to 19·3

ALKALIMETRY.

Alkalimetry is the art of determining the value of the alkaline bodies which have been described above, the carbonates and hydroxides of potassium and sodium.

As usually carried out the process depends upon the fact that when any of the alkalative compounds in question are brought into contact with sulphuric acid combination takes place, sulphates of the alkali metals being formed according to the following equations:—

$$\underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} + \underset{\substack{\text{Potassium}\\\text{hydroxide}}}{2\ KOH} = \underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + 2H_2O$$

$$H_2SO_4 + \underset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} = K_2SO_4 + CO_2 + H_2O$$

$$H_2SO_4 + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH} = \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + 2H_2O$$

$$H_2SO_4 + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} = Na_2SO_4 + CO_2 + H_2O$$

which show the action of the acid on the four alkaline compounds which are of importance in soap-making.

From these equations it is seen that one molecular proportion 98 parts by weight of sulphuric acid is equal to two molecular proportions 112 parts by weight of potassium hydroxide, or to one molecular proportion 138 parts by weight of potassium carbonate, or to two molecular proportions 80 parts by weight of sodium hydroxide, or to one molecular proportion 106 parts by weight of sodium carbonate.

Taking one molecular or one equivalent proportion, 40 parts by weight, of sodium hydroxide as a standard, then

49 of sulphuric acid = 56 of potassium hydroxide.
" " = 69 of potassium carbonate.
" " = 40 of sodium hydroxide.
" " = 53 of sodium carbonate.

Knowing then the proportions in which sulphuric acid and the alkalies react with one another, it follows that to ascertain the quantity of actual alkali in a commercial sample, it suffices to ascertain the quantity of acid required to neutralise a known weight of the alkaline body. This is most easily and simply done by the use of a solution of sulphuric acid of known strength to a solution of the alkali until neutrality is attained. The latter point is readily ascertained by making use of certain bodies which are altered in colour according as they are in the presence of alkalies or acids; some of these bodies are excessively sensitive, and will readily show the presence of the minutest trace of either acid or alkali. These indicators, as they are called, will be dealt with in detail shortly.

This system of analysis is known as volumetric analysis, because its essential feature is the measurement of the volume of certain solutions of known strength.

These solutions are called standard solutions, and may be made of any strength, but there has grown up with the development of volumetric analysis a system of making the various standard solutions of recognised strengths, what are called normal solutions; these are supposed to contain an equivalent weight in grammes in each litre or 1000 cubic centimetres of the reagent. Thus normal sulphuric acid contains 49 grammes actual H_2SO_4 per litre. Normal sodium hydroxide contains 40 grammes actual NaOH per litre. Normal sodium carbonate 53 grammes actual Na_2CO_3 per litre. Normal potassium hydroxide 56 grammes per litre of actual KOH. Normal potassium carbonate 69 grammes of actual K_2CO_3 per litre, and so on with other reagents. It therefore follows that 1 c.c. of any one of these normal standard solutions is equal to 1 c.c. of any other.

For the purpose of measuring the volume of the standard solutions there are used measuring glasses known as burettes, of which the best form is that known as Mohr's, with a stopcock, and one or two should be provided; the best size is one to hold 50 c.c. and graduated in tenths of a c.c. These are supported in suitable stands, and the volume of liquid in them is noted where the bottom of the meniscus of the upper surface of the fluid appears to be adjacent to a mark on the burette. This is done before and after using the solution, and the difference between the figures gives the volume or number of c.c.'s of solution used. To facilitate the reading of the burette, small glass floats—Erdmann's floats—may be used; a line round these comes up close to the sides of the burette, and the reading is much easier and more accurately made.

Besides the burette there are used in volumetric analysis pipettes for measuring off definite volumes of liquids and flasks marked to hold a definite quantity of liquid when filled up to certain marks on the neck.

The standard solution most in use in alkalimetry is one of sulphuric acid of normal strength, that is 1000 c.c.'s of it contain 49 grammes of pure H_2SO_4. It can be bought from all dealers in analytical chemicals, ready prepared ; that is a convenient but most expensive manner of procuring it. The best and cheapest plan is to make it for one's own use.

To do this, procure a supply of pure bicarbonate of soda or pure carbonate of soda ; place a quantity in a crucible and heat to redness, allow to cool in a desiccator, weigh out exactly 53 grammes of the dried carbonate, dissolve in water, place the solution in a litre-measuring flask and fill up to the mark with water. There will be now prepared a normal standard solution of sodium carbonate, each c.c. of which contains 0·053 gramme of Na_2CO_3 and is equal to 0·049 H_2SO_4.

Measure out 55 c.c.'s of pure strong sulphuric acid and dissolve in two litres of water. This solution will be a little stronger than normal strength, but much depends upon the actual strength of the acid used.

Place the sulphuric-acid solution which has been made in a burette, and note the reading. Then measure with a pipette 10 c.c.'s of the normal soda solution into a beaker, add a few drops of methyl-orange solution, then turning on the tap of the burette, allow the acid to drop into the soda solution, constantly stirring the latter. When the colour of the soda solution changes from yellow to red, the operation, or titration as it is called, is finished. If the acid solution is of the right strength 10 c.c.'s of it ought to have been used. If less is required it is too strong; if more, it is too weak. From the quantity of acid solution required, make a calculation as to how much water or how much acid is required to bring it up to the right strength. Then test it again, and, if necessary, again, with 10 c.c.'s of the soda solution, and add water or acid as required until you have prepared a standard acid solution, 10 c.c.'s of which will just neutralise 10 c.c.'s of the soda solution. The acid solution will then be of normal strength and will contain 49 grammes of actual H_2SO_4 per litre.

The methyl orange which has been directed to be added to the soda solution is what is termed an indicator; it is very sensitive to acids, the merest trace of which turns it pink.

It may be convenient here, before proceeding to describe fully the various alkalimetrical processes, to briefly note the various indicators which are used in this branch of chemical analysis.

One of the oldest indicators is litmus. This body forms a violet blue solution, which turns red on the addition of acids, while alkalies change the shade a little bluer. It is a good indicator to use when testing alkaline liquors with acid; it has, however, one drawback when using it in the testing of alkaline carbonates, and that is the carbonic acid which is evolved from the carbonates by the action of the standard acid, and which tends, by its solubility in water, to remain in solution in the liquid, has the property of turning the litmus red, and consequently there is a tendency to obtain too low results when testing carbonates with litmus. This trouble can only be got over by boiling the solutions before titrating, so as to prevent the carbonic acid from becoming dissolved in the solution. This boiling is rather objectionable and inconvenient, although excellent results are obtained when it is resorted to.

Litmus is, however, being rapidly replaced by methyl orange. Methyl orange is one of the coal-tar azo-oranges; it dissolves freely in water, forming an orange solution, which is turned yellow by alkalies, and red by the merest presence of acids such as sulphuric, nitric, hydrochloric, acetic, oxalic acids, but not with carbonic and some weak organic acids. This want of sensitiveness to carbonic acid enables it to be used in the analysis of alkaline carbonates in cold solutions, which are more convenient to work with than hot solutions.

Phenol phthalein is a preparation of phenol and phthalic acid; it is a yellowish powder insoluble in water, but soluble in alcohol or methylated spirits to a colourless solution. It has the property of producing an intense red colour with the caustic alkalies, and a weaker red with the alkaline carbonates. Its sensitiveness is great; it can be used with advantage in the testing of acids with standard solutions of sodium or potassium hydroxide, the merest excess of the latter producing a pink coloration, or it may be used in the testing of pure potassium or sodium hydroxides (caustic alkalies) with standard acid. It does not work well with the alkaline carbonates, it shows the normal carbonates to be alkaline, but the acid carbonates are neutral to it. It does not work well in ammonia. A weak solution in methylated spirit is used in analysis.

Lacmoid is a preparation of resorcin, and behaves like litmus, over which it has the advantage of being a little more sensitive to acids.

There are other indicators which may be used, but the above are sufficient for all purposes in alkalimetry. Methyl orange is the indicator which the author prefers to use.

The operation of testing the alkaline carbonates and hydroxides is practically alike for all, so that one description will suffice.

Testing Sodium or Potassium Carbonate.—Weigh out five grammes of the alkali, transfer to a 250 c.c. measuring flask, fill this up to the containing mark with water. It is not advisable to heat, as the volume of the liquid may thereby be affected, for although it might measure 250 c.c. when made, it will measure less on becoming cold, due to the contraction in volume that will occur, and then the results will not come out right. All volumetric apparatus is understood to be correct at a uniform temperature of 60° F., which is not the best; 70° F. is much more nearly the average working temperature of a laboratory, and is much easier to obtain in practice.

Fill the burette with the normal sulphuric acid, measure by a pipette 25 c.c.'s of the alkali solution into a beaker, add a little methyl-orange solution, just enough to give a faint yellow tint to the liquid, then drop in (titrate) from the burette the acid until the colour of the liquid changes from yellow to pink. To be able to observe the colour change more quickly, it is best to place a white tile or plate under the beaker, and to carry out the work in a good light. Methyl orange does not work well in gaslight, the change is not so easily perceptible; when working by gaslight it is best to use litmus or lacmoid, then the alkali solution must be boiled previous to titrating. Note the number of c.c.'s of acid used.

Repeat the test two or three times; the various readings should not differ more than 0·05 c.c. from one another. If an Erdmann's float is not used, a sheet of white paper held behind the burette enables the readings to be more easily taken.

Having ascertained the number of c.c.'s of acid used, these can be calculated to the equivalent of alkali by multiplying by 0·053 if sodium carbonate is taken, or by 0·069 if potassium carbonate is being tested; this gives the weight in grammes of the alkali in the quantity taken for titration, and from the figures obtained the percentage can be calculated.

Testing Sodium or Potassium Hydroxide (Caustic Soda or Caustic Potash).—The process is exactly identical with the above. In calculating the results, the factors 0·04 for caustic soda and 0·056 for caustic potash are made use of.

Caustic Soda Ash or Commercial Caustic Soda.—These articles are rarely pure; soda ash is or should be sodium carbonate, but it invariably contains some caustic soda. Then commercial caustics, especially the lower grades, invariably contain some carbonate in addition to the caustic. In the case of the caustic alkalies it is advisable that when used in soap-making they should contain as little carbonate as possible. Since this takes very little, if any, part in the actual process of saponifying the fats, it is therefore frequently necessary to examine samples of soda ash for the presence and amount of hydroxide, and caustic for the presence and amount of carbonate. The method is the same in both cases.

Five grammes are weighed out and dissolved in 250 c.c.'s of a neutral solution of barium chloride; this gives a precipitate of barium carbonate; the volume of the mixture is made up to 100 c.c.'s, then it is filtered as rapidly as possible. Fifty c.c.'s of the filtrate, which equal 25 c.c. of the original solution, are taken and titrated as before. This titration gives the alkali present as caustic (hydroxide). The difference in the amounts of normal acid used in the two titrations represents the amount of carbonate in the sample. To make the calculations the c.c.'s of acid used in the two titrations are multiplied by 0·053 when caustic soda or soda ashes are being tested, or by 0·069 when caustic potash or potashes are being tested.

It is customary in the alkali trade to represent the strength of soda not by the percentage of actual carbonate or hydroxide they may contain, but by the percentage of sodium oxide, Na_2O, they contain. There is no difference in the mode of testing, but when the amount of sodium oxide only is required the factor for multiplying the acid is 0·031.

The amount of sodium oxide so calculated may be expressed as "total alkali," "alkali as carbonate," or "alkali as caustic". The same can be done with the potash compounds, the factor in that case being 0·047.

In alkali works it is customary to adopt a method of working the tests by means of which the reading of the number of c.c.'s of normal acid used gives at once the percentage of alkali present. This is done by weighing out 3·1 grammes of the alkali, dissolving in 250 c.c.'s water, titrating with the alkali as before; the number of c.c.'s used multiplied by 10 gives at once the percentage of Na_2O present. This saves a good deal of time by avoiding the trouble of making elaborate calculations.

In the case of potashes, 6·9 grammes should be weighed out, when the percentage of carbonate, K_2CO_3, is given at once by the acid.

The following table of factors may be found useful for reference in alkalimetry:—

1 c.c. normal sulphuric acid contains	0·049	grm.	H_2SO_4.
,, ,, ,, ,, equals	0·031	,,	Na_2O.
,, ,, ,, ,, ,,	0·040	,,	NaOH.
,, ,, ,, ,, ,,	0·053	,,	Na_2CO_3.
,, ,, ,, ,, ,,	0·047	,,	K_2O.
,, ,, ,, ,, ,,	0·056	,,	KOH.
,, ,, ,, ,, ,,	0·069	,,	K_2CO_3.
,, ,, sodium carbonate contains	0·053	,,	Na_2CO_3.
,, ,, sodium hydroxide ,,	0·040	,,	NaOH.
,, ,, potassium hydroxide ,,	0·056	,,	KOH.
,, ,, sodium carbonate equals	0·049	,,	H_3SO_2.
,, ,, sodium hydroxide ,,	0·049	,,	H_2SO_4.

BORAX.

This salt has from time to time been added to soaps of various qualities for the purpose of increasing their detergent properties; borax is a borate of sodium, having the formula $Na_2B_4O_210H_2O$, and occurs in fine crystals containing 47 per cent. of water. It occurs naturally in various forms, and from this natural borax or tincal the commercial article is now largely manufactured. In Tuscany boracic acid is found, and from this borax is made by combining it with soda. Borax crystals are rather efflorescent, are soluble in about half their weight of boiling water and about 12 parts of cold water; it has a feebly alkaline taste and reaction when hydrochloric acid is added to strong boiling solutions of borax; on cooling boracic acid crystallises out. It is owing to the feebly alkaline properties of borax that it is used in soap-making.

PHOSPHATE OF SODA.

This substance is often added to soaps with a view also of increasing its detergent properties; it has the composition shown in the formula $Na_2HPO_412H_2O$ and forms large transparent, somewhat efflorescent crystals, soluble in about four parts of cold water, and in boiling water to an unlimited extent, the solution having a faint alkaline reaction.

SODIUM AND POTASSIUM SILICATES.

The use of the silicates of potassium and sodium or, as they are frequently called, water glass or soluble glass, on account of their glassy appearance when in the solid state, and being soluble in water, was suggested by Sheridan in 1838, since which time they have been largely used by soap-makers in the preparation of the cheaper qualities of soaps. The soap-maker also knows these products by the name of "runnings".

They are made by fusing sand or powdered quartz of good quality with potash or with soda ash, according as either silicate of potash or silicate of soda is required; the operation being conducted at a high temperature in a suitable furnace. They may be made by heating sand with aqueous solution of the alkalies. The silicate of soda is by far the more important of the two bodies.

Silicate of soda is offered to soap-makers in two forms, solid and liquid.

Solid silicate of soda occurs in the form of glassy-looking masses of a brownish or greenish colour. This colour is due to metallic impurities, usually iron, which are present in the sand from which the product is made. It is brittle, breaking with a conchoidal fracture, and closely resembles glass in appearance, and it is this body that is generally understood when soluble glass or water glass is spoken of.

The liquid caustic soda is the form mostly patronised by soap-makers. It is a viscous liquid, whose specific gravity ranges from 1·500 to 1·546 (100° to 109° Tw.). Generally it is of an alkaline character, and contains 15·9 per cent. of sodium oxide, Na_2O; 29·3 per cent. silica, SiO_2; 54·8 per cent. of water. The formula of the dry silicate contained in this solution would be Na_2O2SiO_2, so that although nominally "alkaline," it is really an acid silicate in character. Normal silicate of soda in which the base and acid are exactly equivalent to one another has the formula Na_2OSiO_2.

A "neutral" silicate containing a smaller proportion of soda is often made. It is advisable that the ratio between the silica and the soda should be kept as 2 to 1, shown in the first of the formula given above; if the silica is in greater proportion then it cannot be concentrated to so strong a solution as 100° Tw. without decomposition. When it is less than 2 to 1, it becomes of too caustic a character for soap-making. Usually about 5 per cent. is the quantity employed in making pale soaps, and such a quantity will harden a soap. If, however, the proportion largely exceeds this, then the tendency is for the soap to become pasty and very wasteful in use. Silicate of soda is not used now as often in soap-making as it formerly was.

Silicate of potash is sold as a "neutral" solution, which has usually a specfic gravity of 1·38 (76° Tw.) and contains

13·43 per cent. of potassium oxide, K_2O, 24·40 per cent. of silica, SiO_2, 62·17 per cent. of water.

The proportions of alkali and silica in this approximate to the formula K_2O3SiO_2. It is also sold as "neutral" silicate in a solid form, this usually containing 30·78 per cent. of potassium oxide, K_2O, 68·73 per cent. of silica, SiO_2, which corresponds approximately to the formula K_2O4SiO_2.

While silicate of soda is used for mixing with hard soaps, silicate of potash is used for mixing with soft soaps.

The effect of employing the silicates in soap-making will be discussed in another place.

COMMON SALT.

One of the materials which find extensive use in soap-making is salt, sodium chloride. This is a compound of the metal sodium and the gaseous element chlorine, in the proportions—

39·32	per cent.	Sodium
60·68	„	Chlorine

and having the formula NaCl.

It occurs in sea-water to the extent of 2·7 per cent., and it is to this substance and the magnesium chloride that sea-water owes its saline taste. Salt occurs in large deposits in a solid form—rock salt—in many places in this country: at Northwich, Middlewich, Winsford, and other localities in the county of Cheshire, at Droitwich in Worcestershire, Fleetwood in Lancashire, Middlesbrough in Yorkshire, and in other places, at all of which it is either mined or pumped up in the form of brine. Rock salt contains a few impurities, as shown in the following analysis of a Cheshire sample:—

Sodium chloride	98·3	per cent.
Magnesium chloride	0·05	„
Calcium sulphate	1·65	„

while the brine usually has the composition:—

Sodium chloride	25·22 per cent.
Calcium sulphate	0·39 „
Sodium sulphate	0·14 „
Magnesium carbonate	0·11 „

but varies considerably.

Salt is purified for domestic and industrial purposes by dissolving the rock salt in water, or taking the brine as it is pumped, clarifying by filtration or settlement from any insoluble matters, boiling down in large pans and fishing out the salt which deposits as the boiling continues. Upon the rapidity of the boiling depends the form of salt which is obtained. A rapid boil gives the fine-grained salt used for domestic purposes, while a slow boil gives rise to the large-grained salt used for other purposes. In the soap industry the latter is the form usually employed.

Salt thus prepared is almost pure, and contains but small traces of other substances.

Pure salt is a colourless and transparent solid, crystallising in cubes. These are slightly hygroscopic on exposure to the air. They are soluble in water. The solubility is not great, nor does it increase to any marked extent with the rise of temperature, as is the case with most other soluble bodies. At 0° C. 100 parts of water will dissolve 35·5 parts of salt, at 25° C. 36·1 parts, and at 110° C. (the boiling point of salt solutions) 40·3 parts of salt.

The following table gives the specific gravity and percentage contents of salt of saline solutions at 15° C.:—

Specific gravity.	Degrees Twaddell.	Per cent. of salt.
1·00725	1·4	1
1·01450	2·9	2
1·02174	4·3	3
1·02899	5·8	4
1·03624	7·2	5
1·04336	8·7	6
1·05108	10·2	7
1·05851	11·7	8

Specific gravity.	Degrees Twaddell.	Per cent. of salt.
1·06593	13·2	9
1·07335	14·7	10
1·08097	16·2	11
1·08859	17·7	12
1·09622	19·2	13
1·10384	20·7	14
1·11146	22·3	15
1·11938	23·8	16
1·12730	25·5	17
1·13523	27·4	18
1·14315	28·6	19
1·15107	30·2	20
1·15931	31·8	21
1·16755	33·5	22
1·17580	35·1	23
1·18404	36·8	24
1·19228	38·4	25
1·20098	40·2	26

Salt is used in the soap trade for freeing the soap formed by the saponification of the fats with alkali from the excess of alkali used in the manufacture, and from the glycerine formed in the operation. Its use depends upon the fact that while soap is soluble in pure water, or in water containing a small quantity of caustic soda, etc., in solution, it is not soluble in water containing much salt in solution, hence when salt is added to the soap-pan, and becomes dissolved in the lye, or brine is added, the soap is thrown out in curds when sufficient salt or brine is added for the purpose. The quantity cannot be definitely fixed, as it varies with the character of the soap and the fats it is made from. Coconut-oil soap takes much more salt than a cotton-oil soap, and this more than either a tallow or palm-oil soap. Then the excess of alkali employed has some influence by reducing the quantity of salt required, while also the proportion of water to soap in the pan causes a variation in the quantity of salt according as it is much or little.

The salt may be recovered from the spent lyes by a process of evaporation.

LIME.

Lime, or quick-lime, or caustic lime, as it is indifferently called, is the oxide of the metal calcium, and has the formula CaO. It is used in soap-making only for the purpose of causticising the soda or potash lyes to make the necessary caustic lyes for soap-making. Quick-lime is a white body which when exposed to the air absorbs moisture rapidly, and falls to a white powder. Air-slaked lime, as it is called, when mixed with water combines energetically therewith, giving rise to the production of considerable heat, and producing a white pasty mass called slaked lime. This slaked lime is used for a variety of purposes, chiefly for making mortar and cement, and also is the form employed in causticising the alkaline lyes. Mixed with a quantity of water it forms what is known as milk of lime. The following table taken from Lunge and Hurters' *Alkali-makers' Handbook* shows the amount of calcium oxide in milk of lime of different strengths:—

TABLE SHOWING AMOUNT OF LIME IN MILK OF LIME.

(Calculated from Blattner.)

Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.
2	11·7	0·7
4	24·4	1·5
6	37·1	2·3
8	49·8	3·1
10	62·5	3·9
12	75·2	4·7
14	87·9	5·5
16	100	6·3
18	113	7·1
20	126	7·9
22	138	8·7
24	152	9·5
26	164	10·3
28	177	11·1
30	190	11·9
32	203	12·7
34	216	13·5
36	229	14·3
38	242	15·1
40	255	15·9
42	268	16·7
44	281	17·6
46	294	18·4
48	307	19·2
50	321	20·0

When milk of lime is boiled with fatty acids, combination takes place, and what are known as lime soaps are formed which are insoluble in water, and lime is also, when both heat and pressure are applied, capable of saponifying fats, and is therefore used in the Autoclave process of decomposing fats. The quality of quick-lime and slaked lime may be determined in the following manner:—

1. *Free CaO.*—Weigh 100 grms. of an average sample carefully taken, slake it completely, put the milk into a half-litre flask, fill up to the mark, shake well; take 100 c.c. of the contents, equal to 1 grm. quick-lime, for the test. Titrate with normal oxalic acid and phenolphthalein as an indicator. The colour is changed when all free lime has been saturated, and before the $CaCO_3$ is attacked.

2. *Carbon Dioxide.*—Titrate CaO and $CaCO_3$ together by dissolving in an excess of standard hydrochloric acid and titrating back with standard alkali. By deducting the CaO estimated as in No. 1, the quantity of $CaCO_3$ is obtained. For very accurate estimations the CO_2 is expelled by HCl, absorbed in soda lime and weighed as described.

CHAPTER III.

FATS AND OILS USED IN SOAP-MAKING: THEIR PREPARATION AND PROPERTIES.

THE fats and oils used by the soap-manufacturer are derived from both vegetable and animal sources; none, so far known, are derived from the petroleum oils or paraffin shales. There is no very essential difference between an oil and a fat; it is purely a question of climate, or rather of temperature, as to whether a particular body makes its appearance in a solid form—a fat, or whether it is liquid—an oil, at the ordinary temperature of the place in which it is. Palm oil is here a fat, *i.e.*, solid; in Africa it is an oil, *i.e.*, liquid. Coconut oil is in this country a white solid; in India it is a water-white liquid. Olive oil is here an oil; in Greenland it is a fat. That it is simply a question of temperature is proved by the fact that if tallow or palm oil or coconut oil can be kept in a sufficiently warm place they are converted into liquids; while, on the other hand, by artificially cooling olive oil, or cotton-seed oil, or lard oil, they are solidified, and are then in no wise distinguishable from a solid fat.

These few examples will suffice to show the relation between fats and oils, and in these pages when these bodies are generally referred to, the term fat may be taken to include oils, and *vice versâ*.

The oils and fats are characterised by being lighter than water, their specific gravity ranging from 0·878, which is that of sperm oil, the lightest of natural oils, to 0·964, that of castor oil, the heaviest of natural oils. In water they are quite insoluble; on shaking up with it they form an emulsion in which the oil is distributed throughout the body of the water in the form of minute globules; on standing, the oil gradually separates out and rises to the surface. They impart a greasy stain to paper, causing it to become more or less transparent; this stain is permanent. They are readily soluble in ether, chloroform, carbon bisulphide, turpentine, petroleum spirit, benzol; in alcohol their solubility varies very much; castor oil is readily soluble; linseed oil is soluble in about ten times its volume of strong alcohol, while the solubility of tallow oil is but slight; a great deal depends upon the freedom of the oil from acidity, which increases its solubility in alcohol.

On being heated to 500° to 600° Fahr. they decompose, and under ordinary atmospheric pressure they cannot be distilled unchanged; at a reduced pressure and with the air of superheated steam they may be distilled. The products of decomposition are rather variable, but include water, carbonic acid, acrolein, acetic acid, sebacic acid, etc.

The oils are compounds of the three elements, carbon (C), hydrogen (H), and oxygen (O), the proportions varying in different oils; for linseed oil these are—carbon, 77·40 per cent.; hydrogen, 11·10 per cent., and oxygen, 11·50 per cent.

When boiled with caustic soda, caustic potash, or lime, they are decomposed and two bodies are formed, one glycerine, the other the familiar article soap; this operation is known as saponification—but of this more hereafter.

On exposure to air all oils become more or less oxidised; some, such as olive oil and lard oil, are but slightly affected; these are known as the "non-drying oils": while linseed oil and some other oils on exposure to the air gradually become hard, "dry" as it is called; these are known as the "drying oils". There is no hard or sharp line between these two classes of oils; the transition is very gradual between, say, sperm and olive oils, which are types of non-drying oils, through cotton-seed oil and niger-seed oil, partially drying oils, to linseed oil and poppy-seed oils, types of the drying oils. This property of drying has a material influence on the uses to which the oils are put in practice: the non-drying oils find extensive use in lubricating machinery, the partially drying oils are used as food oils, while the drying oils are used primarily as painting oils. Even in soap-making the drying oils are the best for making soft soap, while the non-drying oils make the best hard soaps.

Two other kinds of oil are commonly distinguished in commerce; these only resemble the oils proper in their appearance; the essential oils are almost entirely derived from vegetable sources, and it may be mentioned in passing that a plant may yield both an essential oil and an ordinary fat oil; to the essential oil it owes its characteristic odour and taste; the essential oil only exists in small quantities, while the fat oil may occur in large proportion. The essential oils vary in specific gravity very much—some are lighter, others are heavier than water, in which some are slightly soluble; they are soluble in alcohol and other solvents, and as a rule they can be distilled without decomposition; alkalies have little or no action on them; they contain carbon, hydrogen, and oxygen, but the proportion of the latter element is less than in the fixed oils; these are used in soap-making to impart a perfume to soap.

The second class of oils referred to above are the so-called hydrocarbon or mineral oils derived from the Scotch paraffin shale and American or Russian petroleum; these oils are lighter than water, have an oily appearance, will give a permanent stain to paper; they are insoluble in water and alcohol, they can be distilled without decomposition, are not acted on by caustic alkalies and are composed only of carbon and hydrogen, whence they are called hydrocarbon oils;

these are not used in soap-making, but find a most extensive use in lubricating machinery.

COMPOSITION OF OILS AND FATS.

It has been mentioned above that oils when they are boiled with caustic soda form two bodies—soap and glycerine.

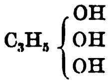
Glycerine is a water-white, very viscid, liquid having a specific gravity when pure of 1·2665; but it has such an affinity with water that it is difficult to obtain absolutely anhydrous glycerine, and the ordinary commercial glycerine generally has a specific gravity of 1·260 to 1·263, and contains a little water. It has a sweet taste, and was originally known in consequence as the "sweet spirit of oils," and in the glycerine industry the crude material is known as the "sweet water". With water it mixes in all proportions. The following table showing the specific gravities and strengths of various mixtures of these two liquids will be found useful:—

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF AQUEOUS SOLUTIONS OF GLYCERINE.

Specific gravity. 15°C.	Per cent. of glycerine.	Specific gravity. 150°C.	Per cent. of glycerine.
1·2650	100	1·1990	75
1·2625	99	1·1855	70
1·2600	98	1·1715	65
1·2575	97	1·1570	60
1·2550	96	1·1430	55
1·2525	95	1·1290	50
1·2499	94	1·1155	45
1·2473	93	1·1020	40
1·2447	92	1·0885	35
1·2421	91	1·0750	30
1·2395	90	1·0620	25
1·2341	88	1·0490	20
1·2287	86	1·0365	15
1·2233	84	1·0240	10
1·2179	82	1·0120	5
1·2125	80		

Glycerine is also soluble in alcohol, but only slightly so in ether. A mixture of equal volumes of chloroform and alcohol dissolves it, but it is insoluble in chloroform, benzene, petroleum spirit and oils. It is a powerful solvent for salts, etc., being nearly equal to water in this respect.

It is composed of carbon, hydrogen, and oxygen in the proportions indicated by the formula $C_3H_8O_3$; in its relationships it belongs to the alcohol group of organic compounds, has basic properties, and with the monobasic acids such as hydrochloric acid, oleic acid, stearic acid, it is capable of forming compounds containing one, two, or three equivalents of the acids, the compound containing three equivalents being the normal one; hence glycerine must be a tribasic alcohol, containing three equivalents of the radicle hydroxyl, OH, and therefore having the formula—



$$C_3H_5\begin{cases}OH\\OH\\OH\end{cases}$$

and is essentially the hydroxide of the radicle glyceryl.

It may be mentioned that although by a looseness of expression which is very common, glycerine is often spoken of as the base of the oils and fats, yet glycerine as such does not exist in the oils, but is formed during the various processes of saponification by the combination of the real base glyceryl, C_3H_5, with the radicle hydroxyl. The oils and fats are salts of this basic radicle glyceryl. Heated with strong sulphuric acid or with acid potassium sulphate it is dehydrated, and acrolein (acrylic aldehyde), $C\ H_3COH$, is evolved, recognisable by its peculiar odour.

Nitric acid acts on it energetically, forming a variety of products, nitro-glycerine, oxalic acid, glyceric acid, etc., being formed according to the strength of the acid used, and the manner in which the operation is carried out. Heated with potassium permanganate in the presence of caustic potash, glycerine is converted into oxalic acid and carbonic acid; and as this reaction takes place in a definite manner, it is taken advantage of for the quantitative estimation of glycerine.

When glycerine is heated with organic acids combination takes place, and ethers are formed known as glycerides, and these have the special termination *in*, as acetin, olein, stearin, and palmitin, with the prefixes *mono*, *di*, and *tri*, to show how many equivalents of the acid are combined with one equivalent of the base. Chemists, to show the analogy between glycerine and the alcohols, have given to it the systematic name glycerol, but it has been thought better to use the more familiar name glycerine here.

SOAP.

Some of the properties of this, the second body formed by the action of alkalies on the fats, have been given, and more will be given after the fats themselves have been fully described.

Soap is, to a more or less degree, dependent on the nature of the fats and on that of the alkali used, soluble in boiling water; if this solution be allowed to cool it sets into a jelly-like mass provided that there be sufficient soap dissolved in the water. If the soap be ignited it leaves behind about 7 per cent. of a white ash consisting entirely of a carbonate of the alkali, soda or potash used in making the soap, thus proving that soap is an alkaline compound.

If to a boiling aqueous solution of soap a slight excess of dilute sulphuric acid be added, the soap is decomposed, and there is obtained an aqueous solution of the sulphate of the alkali, and a fatty or oily matter rises to and forms a layer on the surface of the liquor; the character of this layer of fat depends a great deal on the fat used in the preparation of the soap, but is, as a rule, more solid.

This fatty matter, although resembling the fat or oil from which the soap has been made, possesses very different properties. In specific gravity it is lighter than water. It is soluble in petroleum spirit, ether, benzene, and is distinguished from fat by being soluble in alcohol and glacial acetic acid.

It is capable of combining with and neutralising caustic soda or caustic potash, re-forming soap, which it will do in the cold. It is also on heating capable of decomposing the carbonates of the alkalies with the evolution of carbonic-acid gas, a very characteristic feature of acids. The fatty matter liberated from soap by the action of sulphuric acid is therefore acid in character and is the fatty acids of soap.

As soap is formed by the union of an acid or acids with a base (the alkali) it belongs to the class of compounds known as salts; for the same reason, as oils and fats are compounds of a base-glyceryl, with these acid bodies they must be salts too.

The acid body obtained by the decomposition of the soap is not a simple body, but is a more or less complex mixture of several fatty acids, showing that the oils are compounds of two or more glycerides. The researches of Chevreul and others on the oils have revealed the existence of a large number of fatty acids; some of these, oleic, stearic, palmitic, are present in various proportions in most oils; as, for example, ricinoleic acid in castor oil, arachidic acid in arachis (ground-nut) oil, doeglic acid in sperm oil, brassic acid in rape oil, etc. These fatty acids are monobasic acids, and the glycerides present in the oils contain one equivalent of the base to three equivalents of the fatty acids.

The fatty acids so far known belong to five groups; which from that of the most important member of the series may be called the stearic, oleic, linolic, linolenic and ricinoleic groups. The various members of these groups, while differing from one another in the proportion of carbon, hydrogen, and oxygen they contain, in their specific gravities, melting-points, combining equivalents, yet possess a family resemblance in the matter in which they undergo decomposition and combine with various other bodies in a similar way.

THE STEARIC SERIES OF FATTY ACIDS.

General formula $\left\{ \begin{array}{l} CnH_2n + 1. \\ COOH. \end{array} \right.$

Name.	Formula.	Boiling-point.	Combining equivalents.	Oils and fats in which found.
Formic	$HCHO_2$	105°C.	46	
Acetic	$HC_2H_3O_2$	117°C.	60	
Propionic . . .	$HC_3H_5O_2$	—	74	
Butyric	$HC_4H_7O_2$	164°C.	88	Butter.
Valerianic . . .	$HC_5H_9O_2$	—	102	Whale oil, oil valerian root.
Caproic	$HC_6H_{11}O_2$	200°C.	116	Volatile acids found in coconut oil, palm-kernel oil, etc.
Enanthylic . .	$HC_7H_{13}O_2$	212°C.	130	
		Melting-point.		
Capryllic . . .	$HC_8H_{15}O_2$	15°C.	144	
Pelargonic . . .	$HC_9H_{17}O_2$	12·5°C.	158	
Capric	$HC_{10}H_{19}O_2$	30°C.	172	
Cocinic	$HC_{11}H_{21}O_2$	35°C.	186	Geranium oil, oil of rue, chaulmugra oil, oil of Californian bay-tree.
Lauric	$HC_{12}H_{23}O_2$	43°C.	200	Coconut oil, palm-kernel oil, laurel oil.
Tridecatoic . .	$HC_{13}H_{25}O_2$	47°C.	214	
Myristic . . .	$HC_{14}H_{27}O_2$	53°C.	228	Nutmeg oil, coconut oil, palm-kernel oil.
Pentadecatoic .	$HC_{15}H_{29}O_2$	56°C.	242	
Palmitic . . .	$HC_{16}H_{31}O_2$	62·5°C.	256	Palm oil, Japan wax.
Margaric . . .	$HC_{17}H_{33}O_2$	66°C.	270	Olive oil.
Stearic	$HC_{18}H_{35}O_2$	69°C.	284	Tallow, cotton-seed oil.
Arachidic . . .	$HC_{20}H_{39}O_2$	75°C.	212	Ground-nut oil.
Medullic . . .	$HC_{21}H_{41}O_2$	72·5°C.	326	Beef marrow.
Behenic	$HC_{22}H_{43}O_2$	76°C.	340	Ben oil, black mustard oil.
Lignoceric . . .	$HC_{24}H_{47}O_2$	80·5°C.	368	Beechwood tar.
Geoceric . . .	$HC_{26}H_{51}O_2$	—	396	Distillate from brown coal.
Cerotic	$HC_{27}H_{53}O_2$	79°C.	410	Bees' wax, spermaceti.
Melissic	$HC_{30}H_{59}O_2$	89°C.	452	Bees' wax.

This series is also known as the acetic series, acetic acid being, perhaps, the most important member of the series, although it is not known to be present in oils and fats, but is often a product of their decomposition. They are saturated acids and will not combine directly with iodine or bromine; a distinguishing feature from the other series of fatty acids.

The lower members—formic, acetic, propionic—are liquids, volatile without decomposition, miscible with water, and have a pungent, acrid odour; the next few members are more or less oily in appearance; those below the eleventh member, cocinic acid, are soluble in water, and are hence known as the soluble fatty acids, and can be distilled without change in the presence of water. The higher members of the series are solid bodies, whose hardness and melting-point increase with the complexity of their molecule; they are insoluble in water, and they cannot be distilled in its presence. Heated with solid caustic alkalies they undergo no change.

These acids are more fluid than the corresponding acids of the stearic series. With bromine or iodine they form additive compounds, one equivalent of acid taking up two equivalents of bromine or iodine, forming compounds of the type of bromo-oleic acid, $HC_{18}H_{34}Br_2O_2$. Heated with caustic potash to a temperature of 300°C., they undergo decomposition, potassium acetate and a potassium salt of a fatty acid of the stearic series being formed. This acid has two atoms of carbon less than the original acid, thus oleic acid is converted into potassium acetate and potassium palmitate:—

$$HC_{18}H_{33}O_2 + 2KOH = KC_2H_3O_2 + KC_{16}H_{31}O_2.$$

Under certain conditions some of the acids give sebacic acid, the formation of which serves as a distinguishing test for oleic acid and the higher acids of this series.

One very characteristic reaction of the oleic series is the conversion by means of nitrous acid into a more solid but isomeric compound: thus oleic gives elaidic acid; hypogæic acid, gaidic acid. This reaction also occurs with the glycerides, and is a very useful means of detecting the presence of much olein and its homologues in oils.

OLEIC SERIES OF FATTY ACIDS.

General formula $\left\{\begin{matrix}C_nH_{2n} - 1.\\ COOH.\end{matrix}\right.$

Name.	Formula.	Melting-point.	Combining equivalents.	Oils in which found.
Acrylic . . .	$HC_3H_3O_2$	—	72	Produced by decomposition of oils.
Crotonic . . .	$HC_4H_5O_2$	—	86	Croton oil.
Angelic . . .	$HC_5H_7O_2$	—	100	Angelica oil.
Pyroterebric. .	$HC_6H_9O_2$	—	114	
Damaluric . .	$HC_7H_{11}O_2$	—	128	
Damolic . . .	$HC_{13}H_{23}O_2$	—	212	
Moringic . .	$HC_{15}H_{27}O_2$	0°C.	260	Oil of ben.
Cimicic . .		44°C.		
Hypogæic .	$HC_{16}H_{29}O_2$	33°C.	254	Earthnut oil.
Gaidic . . .		39°C.		Produced from hypogæic acid by nitrous acid.
Physetoleic .	$HC_{16}H_{29}O_2$	30°C.	254	Sperm oil.
Physetelaidic				Produced from physetoleic acid by nitrous acid.
Oleic . . .	$HC_{18}H_{33}O_2$	14°C.	282	All oils and fats.
Elaidic . .		45°C.		Produced from oleic acid by the action of nitrous acid.
Doeglic . .	$HC_{19}H_{35}O_2$	16°C.	296	Bottlenose oil.
Doeglaidic .				Produced from doeglic acid by the action of nitrous acid.
Erucic . . .	$HC_{22}H_{41}O_2$	34°C.	338	Mustard oils, grape-seed oil.
Erucaidic .		56°C.		Produced from erucic acid by the action of nitrous acid.
Brassic . .	$HC_{22}H_{41}O_2$	34°C.	338	Rape and colza oils.
Brassaidic .				Produced from brassic acid by the action of nitrous acid.

The lead salts of the oleic fatty acids are soluble in ether, while the lead salts of the stearic fatty acids are insoluble in that solvent.

LINOLIC SERIES OF FATTY ACIDS.

General formula $\left\{\begin{matrix}C_nH_{2n} - 3.\\ COOH.\end{matrix}\right.$

This series of fatty acids are few in number: they are characterised by readily combining with bromine or iodine in the proportion of either two or six equivalents of the halogen element to one equivalent of the fatty acid.

Name.	Formula.	Combining equivalents.	
Elæomargaric . .	$HC_{17}H_{29}O_2$	280	Liquid body occurs in linseed and other drying oils.
Linolic	$HC_{18}H_{31}O_2$		
Tariric	$HC_{18}H_{31}O_2$		

They are not affected by nitrous acid ; their lead salts are soluble in ether.

Myristolic acid, $HC_{13}H_{23}O_2$; palmitolic acid, $HC_{16}H_{27}O_2$; stearolic acid, $HC_{18}H_{31}O_2$, are isologous acids formed by the action of caustic potash on the dibromo-derivatives of the corresponding acids of the stearic series :—

$$HC_{18}H_{33}Br_2O_2 + 2KOH = HC_{18}H_{31}O_2 + 2H_2O + 2KBR.$$

LINOLENIC SERIES OF FATTY ACIDS.

General formula $\left\{\begin{matrix} CnH_2n - 6. \\ COOH. \end{matrix}\right.$

Acid.	Formula.	
Linolenic	$HC_{18}H_{29}O_2$	Occurs in linseed oil and other drying oils.
Isolinolenic.	$HC_{18}H_{29}O_2$	
Jecoric . . . . . , .	$HC_{18}H_{29}O_2$	

These acids are characteristic of drying oils, have a great affinity for iodine and bromine and are readily acted on by hydrolytic agents, such as alkaline, permanganate of potash being converted into hydroxy acids.

RICINOLEIC SERIES OF FATTY ACIDS.

General formula $\left\{\begin{matrix} CnH_2n - 1{\cdot}OH. \\ COOH. \end{matrix}\right.$

Name.	Formula.	
Ricinoleic	$HC_{18}H_{32}OHO_2$	Present in castor oil.
Ricinisoleic.	$HC_{18}H_{32}OHO_2$	
Rapic	$HC_{18}H_{32}OHO_2$	Found in rape and colza oils.

These acids are hydroxy acids, monobasic, easily combine with bases to form very soluble soaps, combine readily with bromine and iodine, are soluble in alcohol and ether, but not in petroleum oils. Nitrous acid converts them into elaidic acids.

Having so far dealt with the fatty acids, and the base glyceryl, the general composition of the oils and fats may now be dealt with in detail, and their decomposition by alkalies fully pointed out.

Glycerine being a tribasic radicle, and the fatty acids without exception monobasic acids, it follows that the normal compound of these bodies must contain one equivalent of the base with three equivalents of the acid. Thus olein, stearin, palmitin, laurin, and linolein, to take the five most common and important glycerides used in soap-making, have the following formulæ :—

$$\text{Olein, } C_3H_5\left\{\begin{array}{l} C_{18}H_{33}O_2 \\ C_{18}H_{33}O_2 \\ C_{18}H_{33}O_2 \end{array}\right.$$

$$\text{Stearin, } C_3H_5\left\{\begin{array}{l} C_{18}H_{35}O_2 \\ C_{18}H_{35}O_2 \\ C_{18}H_{35}O_2 \end{array}\right.$$

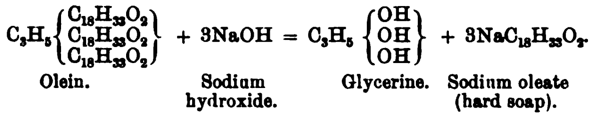
$$\text{Palmitin, } C_3H_5\left\{\begin{array}{l} C_{16}H_{31}O_2 \\ C_{16}H_{31}O_2 \\ C_{16}H_{31}O_2 \end{array}\right.$$

$$\text{Laurin, } C_3H_5\left\{\begin{array}{l} C_{12}H_{23}O_2 \\ C_{12}H_{23}O_2 \\ C_{12}H_{23}O_2 \end{array}\right.$$

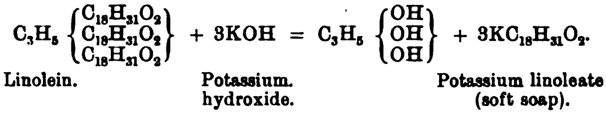
$$\text{Linolein, } C_3H_5\left\{\begin{array}{l} C_{18}H_{31}O_2 \\ C_{18}H_{31}O_2 \\ C_{18}H_{31}O_2 \end{array}\right.$$

Oils and fats are mixtures of these and other glycerides. Some contain only two, others a much larger number. It will be more convenient to state the composition when dealing with each individual oil and fat.

When the glycerides are boiled with caustic soda or caustic potash (sodium or potassium hydroxide), the stronger base combines with the fatty acid to form a soap, while the glyceryl combines with the hydroxyl to form glycerine, as illustrated by the following equations :—



$$\underset{\text{Olein.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{33}O_2\\C_{18}H_{33}O_2\\C_{18}H_{33}O_2\end{matrix}\right\}} + \underset{\substack{\text{Sodium}\\\text{hydroxide.}}}{3NaOH} = \underset{\text{Glycerine.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right\}} + \underset{\substack{\text{Sodium oleate}\\\text{(hard soap).}}}{3NaC_{18}H_{33}O_2.}$$



$$\underset{\text{Linolein.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{31}O_2\\C_{18}H_{31}O_2\\C_{18}H_{31}O_2\end{matrix}\right\}} + \underset{\substack{\text{Potassium.}\\\text{hydroxide.}}}{3KOH} = C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right\} + \underset{\substack{\text{Potassium linoleate}\\\text{(soft soap).}}}{3KC_{18}H_{31}O_2.}$$

These two equations, with, of course, any necessary alterations, represent the action of sodium and potassium hydroxides on all fats and oils. The process is termed saponification, and on the principle here given the operation of soap-making is based.

Chemists perceive in these reactions the principle of the separation of a glyceride into its two approximate components, glycerine and acid, and as this can be brought about by other means, as by the agency of superheated steam when the bodies are directly formed, they include under the term saponification any process which splits an oil up into glycerine and fatty acid.

OCCURRENCE OF ANIMAL AND VEGETABLE OILS AND FATS.

1. ANIMAL FATS.

In the animal body are comparatively large deposits of fatty matter. Nearly all the internal organs are covered with a coat of fat. In and about the joints of the bones deposits of fat occur. The muscles are also separated from one another by layers of fat. In some cases these deposits of fat are of particular note. This is the case with what is known to anatomists as *omentum* of animals, a layer of fatty matter which covers the intestines, known commonly by various names—"leaf" in the case of the pig, "skin" in the case of sheep and oxen. The bodies of whales and seals are covered with a thick layer of fat known as the "blubber". The fat occurs in the animal body enclosed in small cells of animal tissue in a liquid condition, so that it does not interfere with the motions of the body. It is maintained in this liquid condition by the natural heat of the body. When the animal dies the body becomes cold, and the fatty matter sets into a solid mass, to which circumstance is due the stiffness or *rigor mortis* of dead bodies.

The purpose of fatty deposits in the animal kingdom is threefold. First it preserves, especially in the case of the *omentum*, the internal organs from injury and serves to lubricate them in their various motions. It also serves as a store of warmth for the body and as a store of food.

2. VEGETABLE OILS AND FATS.

In the vegetable kingdom oils and fats occur in a variety of ways. All seeds contain oil to a greater or less extent, some as much as 60 per cent. This oil acts as a food for the young plant until it reaches such a period of its growth that it can extract its sustenance from the earth. The pulp of certain fruits, *e.g.*, olives, oil-palm nuts, contains a good deal of oil. The vegetable oils here referred to are those fixed or fatty oils, and not the essential oils, to which in many cases any particular odour or taste of the plant is due.

EXTRACTION AND PURIFICATION OF ANIMAL AND VEGETABLE OILS AND FATS.

It is obvious that as the circumstances under which any particular animal or vegetable oil occurs are so varied the methods adopted for the purpose of extracting them must be varied also. A process which will work well with, say, the fat of the pig, would not suit the blubber of the whale or the oil from the olive. Space will not permit of a very extended description of all the processes which have been devised for the extraction of animal and vegetable oils and fats; but of those which are in common use a full description will be given, while other processes of only special interest will be noted in outline.

1. ANIMAL FATS AND OILS.

The operation of extracting the animal oils and fats, such as tallow and lard, is generally known as "rendering". It may be carried on in various ways. The principle which underlies all the methods is that of liberating the fatty matter from the animal tissue in which it is enveloped by means of heat. This causes the fatty matter to swell, and in so doing it bursts the envelope of tissue and is then ready to flow away. We may carry this operation out by: 1st, direct heat; 2nd, boiling in water; 3rd, steam under pressure.

RENDERING BY DIRECT HEAT.—The housewife renders her lard or suet by placing the rough fat in a tray or dish in the oven. It is scarcely possible to adopt quite so simple a system on the large scale, although one or two plans which will be described very closely resemble the housewife's primitive method.

A simple method occasionally adopted is to heat the rough fat in a large boiler over the fire. The contents of the boiler are kept continually stirred, and when it is considered that the fat has been freed from the tissue, the fire is withdrawn and the fat drawn off into a separate receptacle. This method, though simple, is open to several objections. If great care be not taken there is a liability to char the fat or tissue, the fat thereby acquiring a discoloured appearance and a burnt odour. Not only so, but bad odours are liable to be given off during the operation which are also objectionable.

A much better plan of rendering fats by dry or direct heat is illustrated in figure 3. A large chamber is built of such a size that a workman can conveniently enter it. In this are arranged on each side rackwork shelves placed in an inclined position towards the centre of the chamber. On the floor of the chamber are a number of steam pipes for the purpose of heating the chamber to any required degree. The fat is cut up into small fragments by means of a mincing machine, and spread in layers on metallic trays, which in turn are placed on the shelves in the chamber. At the lower end of each tray is an opening to permit of any fat running out into gutters, which are arranged for the purpose, these gutters conveying the fat into a storage tank placed in a suitable position. When all the shelves are filled with trays of fat the door of the chamber is closed, and steam sent into the pipes, whereby the chamber is heated to from 130° to 140° F. At this heat the fat melts and runs out. When it is seen that no more fat is being obtained the steam is stopped, the melted fat in the trays is allowed to run out and the residual tissue removed, and the trays filled up for another rendering. As the residual tissue still contains some

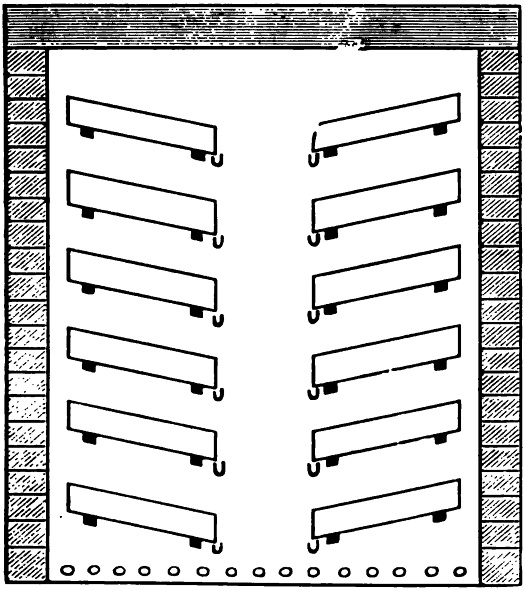


FIG. 3.—Tallow Rendering Chamber.

7 or 8 per cent. of fat, it is sent to another pan for the purpose of extracting this residual fat. The advantage of this process, which has been devised by Messrs. Cook & Hall of the East London Soap Works, is that it yields a fat of very pure quality. On the other hand, it is rather more costly to work than some other processes. There is the labour of mincing the rough fat and filling it into the trays. The cost of heating the chamber is rather high, while the yield is not so great. A better price is however obtainable for the fat.

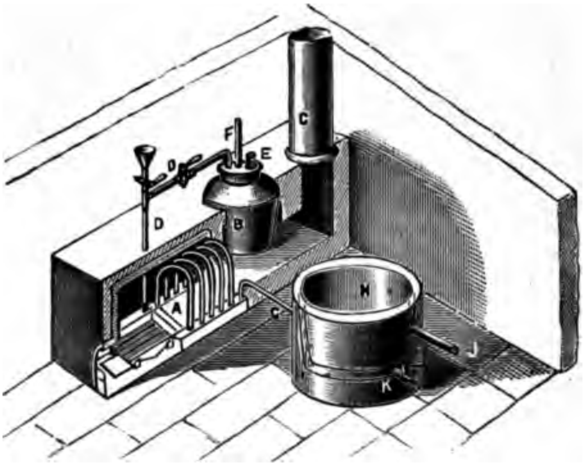


Fig. 4.—Merryweather's Fat Rendering Plant.

Messrs. Merryweather & Sons have devised a plant for the dry rendering of rough fats by superheated steam whereby the overheating of the fats is avoided. This consists of three parts; First, a double-cased or jacketed boiler in which the fat is heated, the steam being sent into the space between the two pans; second, a superheater which is heated in a suitable furnace for superheating the steam; and, third, a steam boiler. This apparatus is very efficient in use. It is shown in figure 4, where H represents the fat pan; B the steam boiler; A, the superheater, consisting of a number of ∩ shaped pipes in a furnace; D is the steam pipe; C, the chimney. In all the dry systems of rendering fats there is left behind the animal tissue, or, as it is called, the "greaves or cracklings". With the best system of rendering the fat, these always contain a certain proportion of fat which it is desirable from economical motives to recover. This may be done in several ways.

One of the most common methods of recovering the fat from greaves is by subjecting them to pressure in a press. One very convenient press for this purpose is the Boomer Screw Joint Press.

A convenient form of this press is made for fat renderers. It consists of a round table with corrugations, and provided with a lip from which the pressed fat can flow. This is supported on a strong iron casting. On the table is fitted a cask made in two halves working on a hinge, with the object of enabling it to be readily discharged. A plunger connected with the screw gear fits the cask. The Boomer press has a right- and left-handed screw, the nuts working on which are connected with the press plunger; the revolution of the screw causes the nuts to travel inwards, and thus by a knuckle joint force the plunger downwards with some force. The greaves or cracklings while still hot are placed in the cask and the press brought into action. The fat is pressed out, while the residual greaves are collected and sold for dogs' food or for manure.

Rendering by Boiling Water.—A very old plan of rendering tallow is to boil it in an open boiler set in a fireplace like an ordinary household washing boiler along with water. The heat of the boiling water causes the fat to expand and melt and flow from the greaves. Being lighter than water, it collects on the top of the boiling water, and should be skimmed off from time to time. The greaves fall to the bottom of the boiler. Some of the animal tissue passes into solution, however, and a little tends to get into the tallow.

This process is simple, but it has the disadvantage of leading to the production of evil odours which are objectionable, so that except for treating small lots of fat it is rarely resorted to, having been largely superseded by processes for rendering fat with steam under pressure.

Such a boiler is shown in figure 5, which represents an improved form of construction. The bottom is double, and the space thus formed is in communication with the outer air. By this means the temperature of the bottom of the pan never gets too high. The boiler is covered with a lid, from one portion of which a pipe conveying the steam, etc., passes into the chimney, thus carrying off all vapours and preventing nuisance.

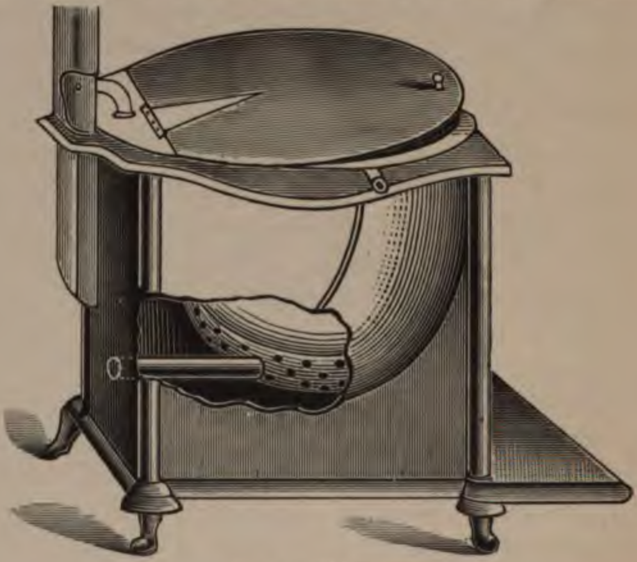


Fig. 5.—Fat Boiler.

Rendering Fats under Pressure by Steam.—A very convenient form of plant for this purpose is shown in figure 6.

This consists of a steam boiler placed vertically as shown, and supported on flanges near its upper portion. The rough fat is fed in through a manhole, M, placed on the top of the boiler, on which also is a safely valve, S. In the bottom is placed a perforated steam coil, C, connected with a steam-pipe and valve, V. In the side of the boiler are placed two gauge or flow-out taps, T, K, lower down is placed a large valve, R, for running off the melted tallow, while at the bottom of the boiler is another valve, T, for running off the water, etc.

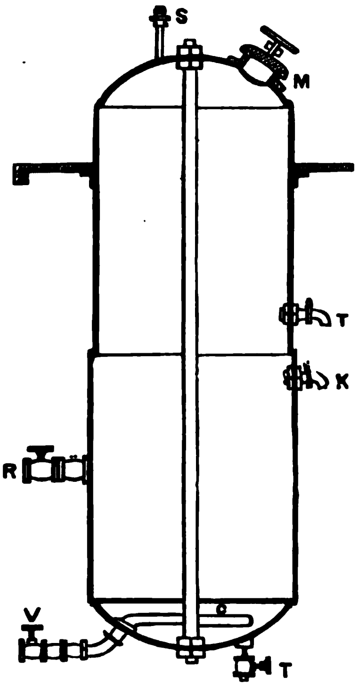


Fig. 6.—Steam Fat Boiler.

This boiler is used in the following manner: The crude fat is broken up into small pieces, and fed into the boiler through the manhole, which is then closed. Water is then run in, and steam at 60 lb. pressure sent in through the steam coil, this being continued for five to six hours; the length of time being regulated according to the amount of charge. When the operation is finished the steam is shut off, the contents allowed to settle, then before the fat has time to get solid it is run off from the flow-out taps. If necessary, water is run in to throw the fat up to the level of the running-off taps. Some renderers will, after turning off the

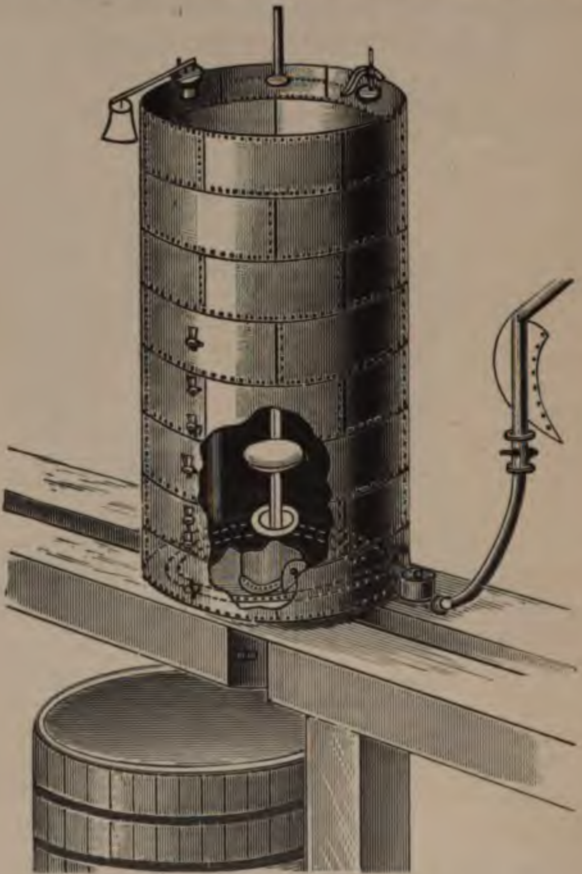


Fig. 7.—Steam Fat Boiler.

steam, run off all the contents of the boiler into a tank, and there allow the fat to settle out and solidify, when it can be removed.

By using such a plant, a larger quantity of fat can be rendered in a given time; there is less chance of objectionable odours arising, and the yield of rendered fat from the crude material is better.

The apparatus previously described is constructed to render the fats at the ordinary pressure, or at all events at but slightly increased pressure. By employing boilers which are constructed to work at a higher pressure, some advantages are secured; the nitrogenous tissue is more completely gelatinised, therefore the fat is better separated from the tissue, and so a greater yield of better quality is obtained. Figure 7 represents such an apparatus, which may be built of any required size; in some cases they are constructed of a capacity of 10,000 gallons. As will be seen from the drawing, it consists of an upright boiler, fitted on the top with a safety valve, manhole for charging, and a stuffing box, through which passes the rod of the discharging orifice or valve. There is a false bottom. Between the two bottoms is a steam coil connected by valve and pipe with an ordinary steam boiler. In the bottom is a discharging orifice, which is kept closed by a plate valve worked by a rod passing through the top of the boiler. In the side of the boiler is placed a number of draw-off cocks, extending from near the bottom to about half-way up, while near the top is a testing cock.

The apparatus is used in the following manner: The discharging valve is closed, and rough fat is thrown in through the manhole until the boiler is filled to within about 2½ feet from the top. The manhole is then closed, and steam sent in until a pressure of 45 to 69 lb. is attained. Generally a good deal of condensation of the steam occurs, and much water is formed, which collects at the bottom of the boiler.

From time to time the top cock is opened. If live steam escapes the boiler is working right; if however fat comes out, then it shows that the boiler is too full, and that water must be drawn off from the lowest cock. This is done from time to time during the progress of the operation. After about twelve to fifteen hours' steaming, the steam supply is cut off, the pressure is relieved by opening the safety valve, and the contents of the boiler allowed to settle. When well settled the water is run off, while the tallow is run into storage tanks. The aqueous liquor contains a good deal of nitrogenous matter, and it may be collected and used as manure. Working with this apparatus, there is a fairly good yield of fat or tallow from the crude material.

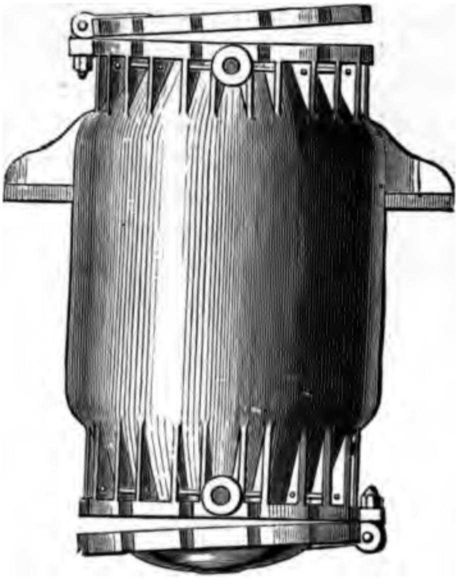


FIG. 8.—Bone Boiler.

BONE TALLOW.

Bones contain a good deal of fatty matter, which it is necessary to extract before the bones can be used for other purposes. This bone fat, or, as it is commonly called, bone tallow, is very largely used in making soaps, especially soaps which are to be used for industrial purposes. The simplest plan is to adopt a boiling process in open vessels, but such a plan is open to great objection on account of the nauseous odours which are developed, therefore it is better to render bone tallow in closed vessels by steam.

Such an apparatus for the purpose is shown in figure 8, and is constructed by Mr. W. M. Fuller. It consists of a boiler measuring about 6 feet by 3 feet 6 inches, fitted with hinged covers at both ends, both of which can be tightly closed by means of suitable nuts and bolts. There are also provided steam connections and draw-off cocks. A charge of about 46 cwt. of bones is put into the boiler through the upper door, which is then closed. Steam at about 50 to 60 lb. pressure is then introduced, and kept up for about forty minutes, when it is shut off; the excess steam being run into a condenser. The contents of the boiler are now allowed to settle for half an hour, when the fat is run off through a cock at the bottom of the boiler. The bones are drawn out by opening the bottom of the boiler and allowing them to drop on the floor. This boiler extracts more fatty and gelatinous matter out of the bones than do most other modes of treatment, while the bones are in a better condition for being converted into manure, being freer and therefore more friable.

In figure 9 is shown a complete plant for the boiling and crushing of bones, as constructed by Mr. Fuller. B is a crushing mill to break up the bones prior to their being placed in the bone boilers, E, E, the crushed bones being conveyed to them by means of elevators; *d*, *d* are the tanks to receive the liquor from the bones, which are passed on to the crushing and sieving mill, F, where they are crushed and sieved prior to being sent out as bone meal.

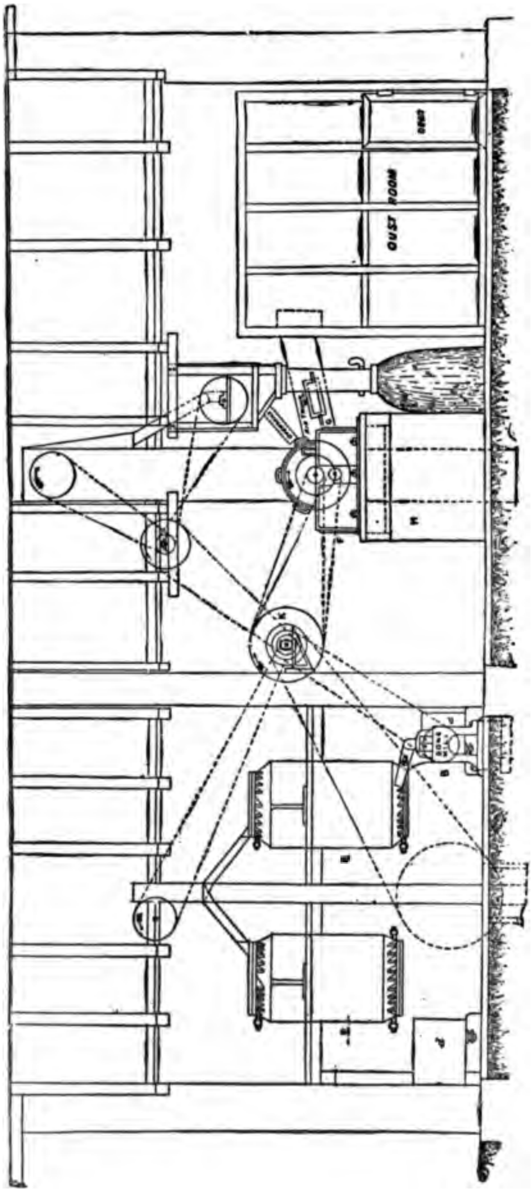


FIG. 9.—Plant for Crushing and Boiling Bones.

Other plans of treating bones have been devised. It is quite possible that no two bone-boiling establishments are arranged alike in their plant for extracting the fat and gelatine from bones.

In one works they boil the bones in pans over a fire. The pans are fitted with covers. Each pan communicates by a flue with a large iron condenser, in which all the matter which is capable of condensing collects and flows away into suitable receptacles. Anything which is uncondensed passes into a flue and away into the atmosphere. It would be better to conduct all gases to the fireplaces to burn up all that is combustible.

In another works they use a bottle-shaped boiler, and heated by steam, both the fat and the gelatine being recovered.

The processes described above are applicable for the extraction of all kinds of animal fats, and are those usually worked. In some cases a special process may be adopted for special fats; any such will be found described under their respective fats.

2. VEGETABLE OILS AND FATS.

There is a greater variety in the methods of extracting oils and fats from vegetable sources than from animal sources. The method generally followed is to extract the oils by pressure, in some cases at the ordinary temperature, in others at a higher one. Some vegetable fats are extracted by a process of boiling with water, as in the case of animal fats, while the property of such bodies as carbon bisulphide, benzoline, benzol, of readily dissolving oils, is taken advantage of for obtaining vegetable oils by a solvent process.

EXTRACTION OF VEGETABLE OILS BY PRESSURE.—The process of extracting vegetable oils by pressure is a very ancient one, and it is the one commonly followed by people in a low state of civilisation. Like many other methods it has undergone many changes and developments from the earliest times to the present. It is not intended here to enter into a discussion of the changes which have taken place; attention will rather be given to the methods now in use in this country. If any reader desires to know something of the older methods he is referred to Chambers's *Encyclopædia* or to Spon's *Dictionary of Engineering*.

There are two chief methods of pressing oils in use in this country; the oldest is generally known as the English system, the newest as the Anglo-American system.

The ENGLISH SYSTEM of oil pressing takes place in several stages as follows:—

First, Crushing.
Second, Grinding.
Third, Heating.
Fourth, Pressing.
Fifth, Refining.

The refining of the oil obtained by carrying out the first four operations is the same as in other processes of extracting oils, and will be considered later on.

First: Crushing.—Prior to being submitted to the various operations enumerated above, the seed or other material is first subjected to a cleaning process to free it from dirt, foreign seeds, etc., which have got into it and which might interfere with the proper carrying out of the various operations or with the quality of the oil which is obtained. These cleansing processes consist essentially of winnowings and sievings through various sizes of sieves. Even with all the care that may be taken it is impossible to completely free oil seeds from all other foreign seeds, so that commercially it is doubtful whether an absolutely pure oil exists.

The crushing mills consist of an horizontal frame in which are fixed two rolls; one of these is about four feet in diameter, the other one foot in diameter. The larger roll is the driving roll, the smaller one revolving by friction against it. The two rolls are caused to press against one another with some force by means of screws and springs working against the bearings of the rolls. The seed is fed into a hopper which delivers it between the pair of rolls, in its passage through which it becomes crushed. A mill will crush about 4 tons of seed in a working day of ten hours. It is obvious, however, that the quantity a mill will do will vary with the kind of seed and other circumstances. It is usual to run the mill at such a speed that the large roll makes fifty-six revolutions per minute. One of these crushing mills will keep two ordinary-sized presses at work.

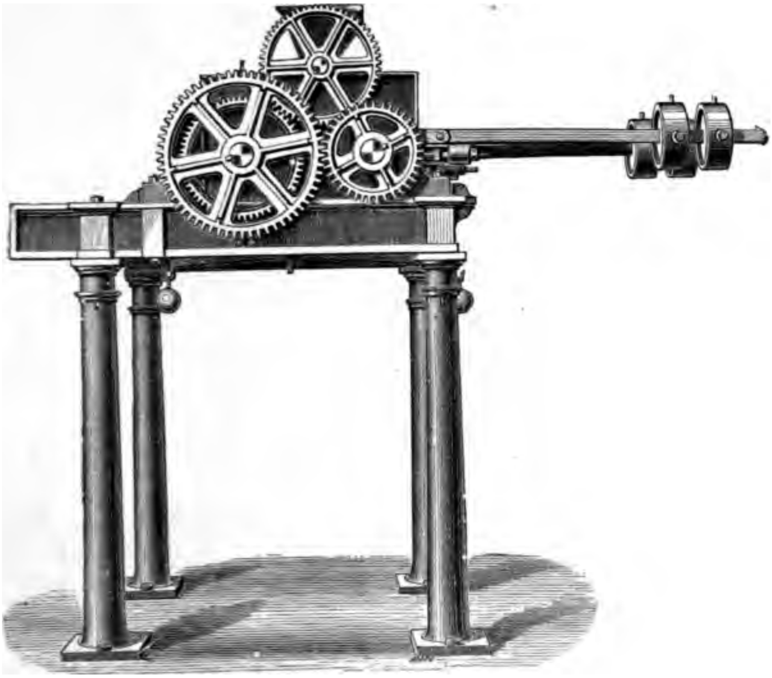


FIG. 10.—Oil Seed Crushing Mill.

Figure 10 is a drawing of such a mill as described above, made by Messrs. Rose, Downs & Thompson of the Old Foundry, Hull, to whom the author is indebted for the engraving of this and other oil machinery.

Second: Grinding.—After being crushed the seed is thrown into the hopper of an edge-runner grinding mill as seen in figure 11, which shows the construction of such mills very well. An oil crushing mill differs from most other edge-runner mills in having a shallow hopper. The usual size for the runners is 7 feet in diameter and 16 inches thick, and they will weigh 6 to 7 tons. The driving shaft makes seventeen revolutions per minute. One of these edge-runner mills

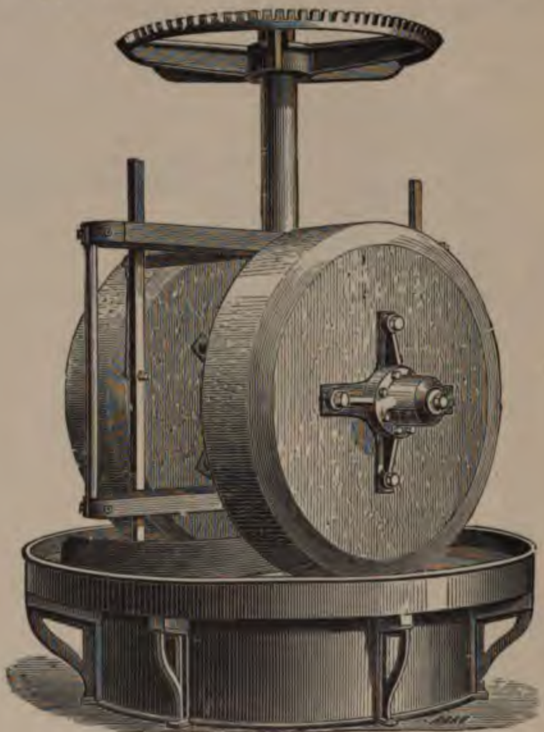


FIG. 11.—Oil Seed Grinding Mill.

will keep two presses at work. The seed is ground for a period of twenty to twenty-five minutes. During the operation care is taken that every part of the seed gets efficiently ground, and it is usual to add from 2 to 3 per cent. of water during the grinding to moisten it and put the seed in the best condition for the succeeding operations.

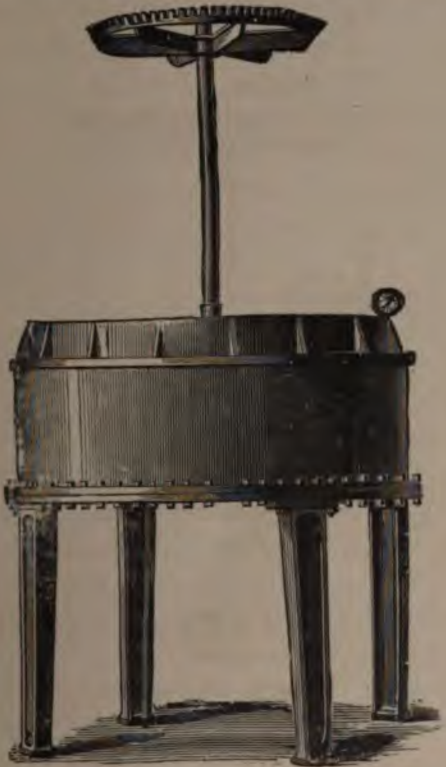


FIG. 12.—Oil Seed Heating Kettle.

Third: Heating.—After being crushed and ground the seed next undergoes a heating operation. This is now done in a large copper steam kettle, shown in figure 12. This kettle varies in size according to circumstances, quantity of seed to be treated, etc. In a large oil mill the kettle will be

5 feet in diameter and 2 feet 6 inches deep. They are usually jacketed so that they can be heated by steam up to a temperature of 160° to 170°. There is also an arrangement for sending steam into the inside of the kettle among the seed which is being treated. This is very important, as the heating in the kettle tends to dry the seed, and dry seed does not give a good yield of oil. The time of heating varies somewhat according to circumstances, but usually is about twenty to twenty-five minutes. The kettle is always fitted with an agitating apparatus to ensure that every portion of the seed is uniformly heated. One kettle of the dimensions given above will keep four presses at work capable of turning out 6 tons of cake in a day.

The previous operations are purely mechanical in their effects, being designed to get the seed into the best possible condition for yielding all the oil it contains. The heating in the kettle has a combined mechanical and chemical effect. The heating more completely breaks up the cells, and thus results in a more ready separation of the oil; while at the same time it leads to the coagulation of the albuminous and other matters present in the seed, and so prevents them from being pressed out along with the oil. It is the great object in oil pressing to obtain an oil as free as possible from extraneous vegetable matters, the presence of which in oil brings about its decomposition sooner than would otherwise be the case.

Fourth: Pressing.—After being heated, the hot seeds are placed in strong bags made of canvas, the usual amount in each bag being 8 lb., or sufficient seed that after pressing the oil out there remains a cake weighing 8 lb. The bags are next enclosed in woollen covers, and are then wrapped again in what are called "hairs," which are strong cloths made of horsehair. The cakes of seed are now placed between the plates of the press and subjected to pressure.

Beyond such primitive methods of pressing oil as have been in existence and still are in use by uncivilised people, there have been three kinds of press in use:—

First, Stamper and Wedge Press.
Second, Screw Press.
Third, Hydraulic Press.

The first and second have almost gone out of use, while now only hydraulic oil presses are made. A few words descriptive of them will however be useful.

The Stamper and Wedge Press.—This old form of oil press consists of two portions. A cast-iron box, long, narrow, but deep, is provided. At one end is placed a perforated iron press plate; against this is put the bag of seed; next comes another press plate, followed by a piece of wood thicker at the bottom than at the top; then comes the wedge, followed by a similar piece of wood to the foregoing. The other end is fitted up in the same way. Between the two sets is what is known as a key arrangement, consisting of three pieces, two pieces thicker at the bottom than the top, with an intermediate piece, the key, shaped like an inverted wedge. The whole of this arrangement constitutes one part. The other portion consists of two hardwood stampers, which can be made to alternately fall upon the wedges with some force, thus driving them further in and causing them to press the seed with some amount of pressure, forcing out the oil it contains. After falling on the wedge the stamper is raised up ready for another drop. When it is considered that all the oil has been extracted, a stamper is allowed to fall upon the key, which loosens the whole arrangement so that the bags of pressed seed, the oil cake as it is now called, can be withdrawn. The oil flows into a receptacle in the lower portion of the box, from whence it is transferred to a storage tank. It is obvious of course that the production of oil in a stamper press is a limited kettle, it is sent into a moulding machine. This machine is shown in figure 14. The moulding machine is one of the novel features of the Anglo-American system. Its object is to ensure uniformity in the size of the cakes of seed, to mould it by a gentle pressure into a level cake, so that the press is not subject to any undue strain due to inequalities in the cakes, while there are secured a greater output from the presses and a better yield of oil. The hot seed is allowed to fall from the kettle into a measuring box, which always ensures a uniform quantity of seed being used. A tray covered with a sheet of woollen cloth is next placed on the table of the moulding machine and surrounded by a frame. Into the mould thus formed the seed is placed, and formed into a smooth cake. The tray and its contents are then pushed under the die of the moulding machine, when a cam is brought into action, and the die caused to fall upon the seed and compress it to a thickness of 3 inches, or even less; the pressure being maintained for about half a minute, when the die rises and the cake of seed is removed and sent into the

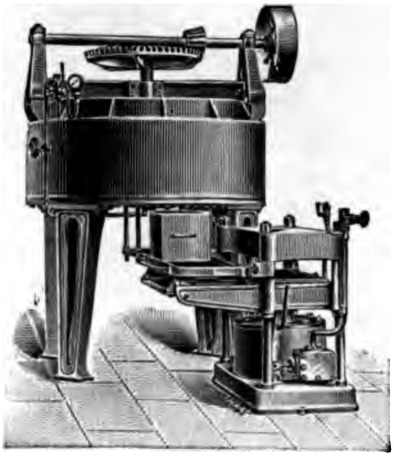


FIG. 14.—Oil Cake Moulding Machine.

hydraulic press. By the use of the moulding machine a larger number of cakes can be dealt with in the press at one time. A cake of unpressed seed has a thickness of about 8 inches, while the moulded seed has a thickness of about 3 inches, and so a press will take rather more than twice as much moulded seed as unmoulded seed.

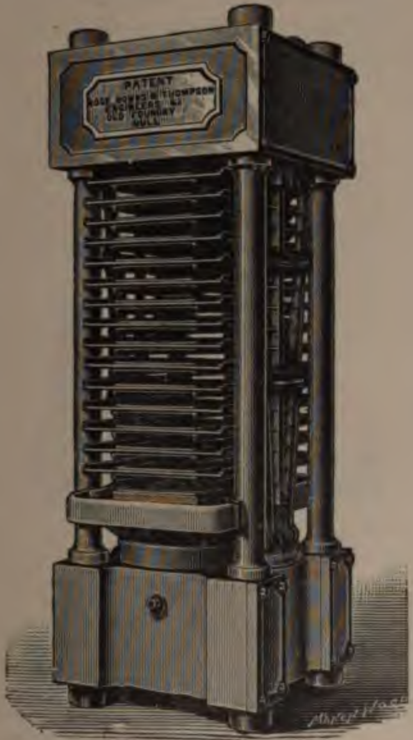


FIG. 15.—Hydraulic Oil Press.

Fourth: Pressing.—This is the final operation of either the Anglo-American or the English system, although in either case the oil after it flows from the press has to undergo a refining operation before it can be sent into the market for sale. The hydraulic press has undergone some changes in detail since it was first applied to the pressing of oil; but it is not intended here to give any historical sketch of these changes, as space does not admit of it.

Figure 15 shows the latest form of hydraulic press for oil pressing, without the pumps which are necessary to work the press. The hydraulic press consists of a very strong cast-iron foundation, in which works a ram connection with a strong iron movable plate. This plate moves up and down between stout iron standards, which also form supports for a very strong iron casting. Between the movable bottom plate and the top are arranged a number of corrugated iron plates which receive the cakes of seed to be pressed.

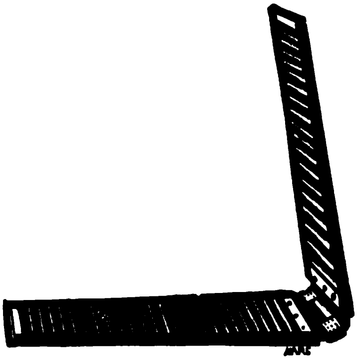


FIG. 16.—Oil Cake Moulds.

The cakes of seed as they come from the moulding machine are placed in a pair of iron covers like a book back (see figure 16), and into the press. This does away with the hairs which were used in the old system, which are very expensive to use owing to the damage which the press does to them in breaking them. The press may be made in various sizes to suit the particular requirements of the oil miller, from a small press capable of pressing four cakes at once to one taking twelve to fourteen cakes.

Two sets of pumps are usually supplied with each press, one to give a pressure of about 700 to 800 lb. per square inch, while the other set will give a pressure of 2 tons.

At first the lower pressure is applied for about fifteen to twenty minutes, during which the great bulk of the oil will flow out. Then the higher pressure is put to complete the extraction of the oil, which will take a further five to ten minutes. The oil flows out of the sides of the cake into the corrugations on the iron plates and into channels which are provided for it to flow away to a storage or receiving tank placed about the base of the press.

Usually from two to four presses are included in one oil plant, as the other portions of the plant are quite capable of keeping more than one press at work.

It is obvious, of course, that the output from the oil press will vary very considerably owing to the varying size of the presses and also of the seed which is being pressed. For, while a press can work through five charges per hour of linseed, it will only do three of rape seed and four of cotton seed in small-sized presses. Larger presses, working perhaps 250 to 320 lb. of seed at one charge, will work through three to four charges in three hours. The size of the cake of seed also varies with the size of the press.

As a rule seeds are only passed once through the press, but there are a few, such as rape and gingelly seed, which are crushed twice, the cake obtained in the first pressing being reground and reheated with a little additional water before being again pressed. Further, what was orginally pressed in two presses is spread in the second pressing over three presses.

Some oil seeds, castor seeds, cotton seeds, arachis seeds, etc., have a very hard shell, besides being of large size. It is necessary for the better extraction of the oil that the shell or husk be removed; this is effected by means of a machine known as a decorticator, the operation being known as "decorticating". Such a mill adapted for the treatment of castor oil seeds by hand, although they may be made to work by steam, is shown in figure 17. These mills have a pair of revolving cylinders carrying blades fixed at a particular distance apart, this distance being dependent upon the seed which is being treated, castor oil seed requiring a different distance than arachis nuts and so on. The knives just cut the seed and allow the kernels to fall out, then by winnowing the husks may readily be separated. In figure 18 are shown at A castor oil seeds before treatment, at B the

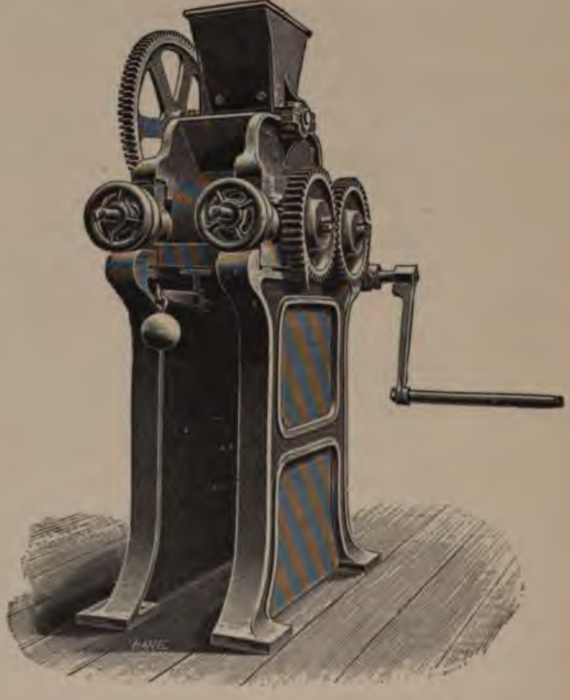


FIG. 17.—Castor Seed Decorticator.

husks, and at C the white kernels ready for the crushing mills.

There is, of course, a great difference in the quantity of oil which is yielded by different seeds. It is found preferable in the case of seeds which give but poor yields to use a smaller quantity of seed in each charge than is done with seeds which are rich in oil.

In some cases, such as castor and olive oils, the seed is subjected to two or three distinct crushings, yielding oil of several qualities. First the seed is crushed cold, when what is known as "cold drawn" or "virgin oil" is obtained; then the seed is heated and reground, when what is called "second pressure" oil is obtained; finally, the seed is warmed with water and again pressed, when a third quality of oil is obtained.

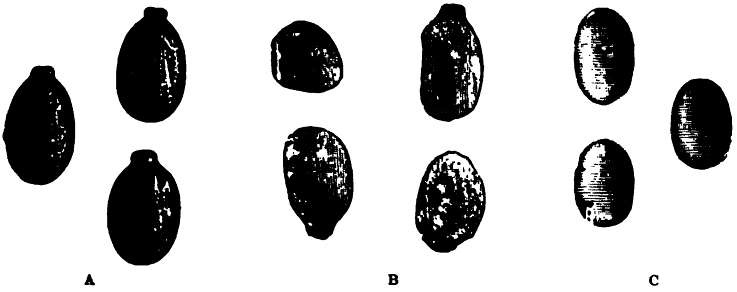


FIG. 18.—Castor Seeds.

In the case of oils which, like coconut and palm-nut oils, are solid at the ordinary temperature, it is customary to heat the presses so as to make the oils fluid. In winter, too, it is desirable to work with heated presses.

The oil cake after coming from the press is passed to a paring machine, where the edges are trimmed to make the cake rather more presentable and therefore more marketable. The parings are sent back to the crushing rolls to be worked through with the next batch of seed.

PRINCIPAL VEGETABLE OILS AND FATS.

Name of Oil, etc.	Botanical Name of Plant.	Native Country.	Percentage Yield of Oil.
Almond	Amygdalus communis	Mediterranean Countries	48 to 50
Arachis (Earth-nut, Pea-nut, or Ground-nut)	Arachis hypogæa	India, Western Africa	43 to 45 (50)
Ben	Moringa oleifera	India, Egypt	35 to 36
Castor	Ricinus communis	East Indies	American, 46 to 49 Indian, 51 to 53
Coconut	Cocos nucifera	Tropical Countries	40 to 45
Colza (Rape)	Brassica campestris; B. napus; B. rapa; B. napobrassica	Europe	33 to 43
Cotton Seed	Gossypium herbaceum	Asia, Africa, America	24 to 26
Laurel Butter	Laurus nobilis	South Europe	24 to 26
Linseed	Linum usitatissimum	Europe, Asia	38 to 40
Maize	Zea mais	America	6 to 10
Mustard Seed (White)	Sinapis alba	Europe	25 to 26
Nut (Walnut)	Juglans regia	Persia, Himalaya	63 to 65
Niger (Ramtil)	Guitia oleifera	Abyssinia, India	40 to 45
Olive	Olea Europea	Southern Europe	Pulp, 40 to 60 Kernels, 12 to 15
Palm	Elais guineensis	West Africa	Pulp or Pericarp, 65 to 72
	E. melanococca	South America	Kernels, 45 to 50
Poppy Seed	Papaver somniferum	Asia Minor	Blue, 48 to 50 White, 41 to 45
Sesame (Gingelly)	Sesamum indicum	India, Levant, Antilles, etc.	50 to 57
Sunflower Seed	Helianthus annuus	Mexico, Peru	21 to 22

Refining and Clarifying Oils.—The oils as they come from the oil press are usually cloudy in appearance, contain much colouring matter, moisture and extraneous vegetable tissue, from which it is desirable they should be freed.

The oil as it comes from the press should be run into large tanks, which are kept at about 100° F., in which it is allowed to remain for some time. The water and solid vegetable matter settle down, leaving the oil bright and clear. This process is however a slow one, and the oil presser often does not care to keep his oils so long, and therefore must adopt a quicker process.

Figure 19 is a drawing of an oil-clarifying tank made by Messrs. Wm. Oxley & Co., of Manchester. It consists, as will be seen, of a long cylinder tank made of tinned iron; the bottom is made conical with the apex to the bottom, from which protrudes to the side of the tank a pipe for drawing off the foots and impurities which settle there. Draw-off and testing cocks are placed on the side of the tank. The oil is placed in the tank and allowed to stand for some time. The impurities collect at the bottom of the tank, the peculiar construction of which is such as to concentrate them in a small space, thus economising the quantity of

FIG. 19.—Oil-Clarifying Tank.

foots obtained. From time to time the testing and draw-off cocks are opened, and when the oil appears clear enough the bottom draw-off cock is opened and the clear oil run off, the foots being then run into a separate vessel, and the tank is ready for another batch of oil. These tanks are made to hold 250 or 500 gallons of oil.

Sometimes oils are clarified by adding to them from 5 to 10 per cent. of their weight of fuller's earth, heating the mixture to about 150° F., and maintaining it at that heat for half an hour to an hour, stirring well all the time. Then the oil is allowed to stand for about twenty-four to thirty hours to settle out. The fuller's earth carries down with it all the impurities in suspension, and at the same time exerts a more or less bleaching action on the oil. The same quantity of fuller's earth may be used several times, especially if its function is simply that of a clarifying agent. Where however it is employed as a bleaching agent, it must be replaced with fresh material from time to time. The fuller's earth absorbs a large proportion of oil, which should be removed by treatment with benzoline or benzine before it is thrown away.

Where large quantities of oil are to be dealt with, it is a good plan to use fuller's earth combined with a filter press. The oil is heated with 2 to 3 per cent. of its weight of fuller's earth, as described above; then the oil is sent through a filter press, which removes the earth and the solid impurities in the oil. Special forms of filter press are made for dealing with oils.

Figure 20 represents a filter press made by Dehne of Halle, which is well adapted for pressing oils. These filter presses are easy to use, while they are efficient in operation.

It is quite possible when using a filter press to render oils, while not quite perfect, yet sufficiently so to be marketable, very quickly, by sending the oil as it comes from the hydraulic press through the filter press. The oil comes out of the latter fairly bright and clear, and will find a ready sale. The solid matter which is filtered out is returned to the kettle to be worked up with the next batch of seed. By this method of working there is produced nothing but oil and cake, no foots of any kind being formed.

Besides fuller's earth, there have been used in clarifying oils other solid matters, such as china clay, infusorial earth, etc., which act mechanically by carrying down the solids in suspension and absorbing the moisture in the oil, so as to leave the latter clear and bright.

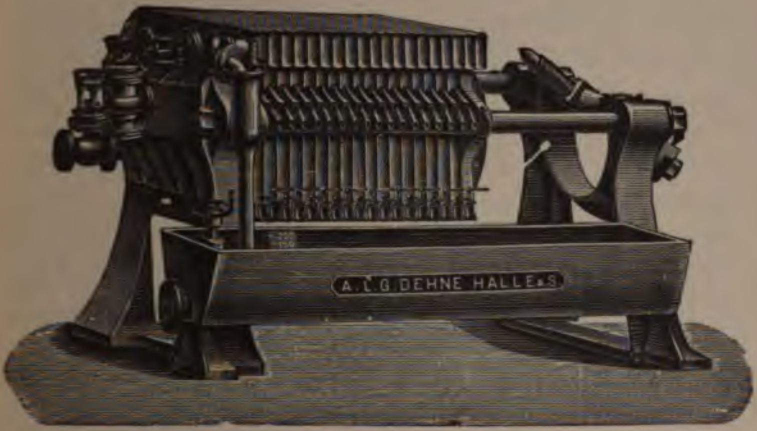


FIG. 20.—Oil Filter Press.

Various processes have been devised for refining oils by chemical means; the two agents most commonly used being sulphuric acid and caustic soda. The general method of using these bodies will be detailed.

REFINING OILS BY SULPHURIC ACID.—Sulphuric acid has a powerful action on all organic bodies, chiefly owing to its great affinity for water, which imparts to it dehydrating properties. As regards its employment in refining oils, its virtue depends on the fact that the extraneous vegetable matters found in crude oils are more easily acted upon by the acid than is the oil itself. Too much acid must not however be used, or otherwise there is risk of it acting on the oil and thus leading to loss. The usual plan of treating the oil is to place it in a suitable receptacle, a copper tank or iron pan, which should either contain a steam coil or, better still, be jacketed; means of agitating the oil and acid together should be provided, which may take the form of a mechanical agitator, or a current of air may be blown in during the operation. It is advisable for the bottom of the tank to be made conical for the purpose of a more effectual separation of the oil and acid, and a tap provided at the bottom of the cone for the purpose of running off the acid which collects. Many modifications of the process have been published from time to time. It will however be found hat the details will have to be varied according to the oil which is being treated. Some oils come from the presses much purer than others. Such oils will require a less severe treatment than those which contain a large proportion of vegetable matter. Strong sulphuric acid should never be used; its action is too severe, and cannot well be controlled. It is always advisable to use a mixture of sulphuric acid and water—the proportion may vary according to the oil which is being treated—1 of acid to 1 of water is a very good ratio, while some oils may require an even weaker acid than this. Hartley recommends for linseed oil 1 of acid to 2 of water; if the oil be very impure, then the ratio 2 of acid to 1 of water may be used.

The oil to be treated is run into the tank and heated to about 110° to 115° F.; the latter temperature should never be exceeded, while it may happen that lower temperatures than 110° F. may be used. Then the mixture of oil, acid, and water is added, with constant agitation and in a slow stream, to the oil. The proportion used must vary according to circumstances, and sometimes 1 per cent. of strong acid will be sufficient, in other cases 3 per cent. may be used. The last-named quantity should, however, not be exceeded. It would be better to give the oil two treatments with a smaller proportion of acid. The oil and acid are thoroughly stirred together for about half an hour, then the mass is allowed to rest for twenty-four hours. At the end of this time 6 or 7 gallons of warm water at 150° F. for every 10 gallons of oil treated are mixed with the oil, and then the mass is allowed to stand for some days until a perfect separation of oil and acid liquor takes place. The oil is drawn off and washed again with water to free it from all traces of acid. The acid "foots," as they are called, are run away.

This method of refining is applicable to almost all seed oils, and is largely used in connection with linseed oil, rape oil, colza oil, nut oil, and also with fish oils. If it be used with any oils intended for lubricating machinery, it is necessary that the oil should be well washed with water to free it from all traces of the acid used in refining, which, if left in, might have a deleterious action on the metal of the bearings to which it is applied.

The acid treatment will not affect any free fatty acid which the oil may contain; any such will be left in the oil after the treatment is finished.

It has been recommended to use a strong solution (100° to 130° Twaddell) of zinc chloride, using from 1½ to 2 per cent. of the oil. This has no action on the oil itself, but it dehydrates it and coagulates all albuminous and vegetable matter the oil contains. It costs more to refine oils by zinc chloride than by sulphuric acid.

REFINING OILS BY CAUSTIC SODA.—A good many oils are refined by using caustic soda, in fact some, cotton-seed oil for example, cannot well be refined by other means, while to obtain certain qualities of oil an alkaline treatment to free the oil completely from acid constituents is necessary. Colza oil, for instance, is much used for illuminating purposes; if it contains any notable proportion of free acid it is rendered unsuitable for this purpose, hence an alkaline refining process must be used with colza and other burning oils.

Alkaline processes not only free the oil from extraneous vegetable matter, but they remove any traces of resin, acid and colouring matters which the oil may contain, leaving a perfectly neutral and pure oil. Greater care is required in carrying out an alkaline process than is required for an acid process. This is due to the fact that, while the acid has no material action on the oil itself, and therefore little loss is likely to take place, the alkali has some action in the direction of saponifying the oil, and thereby a loss may occur. On the other hand, while the foots obtained with the acid treatment are useless, those obtained from the alkaline process may be made use of.

The process is comparatively simple. The oil to be treated is run into a suitable vessel; an iron tank serves very well. The requisite quantity of caustic soda lye is added, and the whole thoroughly agitated together for some time and then allowed to settle, an operation which may take some time, when two layers will form, one of a watery fluid containing much soapy foots, the other of clear oil. The watery fluid is drawn off into a tank, fresh weak alkali is run in, and the mass treated as before, after which the purified oil is well washed with water to free it from alkali.

The strength and proportion of alkaline solution used will depend upon the character of the oil to be treated. With all ordinary oils a lye of 8° to 12° Twaddell may be used. Crude cotton-seed oil requires a stronger lye, one of from 15° to 20° Twaddell, while coconut oil can be refined with a lye of about 5° to 6° Twaddell. The quantity used will depend upon the amount of acidity of the oil which is being treated, the quantity of resinous matter it may contain, and the amount of colouring matter. Hence few rules can be given as regards quantity of alkali to be used. Generally ½ to 1 per cent. of caustic soda will suffice.

Occasionally trouble arises from the formation of emulsions which prevent the proper separation of the oil from the alkaline liquor. When this happens it is best to add a little solution of salt, sufficient to throw out the oil.

In some cases the oil has been treated with soda crystals melted by heat in their water of crystallisation. After being well mixed the mass is allowed to stand, when, as a rule, it easily separates into three layers, one of oil, the second of soapy matter, and the third of watery liquid.

When the oil is fairly free from mucilaginous matters, and is of poor quality in consequence of its containing much free fatty acid, this may be removed by agitating the oils with a weak solution of caustic soda or of carbonate of soda, but usually it will be found easier to treat them with milk of lime or with magnesia, followed by filtering from the lime or magnesia soaps which are formed.

Oil Foots.—In the alkali method of refining oils a large quantity of "foots" is formed. These may be utilised in various ways according to their character. One very good method is to work them up for soap-making in conjunction with other fats. Cases however occur where, owing to their being strongly coloured as in the case of cotton oil foots, this cannot be done. The best plan of dealing with such is to decompose the foots by weak sulphuric acid and distil the liberated fatty acids, etc. There is then obtained a distillate containing glycerine (from any undecomposed glyceride which may be present in the foots) and fatty acid. The residue in the retort takes the form of "pitch," and will consist of the resinous matter present in the foots. The fatty acids which are obtained are not quite pure, but contain small quantities of hydrocarbon bodies produced by decomposition of the fatty matter by the heat employed in distilling.

Other processes for refining oils have been devised, but those just described are what are in common use in oil refineries.

BLEACHING OF FATS AND OILS.

As obtained by the processes described above, the oils and fats are often more or less coloured. In vegetable oils this colour is necessarily due to the presence of natural organic colouring matters, chlorophyll, erythrophyll, etc., present in solution in the oil. Linseed oil, brown rape oil and palm oil are examples of such oils which are strongly coloured. Very often in the processes of refining, such as have been described above, a large proportion of the colouring matters is removed, but traces of them will remain in the refined oils. Animal oils and fats are usually free from colour. Any such that may be present is generally due to exceptional circumstances.

There are a number of ways by which the colour can be removed from oils. A process which may give good results with one oil may not do so with another. In some cases it is sufficient to agitate the oil at a temperature of 120° F. with animal charcoal, followed by filtration. Blowing hot air through will in some cases (palm oil) destroy the colour. Air and light bleaching are sometimes resorted to, but in some cases it is necessary to make use of chemical reactions.

Bleaching by Hot Air.—By blowing a current of hot air at about 130° F. many fats and oils can be decolorised. Tallow, lard, and palm oil may be treated in this way. It is not desirable that the action should be prolonged, or otherwise there is some risk of the oxidation of the oil. It is important that the air should be dry.

Figure 21 is a drawing of an apparatus made for bleaching palm oil by air devised by Messrs. Korting Bros. This consists of a cylindrical vessel of any convenient size to suit the quantity of fat that is being treated. K is a closed steam coil by means of which the fat can be heated up to any required degree. E is a tube open at the top and terminating in a ring at the bottom inside the vessel, this ring having perforations. H is a draw-off valve. C is an injector worked by steam which enters at A, B is the regulating valve.

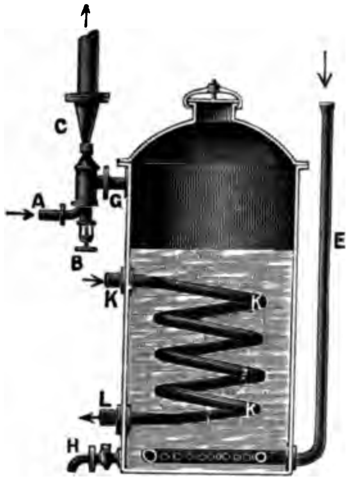


FIG. 21.—Apparatus for Bleaching Palm Oil.

By the action of the injector air is drawn from the upper part of the vessel and therein creates a vacuum which is filled by air being drawn in through E from the outer atmosphere and which rises in bubbles through the fat, bleaching it. The operation is comparatively simple and is continued until a sample of the oil drawn from H shows that the bleaching has been carried far enough. It may be mentioned that the top of the vessel is fitted with a tight-fitting cover so that it may be hermetically sealed up.

BICHROMATE OF POTASH PROCESS.—Watts has devised a process for the bleaching of oils by means of bichromate of potash, which is largely used, especially for bleaching palm oil. It is carried out in the following manner: The oil to be bleached is heated at about 120° to 130° F., then a quantity of bichromate of potash, about 22 to 28 lb. per ton of fat, previously dissolved in a little water and thoroughly mixed with the fat, then hydrochloric acid to the extent of about 2 or 2½ per cent. of fat is added and also thoroughly mixed with the material. In the case of bleaching palm oil, the reddish orange colour changes first to a brownish green, and finally to a light green, the entire operation only taking a few minutes. Wet steam is now blown through for a few minutes, and then it is allowed to stand for some hours. The bleached oil is separated out and is skimmed off, and then washed with clean water to take out all traces of acid and chrome. Instead of hydrochloric acid, sulphuric acid may be used, but it does not give good results. This process can also be used for other fats and oils.

CHLORINE PROCESS.—Chlorine is a powerful bleaching agent which may be employed for the purpose of bleaching fats and oils. It is necessary, however, that great care should be taken in using it on account of the fact that chlorine is a colouring agent in oils and fats, excess resulting in the formation of products which have deleterious effects upon them. The most convenient plan of working is to mix the fat with a solution of bleaching powder, using about 2 lb. to 1 ton of fat or oil, then about three times the quantity of hydrochloric acid is added, and the whole stirred together; then the mixture is allowed to settle, the fat taken off, and the acid liquor run away. One advantage of the chlorine process is that it acts as a deodoriser to rancid fats. In the case of fats and oils which are strongly coloured, it is advisable to give them two treatments rather than to attempt to bleach them at one operation.

In place of using bleaching powder there may be employed potassium chlorate at the rate of 2 to 4 lb. per ton of fat; about twice the quantity of hydrochloric acid is added, and the operation done at a temperature of 150° F.

Sun Bleaching.—This is commonly carried out by exposing the oils and fats in colourless glass bottles to sunlight. From time to time the oil or fat is poured from one bottle to another with a view to exposing fresh portions to the action of the sunlight. This method is slow but is often employed, especially for castor and other oils used for medicinal or food purposes.

The processes above described are those which are commonly employed in bleaching oils and fats. Different refiners, however, have various modifications of different processes, which they have found to work well with the plant and appliances they have in use. Such modifications are often regarded as "trade secrets."

SOLVENT EXTRACTION PROCESSES.

All oils and fats are soluble in such bodies as ether, carbon bisulphide, benzoline, benzol, carbon tetrachloride, etc. This property is taken advantage of both in the laboratory and on the large scale for the purpose of extracting fats and oils from substances containing them. The principle on which all such apparatus works is that of treating the fat-containing substance with the solvent in a suitable vessel, then running the solution into a still or retort and distilling off the solvent. The fat remains behind in the still, while the solvent is recovered and used over again. The best possible solvent is one that has great solvent properties for oils, can be distilled completely by means of steam, is free from odour and non-inflammable. The only substance among those named above which answers these conditions entirely is carbon tetrachloride, but unfortunately it is expensive.

Benzoline is commonly used for this purpose. It is light, has strong solvent action on oils, and is cheap It has one disadvantage, as it does not entirely volatilise by means of steam; consequently there is a tendency for a little of the benzoline to remain behind in the oil; again, it is very inflammable, and great care is needed in working with this solvent. Carbon bisulphide is one of the best solvents to use. It is volatile at the temperature of boiling water. Being heavier than water, it can be kept in tanks under water, thereby reducing the risk of danger from explosion or fire. It has unfortunately rather a noxious odour, which makes it unpleasant to work with. This odour is however largely due to impurities that come from the materials from which the carbon bisulphide is made. By repeated use this odour becomes less offensive and unpleasant.

Benzol is a hydrocarbon obtained during the distillation of coal tar. It is freely volatile at the temperature of boiling water, and has strong solvent properties. It is highly inflammable, and therefore great care must be taken in working with it.

DIETZ APPARATUS.—A very convenient form of apparatus for the extraction of oil by bisulphide is that of Dietz, as shown in figure 22. This consists of an extraction tank B, in which is placed, between perforated plates at top and bottom, the material from which the oil is to be extracted; by means of a pump, carbon bisulphide, contained under water in the tank A, is passed through the extractor, and so abstracts the oil from the materials; from the extractor, the carbon bisulphide containing the oil flows into the still or retort D, where the carbon bisulphide is distilled off by steam, and is condensed in the coil condenser and flows back into tank A to be used over again. Residual oil left in the still D is run off from time to time by means of a discharge pipe. This plant is small and easy to work.

Figure 23 is a drawing of a small plant which can be made in any convenient size and used with any kind of solvent. It consists of three portions. First, the centre vessel which forms the extractor. The material is put in at the top, which is fitted with a lid which can be hermetically closed. In this extractor there is also a perforated false bottom, on which the fatty materials are placed. Under this is a retort or still which can be heated by steam. This still communicates with the extractor by means of a tube, which proceeds from the bottom of the extractor and rises up alongside it to nearly three-fourths of its height, and then turns down and enters into the still, ending near the bottom. From the top of the still a pipe passes to a condenser placed above the extractor, the end of the condenser worm passing into the top of the extractor. This plant is

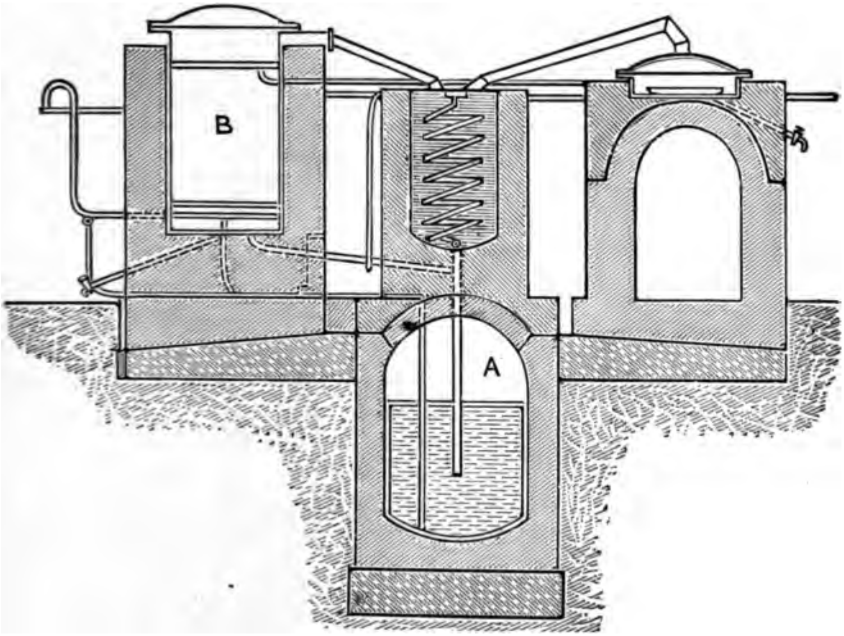


FIG. 22.—Apparatus for Extracting Oils.

used in the following way: The fatty material is placed in the extractor and the required quantity of solvent in the still; by means of a steam coil the solvent is volatilised and passes into the condenser, where it is condensed, and flows as a liquid into the extractor; here it gradually accumulates, dissolving out the fat until its level rises above the level of the bend in the syphon tube, when it flows into the still; here it gets volatilised again and passes through the same cycle of changes. The fatty matter which it had in solution, however, is left behind in the still and can be run off from

FIG. 23.—Oil Extracting Plant.

time to time, as required, through a discharge pipe placed on the bottom of the still.

Another method of extracting, using benzoline, is to have two large upright boilers side by side. Each is divided into three portions by partitions—the middle portion is the extractor and is provided with two manholes, one at the top for charging, the other at the bottom for discharging; the lower portion forms the still and is fitted with steam pipes; the top portion contains a condensing arrangement. This apparatus is used in the following manner. The extractors are filled with the oily material. Benzoline is placed in the still of one and is vaporised by means of a steam coil; the vapour, passing upwards into the condenser of the other boiler, is there condensed to a liquid and flows down through the oily material into the still, carrying with it the oil. When all the benzoline has been vaporised off from the original still, the action is reversed and the benzoline distilled back again; the oil it held in solution is, however, left behind in the still. The action is allowed to go on until all the oil is removed from the raw material. This is then run off from the still to a storage tank.

The extraction of oils by means of volatile solvents is in itself very simple. The crushed seed or other oil-bearing material (dried fish, etc.) is placed in a closed vessel. Benzine, petroleum spirit, bisulphide of carbon, ether or any other suitable solvent is passed through it, and allowed to flow into a retort, carrying with it the oil in solution and leaving the exhausted substances in the extractor or macerator. The solvent in the retort is now distilled off and condensed for re-use, while the pure oil is left behind in the retort. So far, the process is very simple, but there are many difficulties: one consists in recovering the solvent from the waste product in the extractor. This part of the apparatus consists essentially of a large tank, with inlet and outlet pipes or the circulation of the solvent, and steam connections to drive off the residual solvent after the material in it has been exhausted.

These extractors must necessarily be of a considerable size, and, when extraction has been completed, there is left behind a large bulk of residual material, starch and husks (in the case of seeds), saturated with solvent which ought to be distilled off before the extractor is emptied. This is necessary for two reasons. First, because the manufacturer could not afford to lose all this solvent; secondly, because its vapours are inflammable, and might become a source of danger if allowed to escape freely. And herein lies the chief difficulty: the material left in the extractor is a bad conductor of heat, and therefore it is very difficult to heat the mass, when in large bulk, sufficiently throughout to ensure complete volatilisation. To this a second difficulty is added, by the fact that the volatilisation of the solvent has the tendency of greatly depressing the temperature in those parts which are not easily reached by the heat of the steam.

This difficulty is only partially overcome by admitting steam into the extractor, as what volatilises in the lower part condenses again in the upper layers, until the whole mass is sufficiently heated throughout, which, on account of the non-conducting properties of the material, is achieved after many hours only. But, when the solvent has to be thus driven off by live steam, the material is being cooked at the same time, and when taken out is in a moist state, which in many cases is detrimental to what otherwise would be a valuable product.

The residual meal cannot be stored in this condition, as it soon spoils, and is only fit for manurial purposes.

The apparatus shown in figure 24 was designed to overcome all these defects. The difficulty arising out of the

1.

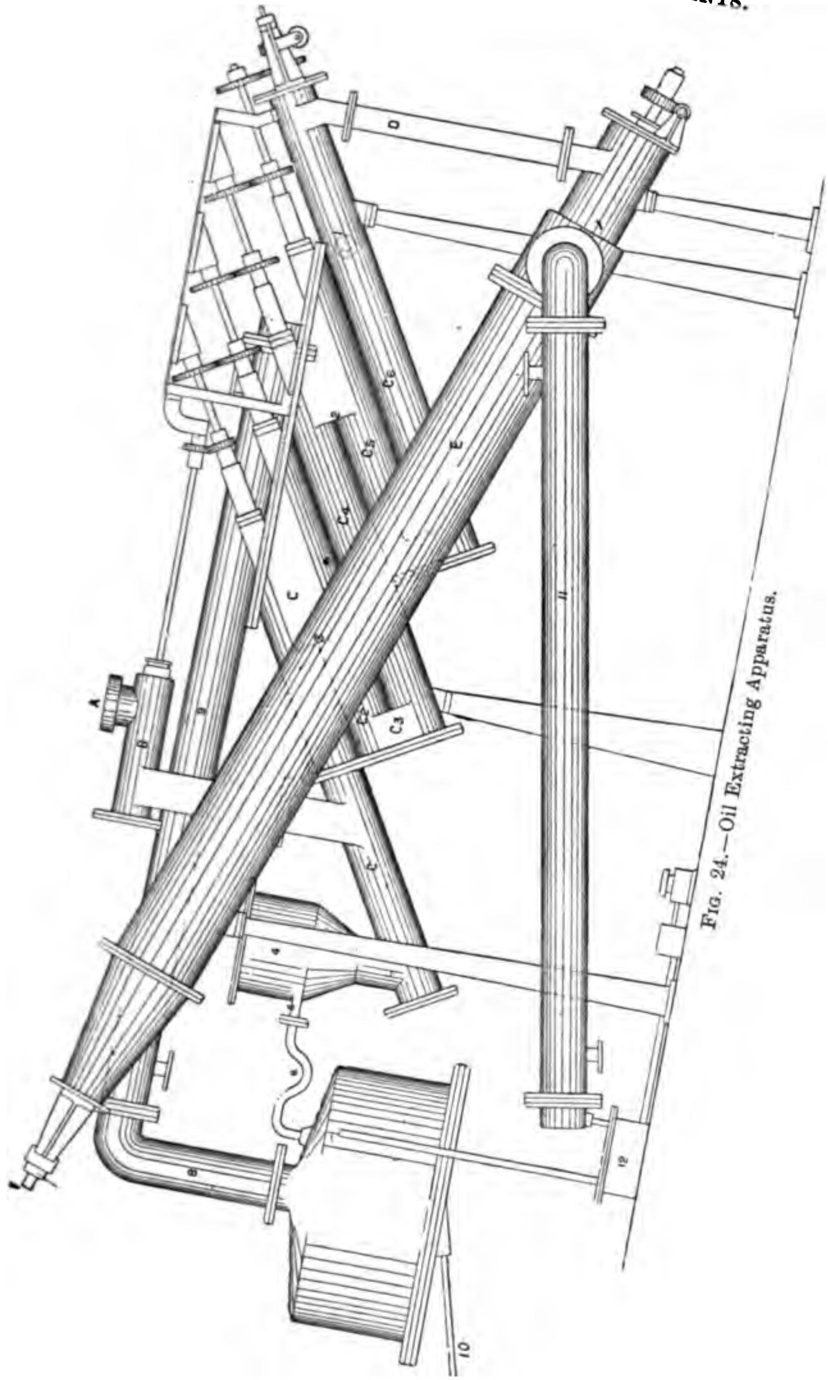


FIG. 24.—Oil Extracting Apparatus.

unmanageableness of the material while in bulk has successfully been conquered by treating small and successive quantities at one time. This is being done by practically reversing the older process. That is, instead of passing the solvent through a large mass of material, here the material to be extracted is passed through the solvent, the latter flowing at the same time in the opposite direction.

In what manner this is effected will be best understood by a reference to the accompanying drawing. C, C2, C4, C5, and C6 are cylinders alternately communicating with each other at top and bottom, in which are working screw carriers. The material is fed in at A (which, when not at work, is hermetically closed by a water seal) and carried forward by a screw working in B, and falls down the vertical shoot into C. Here it is carried upwards by a screw to Cl, where the first cylinder communicates with the second and falls on to the screw working in C2, is carried downwards and falls through communicating channel C3 on to the next screw. This again carries the material in an upward direction and to C4, whence it is carried downwards in C5, up again in C6, in the upper part of which there is a squeezing arrangement to express the excess of solvent, and falls then through D into kiln E, which is provided with a steam jacket and forward screw, where the exhausted material is deprived of the residual solvent. This is easily effected, as the material is spread out in a thin layer over a large heated area. The vapours, which are considerably heavier than the air, and hence have a downward tendency, are allowed to escape at the lower end of the kiln, are condensed in their passage through the condenser 11, collected in receiver 12, and pumped back into the machine at 1. While the material thus travels from left to right, the solvent flows in an opposite direction, whereby the partially extracted meal, etc., meets in each successive cell with a purer stream of solvent, thus ensuring nearly complete exhaustion. On the other hand the solvent comes successively in contact with material richer in oil, finally passing into the first cell (the last as regards the direction of the solvent), where it meets the largest quantity of oil, passes through a filter H, and thence into a retort. This latter part of the apparatus is provided with several trays, each steam-jacketed, over which the mixture of oil and solvent flows in a thin stream; the solvent being volatilised and condensed in 9, while the oil flows out in a continuous stream at 10. The apparatus is sealed by water throughout.

ANIMAL AND VEGETABLE SOAP OILS.

TALLOW.

Tallow is, or should be, derived from the fat of cows, oxen, sheep, goats, and similar animals, the best fat being taken from the thicker deposits which surround the abdomen, known generally among butchers as the skin, although it is known by other names in some places. Anatomists call it the *omentum.* Tallow is also obtained from the fat surrounding the large muscles, the kidneys, and the other organs of the body. Fatty matter can be and is obtained from other parts of the animal, such as the intestines, bones, etc., and such fat is often sold as tallow; sometimes with a qualifying distinction as bone tallow; at other times, and this wherever possible, without such a qualifying description. Whenever tallow is dealt in as tallow, it is always understood to be the fat obtained from the parts above-named, and the sale of any other kind of fat should be regarded as a fraud upon the buyer.

The deposit of tallow as it exists in the animal body is found to be contained in small cells or bladders of animal tissue. The reason for its being in this condition is that being a liquid and therefore able to move with every motion of the parts, yet it is not able to flow from the spot in which it is found. As it is taken from the body, the crude fat is known as butcher's fat, and is usually purchased from the butchers by the tallow refiner, who, if he be located in a large town, often distinguishes between "town fat" and "country fat," the former being usually fresher, and therefore yielding a better quality of tallow than the latter. The idea or principle which underlies all processes for the extraction of the tallow from this rough fat is to separate out by some means the animal tissue from the actual fatty matter, a process which is known as rendering. The various means which have been adopted to do this have been described, p. 68 *et seq.*

Of fatty matters obtained from other parts of the animal body, the intestines give what is called "tripe tallow," the feet yielding "neatsfoot oil". The processes for extracting these greases or fats do not differ essentially from those described above, but, as a rule, they are obtained by simply boiling the various parts of the animal in water, and skimming the fat which is obtained from the top of the water where it collects, whilst the tripe and feet are used as food.

A great deal of fat largely used in making soap is now extracted from bones, and sold as "bone grease," "bone fat," "bone tallow," and not seldom, wherever possible, as tallow. All bones do not contain tallow or fat; the best are cows and bullocks' shank bones, which are hollow, and contain a fairly large proportion of good fat, often separately extracted and sold as "marrow tallow". The more solid bones found in the animals do not contain much fat, and scarcely pay for its extraction. Horses' bones contain so little fat they are not worth the process of treatment. In dealing with bones it is therefore worth while to sort them into those which are worth treating for the fat and those which are not worth so treating. The method of extraction is given on p. 76.

Tallow comes into this country from all parts of the world. Now, it is a well-known fact with regard to natural products obtained from various localities that they vary somewhat in appearance, colour, odour, and consistence, etc., to say nothing of minor differences in chemical composition. Tallow is no exception to this rule, hence in the tallows which are sent into England from North America, Australia, Russia, India, etc., there are certain minor differences by which experts can tell the locality from which the tallow came. There can scarcely be any doubt but what these differences are caused by the character of the food on which the cattle feed in the various localities, and which must vary to a great extent. Commercially, tallows are distinguished according to their country of origin, and of the cattle—oxen or sheep, or into beef or mutton—from which they are obtained. Russian tallow comes chiefly from Cronstadt, Odessa, Taganrog, and St. Petersburg. It is derived chiefly from oxen, and is a hard, yellowish tallow, better suited for candle-makers than for soap-makers. A large proportion of the Russian tallow finds its way from Siberia, but no distinction is made between this tallow and that from other parts of Russia. South America sends both "beef" and "mutton" tallow. It is chiefly shipped from the River Plate ports. It is of a strong yellow colour, and usually of fair quality, and serviceable for all uses. North American tallow is of very good quality, rather paler in colour than South American, and is the favourite tallow of soap-makers. It is mostly "beef" tallow that comes from North America, but "mutton" tallow is also sent over. Australia also sends large quantities of both "beef" and "mutton" tallow of fairly good colour and quality to England. The value of the tallow depends on its consistence—the harder the tallow the higher its melting point, and the more valuable it is. These points vary very much within certain limits, which will be presently pointed out.

The chemical composition of tallow varies somewhat according to the method of feeding and the locality as well as the kind of tallow. Tallow consists essentially of the two glycerides, olein and stearin, the latter predominating, forming from 60 in soft to 80 per cent. in hard tallows. Margarine is also probably present in some tallows, while there are also nearly always small quantities of animal tissue, colouring matter, water; but these should not altogether amount to more than from ½ to 1 per cent. of the total. Beef tallow contains more olein than mutton tallow, so that it is rather softer in consistence, and therefore better adapted for soap-making and lubricating and for making tallow oil, whereas mutton tallow is more suitable for the candle-maker. The specific gravity of beef tallow ranges from 0·935 to 0·939, while that of mutton tallow ranges from 0·937 to 0·940 at 60° F. (15°C.); while at 212° F. (100° C.) the specific gravity is from 0·860 to 0·862. The melting point of tallow varies very considerably, usually ranging from 36° to 49° C. (97° to 120° F.)—the lower limit is that of a soft tallow, while the higher limit is a hard tallow. 39° C. (102° F.) is the average melting point of tallow. After being melted it begins to solidify at rather lower temperatures, from 33° to 46° C. (115° F.), but at the moment of solidifying the temperature rises a few degrees. When pure, tallow should be white, fairly firm, and without much odour and taste. It is soluble in from 40 to 44 times its volume of alcohol. Generally it contains a small quantity of free acid, ranging from 0·75 to 7 per cent., although occasionally samples with larger quantities are met with. For soap-making, the presence of free fatty acid is not detrimental, but rather otherwise; but for lubricating machinery it is decidedly disadvantageous.

When melted tallow is allowed to cool very slowly at a temperature of not less than 27° to 30° C. (80° to 86° F.), it forms a granular mass, the stearin crystallising out in the form of small nodules which can be separated out from the more fluid mass by pressure. The process is known as "seeding," and is largely applied to the separation of the stearin of the tallow for use in making candles, while the liquid which passes through the press is known as "tallow oil," and is used for lubricating machinery and soap-making.

When boiled with caustic alkalies, tallow is converted into soap. Of caustic soda, tallow usually takes about 13·79 to 13·85 per cent. to completely saponify it, while of caustic potash it requires 19·32 to 19·38 per cent. The alkalies being in both cases taken as chemically pure, of the ordinary commercial products more will be required, according to the strength of the article, which varies very much. When the soap formed by boiling tallow and alkali together is treated with acid, the fatty acids of the tallow are separated and usually are found to amount to 95 per cent. of the tallow used. The melting point and specific gravity of these fatty acids vary with the quality of the tallow.

Tallow is frequently adulterated. Among other bodies have been used soft fats from other parts of the animal, such as bone or tripe tallows, cotton-seed oil, seal oil, stearin from wool grease, among fatty matters, to say nothing of china clay, starch and similar products. It is by no means an easy matter to detect some of these adulterants: cotton-seed oil stearin is very difficult to detect. The specific gravity of the fat at 109° C., or the melting point, is some guide, while the large proportion of solid fatty acid would be a clue to its addition. Cotton-seed oil can be detected by its reducing the specific gravity, melting point, and increasing the proportion of liquid fatty acids, as well as by the silver nitrate and iodine test. Stearin from wool grease can be detected by the tallow containing a large proportion of fatty acid, as well as by the silver nitrate test. Bone grease can be detected by the tallow containing phosphate of lime, which is a characteristic ingredient of bone grease. The addition of such matters as china clay and starch can be detected by melting the tallow and allowing these insoluble matters to settle out. Such forms of adulteration are now rare, and show unskilful work on the part of the adulterator. Paraffin wax and scale and mineral oil are sometimes added; these may be detected by their reducing the percentage of potash required to saponify the tallow and by the sample having a low flash point (under 400° F.).

Tallow is now rarely used for lubricating machinery. At one time it was largely used for lubricating steam engine cylinders, but it has been superseded by the petroleum cylinder oils. It is used now in small quantity for lubricating heavy engine bearings—bearings of rolling mills—and for making lubricating greases.

Tallow is more largely used for soap-making than any other fat that is known; it gives a good soap—hard and of a good white colour. This, however, is modified by the colour of the tallow, and the care taken in making the soap. The grain of tallow soap is good and uniform; it is not readily soluble in water, and on that account it does not lather so freely as some soaps do. On the other hand, it is not so wasteful in use: its cleansing powers are excellent, and it keeps well, not acquiring any objectionable odour or becoming rancid on keeping. It is rather troublesome to saponify, but by the exercise of a little care on the part of the soap-maker this can be easily got over.

CONSTANTS OF TALLOW.

Specific Gravity at 15° C. (60° F.) . . 0·943 to 0·942.
„ „ 50° C. (122° F.) . . 0·895.
„ „ 100° C. (212° F.) . . 0·862.
Melting Point, 42° to 46° C. (107° to 115° F.).
Solidifying Point, 36° C. (98° F.).
Insoluble Fatty Acids (Hehner Value), 95 to 96 per cent.
Saponification Value (Koettstorfer Test), 19·3 to 20 per cent. KOH.
Iodine absorbed (Hubl Test), 39 to 44 per cent.
Reichert Value, 0·25 c.c. $\frac{N}{10}$ KOH.
Viscosity at 120° F. . . . . 53.
„ „ 150° F. . . . . 35.
„ „ 212° F. . . . . 25.

CONSTANTS OF FATTY ACIDS FROM TALLOW.

Specific Gravity at 100° C. (212° F.), 0·8698.
Melting Point, 43° to 44° C. (108° to 110° F.).
Solidifying Point, 42° to 43° C. (107° to 108° F.).
Molecular Weight (Combining Weight), 284.
Iodine absorbed (Hubl Test), 40 per cent.

LARD.

Lard, as is well known, is the fat obtained from the leaf and other parts of the pig. It is almost entirely used for culinary purposes and but rarely for industrial uses. It is used to a limited extent in soap-making, and then only in making the best grades of toilet soaps where a good white colour is desired, lard in regard to these points ranking with coconut oil. Lard is a soft fat of a consistency equal to or slightly harder than butter, melting to a clear, water-white oil; its consistency varies slightly in different samples. It is white in colour, although sometimes it may have a faint yellowish or creamy tint; its odour and taste are sweet and pleasant, and if well refined it keeps well; it saponifies freely, forming a good white hard soap with soda, and a white soft soap with potash. It consists essentially of a mixture of stearin and olein in somewhat varying proportions, from 60 to 65 per cent. of olein and 35 to 40 per cent. of stearin; there are also small quantities of palmitin present. Lard is subject to adulteration, the usual ingredients added being fat and cotton-seed oil. Lard soap has a good white colour, uniform texture, and lathers freely in water, being superior in this respect to tallow soap; it is free from any strong smell and does not go rancid.

CONSTANTS OF LARD.

Specific Gravity at 15° C. (60° F.) . . 0·931.
„ „ 50° C. (122° F.). . . 0·881
„ „ 100° C. (212° F.) . . 0·858.
Solidifying Point, 27·1° to 29° C. (80° to 84° F.).
Melting Point, 40° to 42° C. (104° to 108° F.).
Insoluble Fatty Acids (Hehner Value), 96 per cent.
Saponification Value (Koettstorfer Test), 19·5 per cent. KOH.
Iodine Value (Hubl Test), 59 per cent.

CONSTANTS OF FATTY ACIDS FROM LARD.

Specific Gravity at 100° C. (212° F.), 0·844.
Solidifying Point, 39° C. (102° F.).
Melting Point, 43° C. (107° F.).
Combining Equivalent (Molecular Weight), 280.
Iodine Value (Hubl Test), 64·2 per cent.

BONE GREASE.

This fat is largely used in the manufacture of the cheap sorts of soaps, both domestic and manufacturers' soaps, either alone or in admixture with other fats and oils. Its preparation has already been described. As usually sold it is in the form of a greyish-coloured, granular soft fat, its consistence being between tallow and lard. It has a slight odour when fresh, which often develops into an unpleasant one if the fat becomes rancid. It contains some water, the amount varying from 2 to 6 per cent., small quantities of animal tissue, from 0·5 to 1 per cent., the latter being rather an excessive proportion; the proportion of free acid in bone grease is rather higher than in tallow, the amount ranging from 7 to 21 per cent.; then small quantities of phosphate of lime are present—this constitutes a characteristic test for the presence of bone grease. Two samples of such a grease examined by the author had the composition :—

	No. 1.	No. 2.
Water	3·17 per cent. ...	2·28
Free acid	21·71 „ ...	6·97
Unsaponifiable oil ...	0·28 „ ...	0·32
Saponifiable oil ...	74·84 „ ...	90·28
Phosphate of lime ...	Traces ...	·15
	100·00	100·00

Owing to the variable quality of bone fat it is advisable to test it for moisture, etc., before buying.

The water it contains may if thought necessary be got rid of by melting the fat and keeping it in a melted condition for some hours.

The colour of bone fat varies a great deal, but as a rule this is of little detriment to its soap-making properties, as the colour generally finds its way into the soap lyes, and a pale soap, rather softer than a tallow soap and a little more soluble in water, is obtained. Bone-fat soap still retains some of the odour of the fat, and so if used for domestic soaps some scent is required to disguise this odour; if used for manufacturing soap the odour is of little consequence.

ANIMAL SOAP FATS.

Besides tallow and bone grease which are regular articles of commerce there are other solid greases of animal origin which are offered in occasional parcels to soap-makers; such are: tripe tallow, horse fat, skin fat, etc.

These are only fit to be used to make the commonest class of soaps, such as scouring soaps, rough mill soaps; they are usually of a soft consistency, and vary in colour a great deal, some are a shade darker than tallow or bone-fat, but others are of a brownish tint; their odour likewise varies considerably, from being comparatively sweet to having a rancid odour. They make soaps of a consistence and quality rather softer and poorer then tallow. If anything they are rather easier than tallow or bone-fat to saponify. They are very variable in composition, some contain water, others traces of unsaponifiable fats, some contain large quantities of free acid. The author has had occasion to examine many such soap greases during the last few years and the following are the results of some of these analyses:—

	No. 1.	No. 2.	No. 3.	No. 4.
Water, animal tissue ...	0·90	5·69	6·40	3·23
Free fatty acid	51·88	18·76	49·06	34·96
Saponifiable fat	42·42	69·17	44·15	53·07
Unsaponifiable oil ...	4·80	5·38	0·39	8·74

The large proportion of free acid in Nos. 1 and 3 is to be accounted for by the fact that some distilled stearin has been added to them.

TALLOW OIL.

Tallow oil is obtained from tallow by melting and keeping the tallow in a warm room at about 80° to 90° F. for some hours; the stearin it contains crystallises out in the form of small granular particles, hence this process is known as seeding. The seeded tallow is then placed in canvas cloths and put under hydraulic pressure, when the olein it contains comes out, together with a little of the stearin, and forms the tallow oil of commerce. It is also sold under the names of ox oil, animal oil, etc. Its chief use is for lubricating machinery, but it is used for making soap when a white soap, rather softer and more soluble than a tallow soap, is required. Tallow oil varies much in consistence, some samples are more fluid than others; this depends upon the proportion of stearin which the oil contains; if there is much, then the oil is solid; if little, then it is liquid. The specific gravity varies for the same reason from 0·911 to 0·915. Tallow oil contains a varying proportion of free acid from nil in well-prepared samples to 15 or 16 per cent. in others. Tallow oil should be quite white when cold, or have at the most a faint yellow tint. When melted it ought to be quite clear and bright, free from any cloudiness or floating particles of any kind. It has only a slight odour of an animal fat.

LARD OIL.

Lard oil, like tallow oil, is not much used in soap-making, finding its principal use in lubricating machinery. It is prepared from lard by the same process as tallow oil is made from tallow. It resembles the last oil in its properties and uses. It is if anything rather lighter in colour and has less odour, which resembles that of lard.

VEGETABLE SOAP OILS AND FATS.

PALM OIL.

Next to tallow palm oil used to be the fat most used for making soaps, but of late it has been displaced by cotton oil which is cheaper and gives a better soap for the general run of domestic purposes.

Palm oil is obtained from the fruit of various species of palm trees, natives of the oil regions of the west coast of Africa. The tree which yields the largest proportion of the palm oil of commerce is the *Elaiis Guinensis.* The fruit of the palm is about the size of a small plum, and hangs in bunches from the trees. Like the plum it contains an outer pulpy mass and an inner kernel. From the outer pulp is obtained the palm oil, while the kernel yields palm-nut or palm-kernel oil, also used in soap-making, but which has different properties to palm oil.

The natives of the oil regions employ a variety of methods for the purpose of extracting the oil from the fruit. The commonest plan consists in stacking the nuts as they are taken from the tree in heaps for from seven to ten days, when by the decomposition of some of the vegetable tissues surrounding the husk of the nuts the husk can be readily removed, leaving the internal pulp and kernel. The pulp is of a rather hard nature, and to soften it the nuts, after being husked, are thrown into pits and covered over with plantain leaves, then with earth and palm leaves; in this condition they remain for a period varying from three weeks to three months, according to the fancy or practice of the particular tribe of Africans who are making the oil. At the end of the period named the pulp will have been converted into a soft mass; it is now thrown into pits lined with stones, where it is subjected to a pounding process whereby the pulp is separated from the kernels; the former is now thrown into boiling pots and boiled with water, when the oil rises to the top and is skimmed off, any vegetable tissue which may accompany the pulp passing into the water, or the oil may be separated from the vegetable pulp by heating it with water so as to melt the oil, and then squeezing the mass in bags, when the oil flows out.

The quality and consistence of the product depend partly on the particular species of palm from which it is made, but as to this point definite information is required, but more particularly upon the care with which the process of extraction has been carried out, and the length of time the fruit is allowed to remain in the pits.

A long steeping results in the oil being harder, but at the same time its quality is materially decreased; it acquires a rancid odour, its colour is not as bright, and it contains more free acid, indicating that a decomposition into acid and glycerine has taken place; a short steep gives a soft oil of a sweet odour and a bright colour. The process of extracting palm oil being as crude as it can well be, it is evident that the commercial article is far from being all pure fat; it may contain some traces of vegetable tissue, etc., which, being very liable to ferment, will in course of time gradually bring about the decomposition of the oil, resulting in its becoming more or less rancid, and losing its odour and colour.

Palm oil is a solid fat of about the consistence of butter; it has an orange to golden-yellow colour, which is highly characteristic, but is liable to vary very much. Salt Pond and Brass oils have usually a brownish-yellow colour, Lagos oil is a bright orange, Sierra Leone is rather redder, New Calabar oil is a golden yellow; the colour is probably partly dependent upon the species of palm from which the oil is obtained in the first instance, and partly on the process of extraction. Lagos oil is the best and most neutral quality, the proportion of free acid it contains rarely exceeding 10 per cent., and the amount of water and other impurities not more than 2 per cent., and in consistence it is the softest of the palm oils. Brass, so far as freedom from impurities is concerned, comes next to Lagos oil; it is the hardest of the palm oils, and on that account is the quality most in favour with candle-makers; it usually contains a large percentage, 53 to 65, of free fatty acid, and by far the largest proportion of palmitic acid of any variety, hence its hardness.

Salt Pond oil is one of the worst qualities of palm oil to be found in the English market, the amount of impurities often being found to amount to 20 per cent., while the free acid has been recorded by Norman Tait to be as high as 80 per cent., indicating that but little actual oil is present. The colour and odour are usually poor. Half Jack, Bonny, New Calabar oils occupy intermediate positions between these oils in hardness and quality generally. Palm oil has a peculiar violet-like odour, which is communicated to the soap which is made from it.

Chemically palm oil consists of a mixture of palmitin and olein in various proportions, with varying quantities of free palmitic and oleic acids. The specific gravity of palm oil at 15° C. varies from 0·920 to 0·926. The specific gravity at 100° C. ranges from 0·857 to 0·859; the melting point is exceedingly variable, ranging from 25° to 36° C. (77° to 97° F.), the setting point being a few degrees lower. When saponified palm oil yields from 94 to 97 per cent. of fatty acids, the setting points of which range from 41° to 46° C. (106° to 113° F.), the combining equivalent from 273 to 274. Palm oil takes from 19·6 to 20·2 per cent. of caustic potash, KOH, or from 14 to 14·4 per cent. of caustic soda, NaOH, to saponify it.

Palm-oil soap has an orange yellow to yellow colour, depending upon the quality of the oil from which it is made; it also possesses the characteristic odour of the oil which has already been referred to. It is hard, not liable to go rancid, and will keep well, improving in quality in so doing; it lathers fairly well, and is a good cleanser, altogether being a first-class soap. Palm oil may be bleached, which must be done if the oil is to be used for making a white soap. There are many processes available for this work; the best is Watts's by means of bichromate of potash, then it may be bleached by blowing air through it and by other means. These processes have been already described. Adulterated samples of palm oil are scarcely known; the author has not met with one in the course of his practice, nor is the fact that it is adulterated referred to in the text-books on oils.

CONSTANTS OF PALM OIL.

Specific Gravity at 15° C. (60° F.) . . 0·920 to 0·924.
" " 50° C. (120° F.) . . 0·893.
" " 100° C. (212° F.) . . 0·8586.
Melting Point, from 27° to 42° C. (80° to 107° F.)
Insoluble Fatty Acids (Hehner Value), 96·5 per cent.
Saponification Value (Koettstorfer Test), 20·2 per cent. KOH.
Reichert Value, 0·5 cc. $\frac{N}{10}$ KOH.
Iodine Value (Hubl Test), 51 to 52 per cent.

CONSTANTS OF FATTY ACIDS FROM PALM OIL.

Specific Gravity at 100° C. (212° F.), 0·8369.
Melting Point, 50° C. (122° F.).
Solidifying Point, 45·5° C. (113·5° F.)
Saponification Value, 20·6 per cent. KOH.
Combining Equivalent (Molecular Weight), 270.

PALM-NUT OR PALM-KERNEL OIL.

The nuts or kernels of the palm fruit are collected and imported in large quantities into this country for the purpose of pressing the oil from them, which is done in mills similar to those previously described. In some places a very crude method is in use for extracting the oil; the nuts are put into a pan over a fire and charred slightly, some of the oil exudes and is poured off; the roasted nuts are now ground up and boiled with water, the oil they contain rises to the top and is skimmed off; after a short boil the mass of kernel meal is reground up, mixed with a little water and again boiled up, when more oil is obtained. This is skimmed off as before. The oil obtained by this process is of a dark colour and is unsuitable for making good soap.

Palm-nut oil is of white or faintly yellowish colour, of a consistence similar to butter; in odour it resembles coconut oil, from which it can hardly be distinguished. The melting point ranges from 26° to 30° C (78° to 86° F.).

Much depends upon the proportion of oil extracted from the kernel; the first portions which are pressed out are the softest and have the lowest melting point; the last portions are harder and have the highest melting point. It takes from 22 to 24 per cent. of caustic potash, or from 15½ to 17 per cent. of caustic soda to saponify it. In this respect it resembles coconut oil, to which also it approximates in composition, containing a large proportion of the lower fatty acids, lauric, capric, capryllic, and caproic acids, but not to so great an extent as does coconut oil. Oudemans gives the following analysis of palm-nut oil:—

Glyceride of Oleic Acid	26·6.
Glycerides of Stearic, Palmitic and Myristic Acids . .	33·0.
Glycerides of Lauric, Capric, Capryllic and Caproic Acids .	40·4.

Palm-nut oil is fairly clear of free acid and is not liable to go rancid.

In its specific gravity at both 60° and 212° F. it resembles closely coconut oil.

Palm-nut oil is largely used in soap-making in the place of coconut oil; it gives a soap of similar properties.

Palm-nut oil is said to be adulterated with lard, tallow and other cheaper fats and oils. Such adulteration can be detected by means of the saponification value; the distillation test will suffice to detect any adulteration.

CONSTANTS OF PALM-NUT OIL.

Specific Gravity at 15° C. (60° F.) . . 0·952.
„ „ 40° C (105° F.) . . 0·9119.
„ „ 100° C. (212° F.) . . 0·9731.
Solidifying Point, 20·5° C. (71° F.).
Melting Point, 27° to 28° C. (79° to 80° F.).
Insoluble Fatty Acids (Hehner Value), 91·1 per cent.
Saponification Value (Koettstorfer Test), 24 per cent. KOH.
Reichert Value, 2·4 c.c. $\frac{N}{10}$ KOH.
Iodine Value (Hubl Test), 10 to 13 per cent.

CONSTANTS OF FATTY ACIDS FROM PALM-NUT OIL.

Solidifying Point, 20° to 23° C. (71° to 76° F.).
Melting Point, 25° to 28° C. (77° to 80° F.).
Combining Equivalent (Molecular Weight), 211.
Iodine Value, 12·07 per cent.

COCONUT OIL.

The next soap oil which claims notice is that obtained from the coconut, or cocoanut as it is sometimes spelt, the fruit of the coco palm, *cocos nucifera.*

The fruit of this palm is a very useful product. It is of large size. The outer portion consists of a fibrous mass, which is made into ropes, mats and carpets. Inside this is the nut proper, consisting of a hard outer portion, useful as fuel; inside this is a layer of pulpy matter of a white colour, which is that portion of the fruit patronised by the young idea at fair times. The central portion of the nut is occupied by a milky fluid. The pulp is of a very oily nature, the proportion of oil usually averaging over 50 per cent.

This pulp is dried by exposure to air, and in that condition is known as "coprah," and is exported into this country in large quantities for the purpose of extracting the oil out of it. The native method of extracting the oil consists in heating the pulp with water, when the oil rises to the top and is collected. Another method commonly followed when inferior qualities of oil only are wanted, is to heat the pulp with a little water so as to render the oil more fluid, and then to subject the mass to pressure in a rude kind of oil press, worked by oxen. In some places the pulp is dried and then grated by means of cutting machines, and this, after being mixed or heated with water, is pressed, yielding a large quantity of a good quality of oil.

Coconut oil comes into this country from many places in South-eastern Asia; the best is that from Ceylon. Cochin China oil ranks very close behind, Malabar oil is of very good quality, Manilla oil is good; some comes from Mauritius and the Fiji Isles.

In this country coconut oil is pressed from coprah by the machinery which has been described in previous sections, the only difference being that the operation is carried out in either a warmer place or in heated presses.

Coconut oil makes its appearance in this country in the form of a white but soft fat. In Asiatic countries it is a water white, rather limpid oil. It melts at from 20° to 25° C. (68° to 77° F.); its specific gravity at 60° F. is 0·931; at 212° F. it is 0·870. Its odour is pleasant and characteristic, resembling that of the coconut. It is liable to become rancid, when its odour becomes more pronounced.

It is fairly easily saponified, and on that account it is much employed in the manufacture of soaps by the cold process. It gives a white soap, possessing good lathering properties, and one that for reasons which will be pointed out presently works well in hard waters, or in waters which contain a good deal of saline matter in solution. It takes from 24·5 to 26 per cent. of caustic potash, or from 17·4 to 18·7 per cent. of caustic soda to completely saponify coconut oil, a larger amount than is required for any other known fat.

Coconut oil is one of the most complex oils known as far as regards its chemical composition. The principal fatty acid present is lauric acid, $HC_{12}H_{23}O_2$; there is also present caproic acid, $H_6CH_{11}O_2$; capryllic acid, $HC_8H_{15}O_2$; capric acid, $HC_{10}H_{19}O_2$. These acids are all soluble in water and are volatile when distilled with steam or water.

It is the presence of these lower soluble fatty acids which causes coconut oil to require so much alkali to saponify it and to form a soap which works with hard water, for the lime salts of these fatty acids are, comparatively speaking, soluble in water, and the alkali soaps are much more freely soluble in saline solutions than is the case with the alkali salts of oleic or stearic acids for example. There are also present in coconut oil, stearic acid, $HC_{18}H_{35}O_2$; palmitic acid, $HC_{16}H_{31}O_2$, with smaller quantities of other acids of the same series; there are but comparatively small quantities of acids of the oleic series. Of course it should be understood in speaking of fatty acids in coconut oil that these do not exist in it as free acids, but in the form of glycerides.

Lauric acid has a combining weight of 200. The combining of the fatty acids which can be extracted from coconut oil by saponifying and liberating the acids with sulphuric acid, ranges from 196 to 204. When these fatty acids are distilled with water the distillate possesses an acid reaction due to the volatile or soluble acids coming over; the acidity from 100 parts of oil is equal to 0·78 to 0·83 of caustic potash. Butter and palmnut oil have a similiar composition.

Coconut oil has very little power of absorbing iodine or bromine; of the former it takes up 8·9 to 9 per cent., of the latter 5·7 per cent. It yields from 12 to 13 per cent. of glycerine, and from 94 to 96 per cent. of fatty acids.

In soap-making, coconut oil is largely used for making white soft soap in conjunction with tallow, for making cold process soaps, and for making marine and hard water soaps. When it is known that soap is going to be used in districts where hard water prevails it is a good policy to use a little of this oil in making the soap, for then a lather is more readily obtained and there is not so much waste of soap by the action of lime in the water.

Coconut oil is comparatively easily saponified, and will take a stronger alkali than any other fat; thus while with tallow a stronger alkali than 10° Tw. cannot safely be used, with coconut oil the lye may be 20° to 22° Tw. strong. It is this feature of coconut oil that makes it so useful for cold process soaps. It also requires more salt, nearly twice as much, than does tallow or other oil soaps, to salt out.

Coconut oil is rarely adulterated, and then chiefly with animal fats and greases, and with solid vegetable fats and stearins. Any such adulteration would not be very difficult of detection. The odour, alteration of the saponification value, reduction of the specific gravity at 212° F., and reduction of the amount of volatile acids will suffice to detect such adulteration.

CONSTANTS OF COCONUT OIL.

Specific Gravity at 15° C. (60° F.) . . 0·930.
„ „ 40° C. (105° F.) . . 0·9115.
„ „ 100° C. (212° F.) . . 0·8736.
Solidifying Point, 16° to 20° C. (60° to 70° F.).
Melting Point, 20° to 28° C. (70° to 80° F.).
Saponification Value (Koettstorfer Test), 25 to 26 per cent. KOH.
Insoluble Fatty Acids (Hehner Value), 83 to 88 per cent.
Reichert Value, 3·5 c.c. $\frac{N}{10}$KOH.
Iodine Value (Hubl Test), 8·9 to 9·3 per cent.

CONSTANTS OF FATTY ACIDS FROM COCONUT OIL.

Specific Gravity at 100° C. (212° F.), 0·8354.
Solidifying Point, 20° C. (70° F.).
Melting Point, 24° to 25° C. (75° to 77° F.).
Combining Equivalent (Molecular Weight), 196 to 206.
Iodine Value (Hubl Test), 9·3 per cent.

OLIVE OIL.

The olive is the fruit of the olive tree, *Olea Europea*, which grows very abundantly in those countries of Europe, Asia, and Africa that border on the Mediterranean. It is extensively cultivated in Italy, North Africa, Grecian Archipelago, Spain, and Asia Minor, from all which places olive oil is exported. The olive is a fruit resembling the plum and of about the same size. There are certain variations of the olive grown in various localities due to climatical differences and to the mode of cultivation. The fruit is collected when just ripe, and in that condition it yields the finest quality of oil. Olive oil is yielded by the pericarp or pulp which surrounds the kernel. The kernel is also capable of yielding oil, but it is interesting to note that the oil yielded by the kernel is different to that given by the pulp. The olive oil is obtained from the fruit by pressure; some portion is also separated by use of solvents. The simplest method which has been in use for a long time consists in pressing in a primitive mortar, and separating the oil which flows out. Generally the pulp is put into a large tub or tank and subjected to pressure. The oil which flows out is known as "virgin oil". It is of fine quality and used chiefly for edible purposes. There is a considerable proportion of oil left in the pulp, and this is usually extracted by boiling the pulp with water, then subjecting the residual pulp to a second pressure. A rather poorer quality of oil is thereby obtained. This quality of oil is chiefly used for lubricating, soap-making, and general industries. A poorer quality is often got by subjecting the residual cake from this second pressing to extraction by means of bisulphide of carbon. This gives a lower grade of oil, used for the commonest purposes, and generally known as "sulphur" olive oil.

Olive oil varies considerably in its quality. The best oils have a yellowish colour, while some of the inferior qualities are of a greenish-brown tint. In some cases the oil has a greenish tint. The specific gravity ranges from 0·916 to 0·919 at 60° F., the presence of much free acid lowering it. The best quality of olive oil contains usually about 2 per cent. of free acid. Certain grades of what are known as "huiles tournants," prepared from very ripe and fermented fruits which are largely used in dyeing, contain as much as 25 per cent. of free acid. The odour of olive oil is pleasant and peculiar; the taste is sweet and bland. When cooled down olive oil deposits stearin and becomes solid at 6° C. (23° F.). It requires from 19·1 to 19·06 per cent. of KOH to saponify it. It absorbs iodine, and when mixed with sulphuric acid gives rise to an increase in temperature of 41° to 45° C. One property of olive oil is that when mixed with nitrous acid or nitrate of mercury, it becomes solidified, being converted into elaidin. This property is not possessed to the same degree by any other oil. Olive oil is largely adulterated, the usual adulterants being cottonseed oil and mineral oils, but the character of the adulteration varies from time to time. The presence of cottonseed oil tends to increase the specific gravity, while that of mineral oil tends to reduce it, while at the same time their addition reduces the flashing point of the oil. To determine the purity of olive oil, regard must be paid to the specific gravity, flashing point, Koettstorfer test, Hubl iodine value, and the Maumene sulphuric acid test and elaidin test.

Olive oil with caustic soda yields a soap of a smooth texture, hard and somewhat brittle when dry, breaking with a conchoidal fracture. The colour varies with the character of the oil; good oil yields a white to cream-coloured soap, the poorer qualities yellow to greenish soaps. These soaps keep well, have fairly good lathering and cleansing properties. They are much used in the calico printing trade and for boiling-off of silk, owing to their freedom from smell and comparatively easy solubility. The original Marseilles or Castile soap was made from olive oil. A soft soap is often made from olive oil for use in some trades.

CONSTANTS OF OLIVE OIL.

Specific Gravity at 15° C. (60° F.) . . 0·916 to 0·919.
„ „ 100° C. (212° F.) . . 0·862.
Solidifying Point, 6° C. (23° F.)
Insoluble Fatty Acids (Hehner Value), 95·4 per cent.
Reichert Value, 0·3 c.c. $\frac{N}{10}$ KOH.
Saponification Value (Koettstorfer Test), 19·1 to 19·6 per cent. KOH.
Iodine Value, 80 to 83 per cent.
Maumene Test, 41·5° to 45° C.

CONSTANTS OF FATTY ACIDS FROM OLIVE OIL.

Specific Gravity at 100° C. (212° F.), 0·8749.
Solidifying Point, 21° C. (70° F.).
Melting Point, 26° C. (79° F.).
Molecular Weight (Combining Equivalent), 283.
Iodine Value, 86 to 88 per cent.

COTTONSEED OIL.

Of later years the oil obtained from the seeds of the cotton plant, *Gossypium sp.*, originally always known as cottonseed oil, but now simply as cotton oil, finds its way into most of the common household soaps which are now the fashion.

Cotton is obtainable from several species of trees belonging to the genera *Gossypium*, of which the most important is that grown in America, the *Gossypium Barbadense*, but the cotton tree grows in Egypt, India, Siam, China, the tropical portion of South America and in other localities. The seeds of the cotton are of comparatively large size, averaging from

¼ to ⅜ of an inch in length, by ¼ of an inch broad, and ⅛ of an inch in thickness, more or less rounded, and of a greenish-grey colour. To the seeds are attached the fibres which give the cotton tree its value, and which are imported into this country in large quantities, and woven into calico and other textile fabrics. These fibres are separated from the seed by a process known as "ginning".

To extract the oil from the seeds, they are first decorticated, that is they are passed through a mill, whose action is to break open the hull of the seed, and so liberate the kernel which contains the oil of the seed. With clean seed free from much attached cotton fibre, there is no necessity to decorticate the seed, but some varieties of cottonseed retain the fibre with great tenacity, and such seeds must be decorticated. The decorticating machine consists of a hollow cylinder in which revolves another cylinder, the surface of which does not touch the surface of the outer cylinder. The inside surface of the outer cylinder has a number of knives arranged round it, while the surface of the inner cylinder has a similar set of knives. These are so arranged that when a seed passes between the two sets of knives it is cut, the hull falling in two parts, while the kernel falls down whole, or in some mills it is cut in two. By winnowing, the heavy kernels can be separated from the light hulls, which are either used as fuel or as manure.

The cottonseed oil as it comes from the press in either system of crushing is of a dark wine-red colour, owing to its containing a rather large proportion of red colouring matter, amounting, according to Longmore, to 10 to 15 lb. per ton of oil. Before the oil can be used for any purpose this colouring matter must be removed. This is effected by treating the oil with caustic soda, which dissolves out the colouring matter, while having only a slight action on the oil. The quantity of caustic soda used varies in different

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refineries, but amounts to from ¾ lb. to 1 lb. of 77 per cent. solid caustic soda per 100 lb. of oil. It is used in the form of solution of varying strength at different works, from 10 to as much as 40 Twaddell. Perhaps the best plan is to use a lye of from 10 to 12 Twaddell strong. Of this about 10 lb. are required for 11 cwt. of oil. The caustic and the crude oil are mixed together in wooden tubs, and, if thought necessary, they can be heated a little by means of steam, being agitated thoroughly all the time. This is best effected by means of air pumped in by a force pump, the air not only thoroughly, agitating the oil and soda, but to some extent it probably acts as a bleaching agent on the oil. After a few minutes of such treatment the oil is allowed to stand for some time when a curdy mass of soda and colouring matter with some soap which has been formed by the action of the soda on the oil will settle out. The character of the oil is then noted. If not bright enough or free from colour, more soda lye is added, and the treatment resumed. As a rule not more than one such addition is required. The whole mass is allowed to stand to settle. The clear, bright oil is sold as cottonseed oil, while the coloured mass of soda, colouring matter and soap is treated in various ways. One plan is to treat it with acid, when it is decomposed, and a dark greasy mass comes up to the top, which can be used for making very common dark-coloured soaps, or by suitable means the colouring matter can be taken out and used as a dye. But for this purpose it cannot compete with the coal-tar colours, while the fatty matter present is recovered in a form suitable for use in soap-making or candle-making. The loss in refining crude cottonseed oil amounts to from 4 to 5 per cent.

The refined cottonseed oil so obtained contains a large amount of stearin, and hence will, in cold weather, set almost solid. By a process of refrigerating and pressing, this stearin may be removed, and is sold as cotton stearin or oleo-margarine for various purposes, while the liquid oil is often sold under the name of non-congealable cotton oil.

The crude cotton oil has a specific gravity of from 0·928 to 0·930. Refined cotton oil is a clear bright oil of a pale yellow colour, but it can be obtained almost, if not quite colourless. It has a pleasant, sweet taste, somewhat characteristic, while its odour is but slight, and yet characteristic. Its specific gravity varies from 0·922 to 0·926 at 15°C., much depending upon the amount of stearin in the oil, which increases its gravity. It solidifies at from 0° to 2° C. (32° to 35° F.), the more common qualities at even higher temperatures varying with the amount of stearin they contain. Cotton oil contains olein, stearin, palmitin, with small quantities of linolein. In its general properties it lies between the true non-drying oils, like olive, and the true drying oils, like linseed oil, becoming viscid on exposure to the air by absorption of oxygen. Fox, in an article in *The Oil and Colour Trades Journal*, states that one gramme of cotton oil will absorb 26·4 cubic centimetres of oxygen gas, more than olive oil will, but not so much as linseed oil. Consequently cotton oil cannot well be used as a lubricating oil, nor as a drying oil for painting; but as a food oil and for soap-making it has come into rather extensive use.

It takes 19·5 per cent. of caustic potash, KOH, or 14 per cent. of caustic soda, NaOH, to saponify it, giving a rather curdy soap. It is more difficult to saponify than tallow and some other oils, and the soap retains the lyes very much, so that it is difficult to separate the soap and lyes completely and to obtain a perfectly neutral soap. Cotton-oil soap is much darker in colour than tallow soap, the small quantity of the colouring matter of the seed which is still left in seeming to develop a dark colour with the alkali. The soap made from this oil is comparatively easily soluble in water, and therefore lathers freely and does not last as long as a soap made from tallow and some other fats. Another feature of cotton oil soap is that when kept for some time it goes rancid and acquires a peculiar odour, but it takes some months for this odour to develop itself. The fatty acids obtainable from cotton oil are solid acids, insoluble in water; at 100° C. they have a specific gravity of 0·8494, and melt at from 35° to 44° C. (93° to 111° F.).

Cotton oil is rarely, if ever, adulterated, there being no cheaper fat oil, and so any possible adulterant must be one of the mineral oils, the presence of which can be detected by the low flash point, which will be about or less than 400°F., while cotton oil does not flash below 475° F. The quantity of such adulterant can of course be determined by the usual tests.

CONSTANTS OF COTTON OIL.

Specific Gravity at 15° C. (60° F.) . . . 0·922 to 0·925.
" " 100° C. (212° F.) . . . 0·8725.
Solidifying Point, 0° to 1° C. (32° to 33° F.).
Insoluble Fatty Acids (Hehner Value), 96 per cent.
Saponification Value (Koettstorfer Test), 19 to 19·6 per cent. KOH.
Iodine Value (Hubl Test), 106 per cent.

CONSTANTS OF FATTY ACIDS FROM COTTON OIL.

Specific Gravity at 100° C. (212° F.), 0·880.
Solidifying Point, 32° C. (89° F.).
Melting Point, 35° C. (95° F.).
Combining Equivalent (Molecular Weight), 286.
Iodine Value (Hubl Test), 115.

LINSEED OIL.

There is scarcely a more useful plant grown than the flax plant, known to botanists as *Linum usitatissimum*. Its fibres are converted into the textile fabric known from the earliest times under the name of linen, one of the oldest, if indeed not the oldest, of the textiles, while its seed is useful in a variety of ways. In medicine it has wide applications. It yields an oil that has many useful properties, some of which will now be considered; while, after the oil has been extracted, there remains what was at one time quite a useless bye-product. Hundreds of tons of it were at one time annually thrown into the river Hull; it is now the valuable well-known oilcake of commerce, largely used for feeding cattle. The poorer seeds give about three parts of cake and one of oil, and the richer two parts of cake and one of oil. The value of the cakes is sometimes greater than the value of the oil, as oil is often not three times the price of cake. In earlier times this country was practically dependent on Russia for its supply of seed, but at the present day linseed is extensively grown in many parts of the world. The greatest bulk is grown in India. Russia now holds the second place, and the district of the River Plate the third. The seed is flattish in shape, somewhat oval, and varies much in colour, some being pale green, others pale brown, some reddish brown, whilst some others are nearly white; all of it is somewhat lustrous in appearance. Experts can tell, on looking at a sample, whether it has been grown on the borders of the Black Sea, the Baltic, in Calcutta, Bombay, or on the River Plate, and from the appearance of each sample can estimate pretty correctly what quantity of oil each sample will produce. Baltic seed is often mixed very largely with other seeds, several of which do not yield oil, whilst others yield oil with quite different qualities from linseed.

When linseed oil of a high and pure quality is desired, seeds of a different kind have to be removed from the linseed before it is crushed. These admixtures of foreign seed with linseed are sometimes natural, that is, they all grow in the same field together; but they are as often caused through wilful adulteration. Some low-class Baltic seed does not yield more than 20 per cent. of oil, whilst the highest class seed (Bombay) occasionally yields 40 per cent. All the linseed grown in India yields more oil than any of the seed grown in Russia. The difference in temperature is supposed to affect the yield of oil, the warmer climate making the seed richer in oil, whilst the colder one makes it poorer. Linseed is manipulated in various ways, and is afterwards subjected to pressure to expel the oil from it.

Linseed oil is a limpid oil of a greenish-yellow colour, varying a good deal in shade, which depends partly on the care exercised in the pressing of the oil and also on its refining. East India oil is usually paler than other varieties, while Black Sea oil is the darkest, although poor samples of Baltic run very close in colour. The odour and taste of linseed oil are peculiar and characteristic, not to be mistaken for any other oil. In specific gravity linseed oil varies somewhat, the average being 0·935, but the range is from 0·932 to 0·937 at the standard temperature of 60° F.; at the boiling point, 212° F., the specific gravity is about 0·881. It is soluble in about forty times its own volume of alcohol at the ordinary temperature, and in about five times its volume at the boiling point. When exposed to cold it does not begin to become solid until a temperature of − 27° C. is reached.

It is soluble in almost all solvents, like ether, petroleum spirit, turpentine, benzol, etc.

Sulphuric acid has a powerful charring action on this oil. Great heat is evolved, the temperature often rising considerably above the boiling point of water, while a copious evolution of sulphur dioxide takes place and a treacly mass of a dark red-brown colour is obtained. Nitric acid oxidises it readily; much depends upon the strength of the acid which is used.

Iodine and bromine have a strong affinity for linseed oil; it will absorb 156 per cent. of its weight of iodine and 98 per cent. of its weight of bromine. In this respect linseed oil has more energetic properties than any other oil.

Linseed oil is easily saponified by boiling with either caustic potash or caustic soda; it requires for complete saponification 18·9 per cent. of its weight of caustic potash or 13·25 per cent. of its weight of caustic soda. With potash it yields a soft soap, clear and transparent, of a brownish-yellow colour, possessing a peculiar smell, and having good detergent properties. When the proportions of alkali and oil are carefully regulated the soap may be obtained of neutral properties. With caustic soda, linseed oil forms a reddish-coloured soap of a buttery consistency; on this account linseed oil is rarely if ever used in making any of the ordinary domestic hard soaps, although it does find its way into a few of the special soaps.

Linseed oil is the basis from which nearly all the soft soaps of commerce are made, and for this purpose no better oil can be used; a linseed oil soft soap is of a good bright appearance, pleasing in colour and free from any objectionable odour, which is not the case with some other oils which are used for making soft soaps. The soap retains its consistency for a considerable period, which is a point of some little advantage in soft soaps.

When a linseed oil soap is treated with dilute sulphuric acid the fatty acids are separated out; these acids are of a buttery consistency, melting at from 22° C. to 25° C. At the ordinary temperature they have a specific gravity of 0·924 to 0·927, while at the boiling point their gravity is 0·861 to 0·864.

They are insoluble in water, but dissolve readily in alcohol, glacial acetic acid, ether, and other solvents. Their combining equivalent is very high, *viz.*, 306, which points to the presence of acids of high molecular weight.

Some recent researches tend to show that there is present in linseed oil an acid named linolic acid having the same formula as homolinoleic acid, which yields sativic acid when acted upon by an alkaline solution of potassium permanganate; the other is named linolenic acid, and differs from the last acid in containing two atoms less hydrogen. Perhaps the most important property of linseed oil is that of drying upon exposure to the atmosphere; this makes it very valuable in painting, but has no bearing on its use in soap-making.

CONSTANTS OF LINSEED OIL.

Specific Gravity at 15° C. (60° F.) . . 0·932 to 0·935.
" " 50° C. (122° F.) . . 0·920.
" " 100° C. (212° F.) . . 0·881.
Solidifying Point, – 16 to-20° C.
Saponification Value (Koettstorfer Test), 18·9 to 19·3 per cent. KOH.
Iodine Value (Hubl Test), 170 to 175 per cent.

CONSTANTS OF FATTY ACIDS FROM LINSEED OIL.

Specific Gravity at 15° C. (60° F.), 0·923.
" " 100° C. (212° F.), 0·892.
Solidifying Point, 16° C. (62° F.).
Melting Point, 20° C. (68° F.).
Combining Equivalent (Molecular Weight), 307.
Iodine Value (Hubl Test), 179 per cent.

CASTOR OIL.

The next oil which claims notice is castor oil. This is obtained from the seeds of the castor oil plant, *Ricinus communis*, a native of India, where it grows luxuriantly; the plant is a pretty common one in English conservatories and so is familiar to most persons. The seeds are of comparatively large size, of a greyish-green colour and of a lustrous appearance; they contain a large proportion of oil, nearly 50 per cent., which is extracted by pressure in the usual way or by boiling the seeds in water. Several qualities are recognised; that extracted by pressure is the best and sold chiefly for pharmaceutical purposes; the average commerical qualities are imported from Calcutta, Madras, Bombay and France.

What is known as first pressure French is about equal in quality to what is known as seconds Calcutta. Castor oil is a thick, viscid oil; in colour it varies from colourless in the pharmaceutical product to a greenish yellow in the poorer sorts; its specific gravity ranges from 0·960 to 0·970, the average being 0·964—occasionally samples are met with having a specific gravity below 0·960, but such are rare. The odour varies considerably; the best qualities are fairly free, but the poorer sorts have a nauseous odour. The taste also varies in the same way; the common qualities have a peculiar nauseous taste from which the best kinds are free.

It does not begin to become solid until a temperature of - 18° C. (0° F.) is reached, and even then only a few flakes are deposited. This oil is distinguished from other fatty oils by its peculiar physical and chemical properties; it has a very high specific gravity, a high viscosity. The relative viscosities of castor and sperm are 1248 and 58·5 respectively, which figures will convey some idea of the viscid character of this oil. It is readily soluble in alcohol, 1 part in 4 of rectified spirit at 15° C. (60° F.); this enables any addition of other oils to be detected. It is insoluble in petroleum spirit or in mineral oil, though this is only correct at ordinary temperatures; on being heated castor oil will mix with or become soluble in the petroleum spirit or mineral oil, but as the temperature cools down again the two liquids separate out.

Castor oil consists of a little palmitin which separates out when the oil is cooled down and the glyceride of a peculiar acid, ricinoleic acid, which has hitherto been found only in castor oil. This acid has the composition shown in the formula $C_{17}H_{33}OHCOOH$; it differs from the other fatty acids in containing three atoms of oxygen, and there is reason for thinking that this extra atom of oxygen is combined with an atom of hydrogen in the form of hydroxyl, as shown in the formula given above; ricinoleic acid is therefore an hydroxy-fatty acid. The presence of this hydroxyl group gives to ricinoleic acid the property of forming with sulphuric acid ethers; on this property is based the use of castor oil in the preparations of oleine oil for calico printers' use.

Castor oil yields about 9·1 per cent. of glycerine and 96·1 per cent. of fatty acids, these have a combining weight of 306 to 307 and a specific gravity of 0·950 to 0·951 at 60° F.; they are thick, viscid and of an oily appearance, and besides containing ricinoleic acid contain palmitic acid.

It yields a very soluble soap with caustic soda and is easily saponified. By careful treatment a liquid soap may be obtained which at one time was largely in use by dyers and cotton finishers under the name of soluble oil; castor oil soap is very clear and transparent, therefore it is largely used in preparing the cheaper kinds of transparent soaps, but being very soluble in water such soaps are very wasteful in use and while this may be a very good thing for the soap-maker it is not for the soap-user.

Castor-oil soap has often a faint odour of the oil and is apt to go rancid on keeping. It makes a good soft soap, but is not much used for this purpose. It takes from 17·5 to 18 per cent. of caustic potash, from 12·5 to 13·3 per cent. of caustic soda to saponify it, rather less than the majority of fats and oils; a stronger lye, from 15° to 18° Tw., can be used, and it is easily boiled up and lends itself to the cold process of soap-making with great facility.

Although not a part of the subject, the use of castor oil in making what is variously known as oleine, soluble oil, Turkey-red oil or alizarine oil may be touched upon. This is an oily-looking product largely in use among dyers and calico printers as a mordant for many colours, and is of great importance in the dyeing and printing of Turkey and alizarine reds; it mixes freely with water in all proportions and thus presents many advantages over the rancid olive oils which were formerly used for this purpose. This product is made by taking at the rate of 4 lb. of castor oil and mixing with it 1 lb.

of ordinary commercial sulphuric acid, with constant stirring, the object being to avoid any rise in temperature; the mixture is then allowed to stand for not less than twenty-four hours, but longer does not matter; to it is added half a gallon of water, this being well stirred in until the mass has a creamy appearance; this mixture is also allowed to stand for twenty-four or more hours, when it will be found to have separated into two layers, an upper one of oil and a lower one of acid water; this is now run off, and if a good quantity of oil is wanted a strong solution, about half a gallon, of salt is stirred in and the mixture again allowed to stand for twenty-four hours; the bottom layer of salt water is next run off; a lye of caustic soda of about 50° Tw. is then prepared, and this is slowly run in, with constant stirring, until a clear transparent liquid is obtained. The oil is now finished and ready for use.

CONSTANTS OF CASTOR OIL.

Specific Gravity at 15° C. (60° F.) . . 0·960 to 0·966
„ „ 100° C. (212° F.) . . 0·9096.
Solidifying Point, − 17° to − 18° C. (1° to 3° F.).
Reichert Value, 1·6 c.c. $\frac{N}{10}$ KOH.
Saponification Value (Koettstorfer Test), 17·8 to 18 per cent. KOH.
Iodine Value (Hubl Test), 83·6 to 84 per cent.
Acetyl Value, 153·4 per cent.

CONSTANTS OF FATTY ACIDS FROM CASTOR OIL.

Specific Gravity at 15° C. (60° F.) . . 0·9509.
„ „ 100° C. (212° F.) . . 0·896.
Solidifying Point, − 3° C. (27·5° F.).
Melting Point, 13° C. (57° F.).
Combining Equivalent (Molecular Weight), 292.
Iodine Value (Hubl Test), 90 per cent.

So far have been described all the fats and oils which enter most largely into the composition of the ordinary run of soaps, both soft and hard; there still remain for description a few fats and oils which are occasionally used for this purpose, but owing to such circumstances as limited supply, higher price, bad colour, etc., are but rarely applied in soap-making.

As an adjunct, and to make this series of articles complete, a few words will be said about rosin.

CORN OIL.

This oil has of late come into considerable prominence as a soap oil. It is obtained from the seeds of the maize plant (*Zea Mays*) and is extensively produced in America, being largely made as a bye-product in the manufacture of starch and glucose from Indian corn. It is a viscid liquid of a bright amber-yellow colour, has a faint and peculiar odour, and sweetish taste, recalling that of corn-flour; it has a comparatively high specific gravity, being comparable with cottonseed oil in this respect; it is comparatively easily saponified, taking from 18·4 to 19 per cent. of caustic soda to saponify it, yielding a soap of yellowish colour, very homogeneous and of good consistency, very closely resembling a cotton-oil soap in its general properties. With caustic potash it gives a soft soap of a good, bright, transparent appearance, and good detergent properties, and it is for making soft soaps that it will be found of most service. The oil yields on saponification and acidification fatty acids melting at from 16° to 18° C., and solidifying at from 13° to 14° C.

CONSTANTS OF CORN (MAIZE) OIL.

Specific Gravity at 15° C. (60° F.) . . 0·9208.
" " 100° C. (212° F.) . . 0·8694.
Insoluble Fatty Acids (Hehner Value), 96 per cent.
Solidifying Point, – 10° C. (14° F.).
Iodine Value (Hubl Test), 116 per cent.
Saponification Value (Koettstorfer Test), 18·4 to 19 per cent. KOH.

CACAO BUTTER.

In the manufacture of the familiar beverage cocoa, there is obtained a quantity of fatty matter commonly known as cacao or cocoa butter. This is of a white or yellowish-white colour, of a consistency somewhat like butter, but perhaps a trifle harder; it possesses an odour of cocoa and has a pleasant and agreeable taste. By exposure to light and air it becomes bleached, but there is little tendency to become rancid. It melts at about 30° C. (86° F.). Cacao butter has a very complex composition, containing the glycerides of stearic, oleic, lauric, palmitic, myristic and other acids, while some authorities say that it owes its odour to the presence of small quantities of theobromine. It is rarely used in soap-making, although it could be so used with good results, but that its price is rather against it; it yields a good soap fairly soluble in water, lathering well and possessing good detergent properties; it saponifies fairly easily, but takes a little more alkali than tallow.

RAPE OIL.

This oil is pressed from the seeds of various species of rape plants, *Brassicæ Napus*, *Brassicæ Campestris*, etc. It is a brownish-green oil (brown rape oil), or in the refined varieties a yellowish oil having a greenish tone. It has a peculiar and characteristic odour. Its specific gravity varies a little, but usually ranges from 0·913 to 0·916, generally being 0·914 at 60° F. By blowing air through it, it is converted into what is known as "thickened rape oil," a very viscid oil, of specific gravity 0·970 and a peculiar odour. Rape oil takes about 17·25 per cent. of caustic potash or 12·5 per cent. of caustic soda to saponify it. In each case soaps are obtained which are of a greenish-yellow colour and smell strongly of the oil. It is in consequence rarely used in soap-making: then it is a costly oil. Further, the soda soaps are but of a pasty consistency, too soft for hard soaps. This oil is frequently adulterated, chiefly with cotton and mineral oils, both of which are comparatively easy to detect. Rape oil contains three peculiar and characteristic acids—brassic, rapic and erucic acids, which belong to the oleic and linolenic series of fatty acids, and they have a high molecular weight.

WHALE OIL OR TRAIN OIL.

This oil used at one time to be largely employed in the manufacture of soft soap, especially in Scotland, the home of the fish oils, but of late its use even for this purpose has decreased considerably. Whale oil, or, as it is often called, train oil, is obtained from the blubber of various species of whales. It varies very considerably, not only in composition but in quality. There are many species of whales, and each of these may be reasonably suspected of yielding an oil which differs in some respects from the oil of other whales. Generally, however, the whalers mix the products of different whales together indiscriminately; consequently the oil from different whaling ships, capturing a variety of whales, will differ somewhat. Then, again, the methods of extracting the oil from the blubber vary very much, and this has a very considerable influence on the quality of the oil. Of late years there has been more care exercised in the extraction of the oil, and consequently the quality of the product has much improved. The old method used to be to store the blubber in tanks, and extract the oils either on some land or, oftener than not, when the ship arrived home, when the blubber was either boiled in water—the oil rising to the top and being collected—or allowed to drain on racks, the former process giving the best oil, the latter the worst. This method of keeping the blubber for some time before extracting the oil resulted in its decomposition, and the products thereby formed found their way into the oil and decreased its quality by making it of a darker colour and imparting to it a more powerful odour. As a rule whale oil is extracted from the blubber by the process of boiling it in water, whereby a better quality of oil is obtained; one advantage of the process being that the ships can store more oil. Whale oil is a reddish-coloured oil, having a fishy odour and taste; the colour, odour and taste all vary in different oils. Its specific gravity is about 0·925. When cooled down, many samples of whale oil deposit some stearin as a brownish-coloured mass, smelling of fish. It takes about 18 to 19 per cent. of caustic potash, and about 13·5 to 14 per cent. of caustic soda to saponify it. The potash soaps are of a brownish-red colour and have a fishy odour; they are very soluble in water. The soda soaps have a dark-red colour and fishy odour, are rather soft in consistency, and owing to this fact whale oil cannot well be used in the preparation of hard soaps. Whale oil contains notable quantities of valeric acid, which is one of the volatile members of the stearic series of fatty acids.

RECOVERED GREASES.

In various industrial operations fats and oils and soaps are used for a variety of purposes. In currying leather, cod oil, tallow, castor oil, etc., are used for the purpose of softening it. Some of this grease is afterwards recovered and sold as currier's grease. In wool washing, scouring and fulling soap is used in the process, and from the waste soapy liquors the fatty matter they contain is recovered by various processes. After raw wool has been washed and scoured it is necessary to oil it for the purpose of enabling it to spin and weave easily. This oil can be, and is, taken out of the wool again. Some of the greases which are thus recovered may be used in the preparation of soap, but a word of caution is requisite. These greases require very considerable care in buying, and it would be advisable to buy only after a sample has been tested in the chemical laboratory to ascertain its fitness for soap-making, and also only on condition that the bulk was equal to sample. For these greases are of a most variable composition, as will be seen presently, and even professedly the same kind of grease may vary so much that, while one lot will make a fair soap, the next lot may not. The necessity for the soap-maker to be cautious in his buyings will be readily seen. A few of these greases which may find their way into the soap-maker's hands will be briefly described.

Currier's Grease.—This grease is obtained in the currying of leather with oil, for which purpose cod oil is chiefly used, but tallow, castor and other oils are also employed. The grease, as usually sold, is of a soft consistency and varies in colour from a pale brown to nearly black. It has a strong and usually fishy odour, mixed with that of leather. It varies very considerably in composition, containing more or less water, animal oil, fish oil, tallow, animal tissue, bits of leather, hair, skin, etc. Its value as a soap fat will vary very much. In addition to the fatty matter which is present there may also be some unsaponifiable matter and possibly a small proportion of mineral oil; by itself it gives a soft, dark-coloured soap, and it is rarely used alone in soap-making but always mixed with other fats. Before using, it should be melted over hot water and allowed to stand for some time for the impurities to settle out; if these do not do so readily it is best to pass the melted fat through a sieve. In testing such greases the quantity of actual fatty matter they contain should be ascertained by extraction with petroleum ether, and this should be tested as to whether it is all saponifiable or whether it contains any unsaponifiable fat, and as to what kind of soap it gives.

Fuller's Grease.—The next recovered grease which is sometimes offered for soap-making is fuller's grease, and in connection with it mention may be made of what is known as Yorkshire or wool grease.

In the process of manufacturing woollen cloth, the material has to undergo two scouring operations; in the first instance, the raw wool, just as it is removed from the sheep's back, is scoured, usually with soap, or with soap and soda, to remove the natural grease, soapy matters and dirt it contains; after this it is dried, and to facilitate any spinning operations it is oiled with olive oil, oleic acid or some other oil. After being spun into yarn and woven into cloth, the wool has again to be scoured to remove from it the oil and dirt which had been added to or got into it in the process of manufacture: this scouring is necessary, as otherwise the oil, etc., would interfere with the operation of dyeing to a very material degree. These scouring operations are invariably done with the aid of soap, sometimes, but not always, aided by a little soda, but too much alkali must be avoided, as it will act detrimentally on the wool fibre. At one time the liquors containing all the soap used in the operations, together with the grease and oil of the wool, were sent into the rivers to waste; the result being that the Yorkshire rivers were notable on account of their pollution. Then some really bright genius—we do not think that history has recorded his name, at all events we have never come across it—conceived a plan to recover the fat and grease in a usable form, and since then many thousands of tons of grease have been recovered from the soap liquors of the wool scourer, and many thousands more will be so in the future. The process generally followed is to run the soap liquors into large tanks, where all the dirt is allowed to settle out. In these tanks the liquor is first heated by steam, and then hydrochloric acid is run in; this decomposes the soap in the liquors and causes the fatty matter to rise to the top, whence it is removed, pressed, and sent into commerce. A somewhat better process is to treat the waste soapy liquors with just sufficient calcium chloride to decompose any soap present, and form thereby lime soap, which, with any fatty matter, will collect in curds on the top of the liquor; this lime soap is collected, while the liquor will generally be of sufficiently clear and good quality to be run into the river. The lime soap is then heated with sufficient dilute hydrochloric acid, whereby it is decomposed, the fatty matter liberated and collected, while the lime dissolves in the form of calcium chloride, ready to be used for precipitating out more lime soap in a new lot of liquors.

It will be obvious to most persons that at least two kinds of greases are recoverable from the waste liquors of the woollen mills. The first is that obtained from the scouring liquors off raw wool — this is what is generally named Yorkshire or wool grease, usually the latter. The second grease is that obtained from scouring the cloth after manufacture and after it has been fulled—this is known as fuller's grease. This will be considered first.

Fuller's grease varies considerably in appearance from a dirty yellowish-brown to a dark-red grease, of about the consistency of butter, pasty in feel and often sticky and viscid. If prepared from the waste liquors of the fulling mills it will consist simply of the oil used in the batching of the wool, free fatty acid liberated from the scouring soap and some colouring matter; much, however, depends upon the care with which the various operations of batching and scouring have been carried out, while the quality of the batching oil and of the scouring soap used has a material influence. If these are of poor quality, then the recovered grease must be of poor quality too. The following are two analyses of fuller's grease ;—

Moisture . . .	1·25	—
Free fatty Acid . .	2·53	1·49
Saponifiable oil . .	92·62	72·56
Unsaponifiable oil . .	3·60	25·95

The first one is of very good quality, while the second contains too much unsaponifiable matter to make it serviceable as a soap fat.

It can only be used in making very common soft and cheap hard soaps, and even then must be mixed with rosin or other fats in not too large quantity.

Wool Grease.—The grease which is obtained from the liquors of the first scouring operation is of variable quality, as the following analyses by the author will show :—

Water	0·98	1·53	1·21	0·94
Fatty acid	18·61	24·25	24·15	26·43
Saponifiable oil	68·62	58·25	30·02	16·86
Unsaponifiable oil	11·68	15·83	44·44	55·77
Ash	0·11	0·14	0·18	Trace

The unsaponifiable matter in this grease consists chiefly of a peculiar body present in the raw wool and known as cholesterine. This body partakes somewhat of a waxlike character, but is not acted upon by alkalies, although it is more or less soluble in soap liquors and hence is found in the waste liquors and in the greases recovered from them. It imparts to the grease certain undesirable properties, among others that of forming a greasy-looking and rather sticky soap, so that it is not to be recommended, even if a fairly large proportion of some other fats be mixed with it.

A common method of dealing with this grease is to subject it to distillation with the aid of superheated steam, when a pale-coloured somewhat granular grease distils over. This has been used for soap-making; it has about 15 per cent. of unsaponifiable matter, and has a peculiar and rather unpleasant odour; it does not give any satisfactory result.

Oleic Acid.—This product is obtained as a bye-product in the manufacture of candlemaker's stearin by distilling fats with the aid of superheated steam, as in the process invented by Mr. Wilson, of Price's Patent Candle Co., Ltd., or by saponification with lime under pressure in the autoclave, as it is usually carried on now, with subsequent treatment of the lime soap so formed with acid.

In either case the mixture of fatty acids which is obtained is pressed by means of an hydraulic press; the oleic acid comes out, while the solid stearic acid remains in the press. The oleic acid as it comes from the press is a dark-coloured oily liquid, which can be refined into a pale yellowish-coloured, oily-looking fluid. It is sold commercially as pale oleic acid, brown oleic acid, crude oleic acid. In colour it varies from a pale yellow to a dark red, as will have been gathered from what has previously been said; sometimes it may contain small quantities of solid particles. In specific gravity it varies from about 0·889 to 0·907. The following analyses will give some idea of its composition:—

Free acid	96·2	93·8	84·5	89·4
Saponifiable oil . . .	2·5	2·3	5·3	8·6
Unsaponifiable oil . .	1·3	3·9	10·2	2·0

The free acid consists mostly of oleic acid, but there is usually present some stearic acid, and generally acetic, suberic and sebacic acids, which have been formed by the decomposition of the fat during the process of manufacture, this decomposition being greatest in the distillation. The hydrocarbons or unsaponifiable matter have been produced by the decomposition of the fatty matter at the same time; the hydrocarbons formed are probably members of the paraffin series.

Oleic acid combines readily with caustic soda, but unless considerable care is taken in mixing the liquids, and using a dilute solution of the alkali, a very granular mass is obtained, which will require a prolonged boiling to convert it into an homogeneous soap. Oleic acid will also combine with the carbonate of soda to form soap, and a good deal of manufacturer's soap is made in this way.

During the operation a large quantity of carbonic acid is evolved, which causes the mass to fob up very considerably, hence a capacious boiler is required when soap is made from oleic acid and carbonate of soda. By using pale oleic acid and soda ash a fairly good soap can be made.

In the distillation of Yorkshire or wool grease there is obtained an analogous body known as "Oleine"; this contains a large proportion of oleic acid, but there are usually present larger quantities of unsaponifiable oils and of saponifiable oils than are contained in ordinary commercial oleic acid, as the following analyses by the author will show:—

Water	1·12	2·33	—
Free fatty acid	55·02	56·26	64·42
Unsaponifiable oil	34·66	29·46	9·95
Saponifiable oil	9·20	11·95	25·63

These are mostly used for batching wool; they are rarely used in making soap, the large and variable quantity of unsaponifiable oils which they contain rendering them rather unsuitable for this purpose.

When buying the various kinds of recovered greases and oleic acid and oleines soap-makers should always buy from samples and have these tested by an analyst to see that they are suitable for their purpose. Ocular inspection will not distinguish between a grease which will make a fairly good soap and one which contains so much unsaponifiable matter as to render it useless for soap-making.

ROSIN.

Rosin is the residual body left behind in the distillation of turpentine from the resin of pine trees; this rosin is run into barrels and sent into commerce. What comes into this country is almost all of American origin. It is made, of course, in both France and Russia, which are great turpentine-producing countries, but what rosin they produce is used locally, little if any coming into English commerce.

Rosin is a brittle, more or less transparent, resinous body, varying in colour from pale yellow to black. The colour of black rosin is really a dark red when looked through, but it appears black on looking at it. Sometimes the rosin is opaque, and not transparent; this is due to the presence of water, which may be got rid of by keeping in a warm place for a short time. Several qualities of rosin are distinguished in trade—" window glass," "amber," " common," " black," etc. This difference in quality is due partly to the quality of the crude turpentine from which the rosin is obtained, partly to the amount of care exercised in its extraction. The best " virgin " gives window-glass rosin, " yellow dip " gives amber rosin, and " scrapings " the black rosin. Rosin has a faint but characteristic odour, which becomes more highly developed on warming. It is usually homogeneous in structure, quite amorphous, and very friable, readily breaking up into small fragments or into fine powder, which has a rather rough and peculiar feel. Its specific gravity varies, but is about 1·07 to 1·10. It begins to soften at a temperature of 80° C., and melts into a limpid fluid at 100° C. It is quite insoluble in water, but it is soluble in acetone, hot alcohol (on cooling crystals of sylvic acid deposit), benzene, ether, petroleum oils and most fatty oils. Rosin may be distilled in a vacuum almost unchanged, but if distilled under ordinary conditions it is decomposed and yields acid aqueous liquors, a limpid spirit, and a viscid oil with smaller quantities of other bodies.

The chemical composition of rosin has not yet been thoroughly worked out, and authorities differ somewhat on this subject. This, perhaps, is due to the fact that there are several varieties of rosin prepared from different varieties of pine resins, and those chemists who have investigated rosin have not made sufficient allowance for this fact. Some authorities consider rosin to be composed of two isomeric rosin acids, named pinic and sylvic acids, the former of which is soluble both in hot and cold alcohol, the latter only in hot alcohol.

To these acids is assigned the formula $HC_{20}H_{29}O_2$, while other chemists consider that rosin contains as its essential constituent abietic anhydride. This body, when acted on by alkalies, is converted into abietic acid.

Rosin is easily dissolved by solutions of either the caustic or carbonate alkalies forming rosin soaps. These have strong detergent properties, but have a dark colour and are soft and sticky in consistency. As the soap-maker says, they have no body, hence rosin is never used alone to make soaps, but it enters into the composition of most domestic hard soaps and soft soaps of commerce. The quantity of caustic soda or potash required to saponify rosin is very variable, ranging from 17 to 19 per cent. of caustic potash, and from 12 to 13·5 per cent. of caustic soda.

CHAPTER IV.

PERFUMES.

In the scenting of soaps, etc., and in the preparation of perfumes, there are employed essential oils and other substances derived from a great variety of products. The preparation of the essential oils is a comparatively simple process, although to obtain the best product great care has to be taken in the selection of materials, and in carrying out the operations involved in extracting the oil or essence; thus it is impossible to obtain a fine oil of violets from faded flowers, and otto of roses of the finest fragrance can only be obtained from flowers which are just ripe. Generally the oils are obtained either by pressure in a screw press or by distillation with steam, the oils in general possessing the same property as turpentine of being distilled over boiling water or in a current of steam.

Those oils which are mostly in use for perfumery purposes are described in the following brief notes, which for the sake of convenience are arranged alphabetically:—

Anise.—This is obtained from the seed of *Pimpinella anisum*, a plant which grows over a wide extent, and is exported from Russia, Thuringia, Moravia, Chili, Spain, Levant, etc. The yield of oil ranges from 1·3 per cent. to 3 per cent., Levant giving the smallest, and Spanish anise the largest yield. Slight differences are observable in the odour of the oil from seed grown in different localities. It is colourless or at most a faintly yellow oil when fresh. On being kept, especially when exposed to the air, it becomes dark yellow in colour. Badly made and inferior oils may also possess this dark colour. It has a pleasant odour, and an aromatic sweet taste. It solidifies at 50° to 59° F. on account of its containing a stearoptene known as anethol. On exposure to air anethol is converted into anisic aldehyde with some resinification, oxidation taking place. Its specific gravity is 0·980, and it is soluble in an equal volume of alcohol. This oil must not be confounded with oil of star anise, with which it is often adulterated. Sometimes other oils are added, together with a little paraffin or spermaceti, to bring about the solidifying of the adulterated oil at lower temperatures.

BERGAMOT.—This is obtained from the rind of the fruit of the *Citrus limetta*, a species of lemon, which yields about 3½ per cent. of the oil. When fresh it has a pale yellow colour, but may often be met with of a greenish tint, which is due to its having been kept in a copper vessel. It has a strong and agreeable odour. Its specific gravity varies from 0·850 to 0·980; it boils at 118° C. and solidifies at 11° F. It dissolves freely in alcohol. Bergamot oil contains terpenes, linaloöl acetate, and a small quantity of linaloöl. The linaloöl acetate is the odorific principle, and is present to the extent of 40 per cent. and upwards. It can be estimated by means of Koettstorfer's saponification test.

As adulterants refined turpentine oils, or oils derived from oranges and lemons, with rosin are used.

It is advisable to keep it out of contact with air, as it absorbs oxygen, and thereby loses its odour, acquiring that of turpentine. Oil of bergamot is largely employed in the perfuming or scenting of soap.

OIL OF BITTER ALMONDS.—This oil is obtained from the fruit of the *Amygdale amare*, or bitter almonds. The fruit is pressed to separate out all the oil it contains, then the meal is mixed with water, and warmed to 106° to 113° F.

for some hours; a fermentative action sets in, and a vegetable principle, amygdalin, present in the meal, reacts with other constituents and forms the oil together with some sugar and prussic (hydrocyanic) acid. To obtain the oil the fermented meal is distilled, 1 per cent. being the usual amount obtained. When pure it is a colourless, very refractive liquid, having a specific gravity of 1·04, so that it is slightly heavier than water. It boils at 180° C. (350°F.). On exposure to the air the oil gradually undergoes decomposition, and is changed into benzoic acid; hence it must be kept in air-tight vessels. Bitter almond oil is employed to a limited extent in the making of perfumes, but not in scenting soaps, the almond-like odour of which is commonly obtained by using what is known as myrbane (nitro-benzol).

Oil of Caraway.—This is obtained from caraway seeds, which are well known to cooks and confectioners, who delight to add them to their cakes. These are the seeds of the tree *Carum carui*, which is cultivated in various parts of Germany and Holland, while it is found wild in Norway and Russia. The average amount of the oil which can be obtained is 5 per cent., but it is curious that the seeds from the wild variety yield 1 to 2 per cent. more oil than the seeds from the cultivated varieties. Caraway oil has a light yellow colour, and an aromatic odour and burning taste; its specific gravity is 0·960, and it boils at 195°C. (383° F.). It is largly employed in the scenting of soaps, both alone and in combination with other essential oils. Its odour is due to an aldehyde known as carvol.

Cassia.—This oil is obtained from both flowers and the wood of the tree *Cinnamomum cassia*, the former yielding about 2½ per cent. of the oil, the latter only about ¼ per cent. Oil of cassia when fresh is of a yellow colour, but on keeping it becomes of a dark-brown colour. It has a specific gravity of 1·06 and boils at 252° C. (485° F.). It has a pleasant odour not unlike that of cinnamon, but by no means so pleasant. It has a sharp taste, and is employed in the scenting of soap and in the preparation of many perfumes.

CINNAMON.—This oil is obtained from the wood of the cinnamon laurel, *Cinnamomum zeylanicum*, which grows very extensively in China and Ceylon. The wood yields from 1 to 1½ per cent. of oil. Three varieties are recognised in commerce—Ceylon oil of cinnamon, Chinese oil of cinnamon (which is also known under the name of cassia oil), and oil of cinnamon leaves, the first being regarded as the true "oil of cinnamon". This oil is rather viscid, of a golden-yellow or a golden-brown colour, according to the age, and has a burning but sweet taste. The specific gravity is 1·030, and it boils at 240° C. (464° F.), while at 21° C. (− 6° F.) it solidifies. On exposure to the air it absorbs oxygen, becoming thicker, darker in colour, while its flavour deteriorates. The principal constituent is cinnamyl aldehyde.

Chinese oil of cinnamon has a specific gravity of 1·065, and contains about 75 per cent. of the aldehyde. It used to come over very largely adulterated with rosin, etc., but now it is sent over fairly pure. It is not equal in quality to Ceylon oil.

Oil of cinnamon leaves is a very inferior article, used for adulterating the better grades of oil, and in scenting soaps. This oil is rather heavier (its specific gravity being 1·053) than Ceylon oil, although not so heavy as the Chinese oils.

Oil of cinnamon is largely employed in the preparation of perfumes, and in scenting soaps, etc.

CITRONELLE.—In India and Ceylon are grown many species of grass-like plants, which yield oils having an aromatic odour. The oils from these are commonly known as grass oils, of which the following are the chief: citronelle, lemon grass, vetiver, ginger grass. Citronelle is obtained from the grass *Andropogan nardus*, largely grown in Ceylon, where the oil is extracted in large quantities, and exported to this country. It has a pale yellow colour; a peculiar, pleasant odour. It is very largely employed in the preparation of perfumes and the scenting of soaps.

CLOVE.—This is obtained from the fruit buds of the clove tree, *Caryophyllus aromàticus*, which comes from Amboina, Bourbon and Zanzibar. These contain about 18 per cent. of oil. When fresh this oil is colourless, but it soon becomes yellowish to brown. It is rather heavier than water, its specific gravity being 1·030, and it boils at 268° C. (478° F.). It has an exceedingly strong burning taste and a pleasant spicy odour; it is largely employed in the scenting of soaps, either alone or in common with other oils.

CORIANDER.—This oil is obtained from the seeds of the coriander plant, *Coriandum satrium*, which yield from to 1 per cent. of the oil. The tree is grown in Russia, Holland, Italy, India, North Africa and other localities. It is of a pale yellow colour, sharp aromatic taste, and pleasant odour. It is rather lighter than water, its specific gravity being 0·875, while it boils at from 150° to 200° C. It is very largely employed in the scenting of soaps.

LEMON GRASS.—This oil is prepared from the lemon grass, *Andropogon citratus*, a native of Ceylon, while it is also cultivated in India. From these countries are exported large quantities of these oils. It is a colourless oil, possessing a pleasing odour of lemon, with a slight reminiscence of that of roses or geraniums; on this account it is often substituted for the oil of rose geranium. It is rather lighter than water, its specific gravity being 0·870 to 0·898; it boils at 220° C. (428° F.) and solidifies at 22° C. (– 8° F.). It is very much used in the scenting of soaps and in the preparation of soaps of various kinds.

GERANIUM OR ROSE GERANIUM.—In Southern France and Algiers the *Pelargonium roseum*, or geranium, is very largely cultivated, and from its leaves is obtained about ¼ per cent. of an odoriferous oil which has an odour not unlike that of roses, hence the reason why this oil is sold as oil of "rose" geranium to replace the true oil of roses, where the cost of the latter oil prevents its use. Oil of geranium has a specific gravity of 0·895, and a boiling point of 220° C. (480° F.). It is very largely used in the making of perfumes and in the scenting of soaps.

LAVENDER.—Probably no perfume is better known than that of the lavender, the flowers of *Lavandala vera*, which is grown very extensively at Mitcham, in Surrey, and in other localities. The flowers yield about 3 per cent. of their weight of oil. The Mitcham oil is considered the best, having the most delicate perfume, and therefore commands the best price. German lavender oil is of good quality, and is cheaper. An oil is also obtained from the spike lavender, *Lavendara spikum*; this however is not so good as the true lavender oil, although it is sometimes supplied in its stead. Oil of lavender has a light yellow colour and a sharp burning taste; it must be kept in air-tight vessels, as otherwise it undergoes decomposition, losing its fine odour of lavender, and acquiring that of turpentine. Oil of lavender is lighter than water, but its specific gravity is very variable, ranging from 0·870 to 0·940, and its boiling point varies from 186° to 192° C. Oil of lavender is much used in the preparation of perfumes, and in the scenting of soaps, etc.

NEROLI.—This is obtained from the flowers of the orange tree and comes from the South of France, where the orange tree is cultivated for this particular purpose. The oils obtained from different species of orange tree vary a little in quality; that from the Seville orange tree, *Citrus vulgaruis*, is considered the best. On exposure to the air they undergo oxidation and become of a red colour; they ought to be kept in a cool place in well-closed vessels. Oil of neroli is colourless, having an odour of orange, and possesses a bitter taste. It is lighter than water, having a specific gravity of 0·889, and a boiling point of 175° C. (337° F.). This oil is employed in the scenting of soaps and in the preparation of various perfumes.

ORANGE.—Oil of orange should not be confounded with the oil of neroli; while the latter is obtained from the flowers, the former is pressed from the rind of the fruit. Orange oil has a golden-yellow colour, with an odour and taste of the fruit. It has a specific gravity of 0·830 to 0·860, and boils at 171° C. (330° F.). Two varieties are met with in commerce, that from the rind of the bitter orange and that from the rind of the sweet orange; there is very little difference between them. They are employed in the preparation of perfumes, mineral waters, and in scenting soap.

SASSAFRAS.—This oil is extracted from the wood of the sassafras tree, *Sassafras officialnis*, which yields about 2½ per cent. of the oil; it has a yellow colour, a peculiar but pleasant odour and taste. It is rather heavier than water, its specific gravity being 1·082. It contains a peculiar principle named safrol, which is also contained in oil of camphor. Oil of sassafras is largely used for the scenting of soap and other articles.

STAR ANISE.—This oil is extracted from the seed-pods of a Chinese tree (*Illicium anisatum*); it closely resembles oil of anise in all particulars, and is generally preferred by perfumers. It is lighter than water, having a specific gravity of 0·892. These pods yield about 2 per cent. of the oil. A similar oil, but to a smaller extent, is obtained from the seeds of a Japanese tree (*Illicium religiosum*) that possesses family resemblance to the Chinese tree. This oil is, however, not so good in quality.

WINTER GREEN.—This oil is extracted from the leaves and twigs of the winter green, *Gaultheria procumbens*. This oil consists essentially of methyl salicylate; it has a specific gravity of 1·173, and boils at 220° C. (428° F.). It mixes freely with alcohol and other solvents. It is largely used in the scenting of soaps, imparting a pleasant fragrant odour.

MUSK.—One of the most delicate perfumes is that known as musk; quite a number of plants and animals have this odour. A favourite window plant is the common musk (*Mimulosa moschatus*), with its bright yellow flowers and fragrant odour. Others are: *Erodium moschatum*; *Adoxa moschatellina*, the tuberous moschatel; *Nardostachys jutamansi*, the spikenard of the ancients; *Eurybia argophylla*, the silver-leaved musk tree of Tasmania; *Moschoxylum swartzii*, the musk wood of Jamaica; *Guarea trichoilides* and other species of Guarea, the musk woods of Guiana and the West Indies, while the seeds of *Hibiscus abelmoschus* are valuable for perfume, and are commercially known as musk seed. With the exception of the last, none of the other plants are cultivated for their odour.

Among animals which have a musk-like odour, first place must be accorded to the musk deer (*Moschus moschatus*), which is the source of the musk of commerce. There are the musk ox (*Ovis moschatus*), noted for its skin; the musk rat (*Hiber zibethicus*), also valuable for its skin; the Indian musk rat (*Sorex indicus*); the alligator of Central America and the crocodile of West Africa also have musk glands, which are occasionally extracted and employed as a perfume. The excrement of the gazelle (*Gazella dorcas*) has a musk-like odour, and yields 7 per cent. of an odorous extract to alcohol.

The musk deer, from which nearly the whole of the musk of commerce is obtained, is a native of the Himalayas, where it may be found on every hill having an altitude of over 8000 feet, and lives on the underwood of the forests abounding on the Himalayan range. It is an animal of about the size of a greyhound, shy, but very agile, and somewhat nocturnal in its habits. The musk pod from which the odorous secretion is obtained is found only in the males, the females being devoid of any odour; the pod is found near the navel between the flesh and the skin, and is composed of several layers of thin skin in which the musk is found in the form of grains, of irregular shape, roundish and ovoid, varying in size. The pod is developed before the animal is born; at first, and for two years after birth, the contents of the pod are soft, milky in appearance, and have rather an unpleasant odour; at the end of the two years the contents change into musk and increase in quality afterwards; at first the weight averages 8 oz., and at full growth may reach 2 oz.; the average is, however, 1 to 1¼ oz. It varies also with the seasons, being greatest in the rutting season.

The animals are usually snared in specially constructed snares of fences and ropes, then killed, and the pod extracted and dried in the sun, although other methods are occasionally adopted.

Musk makes its appearance in two forms in commerce—"musk in pod" and "musk in grain"; the former is the material in its natural receptacle, while the latter is that removed from the pod. It is imported from (1) Tonquin, China, and Tibet in small chests, containing twenty-five packets of musk encased in lead. This is considered the best quality, and commands the highest price, but is most adulterated. (2) Assam, which comes in bags packed in a box, containing 200 pods, rather irregular in size and form, and having a strong odour. (3) Kanardin or Russian, which is very inferior in quality and poor in odour.

Musk for use in perfuming is prepared as an extract or tincture by means of alcohol; it is rarely used alone, but is combined with other perfumes. It is an exceedingly permanent perfume; one grain of musk will emit its scent for years, and it appears to impart some of its permanence to other perfumes. It cannot be mixed with all substances without deterioration; some, such as bitter almonds and ergot, destroy it, while camphor and valerian change its character very much.

Tincture of musk is prepared in the following manner Take 1 oz. musk in grain, 10 oz. alcohol, ⅛ oz. ammonia. Grind the musk with a little of the alcohol, then mix all together and allow them to digest for several days, shaking at intervals, then filter. Add to the residue 5 oz. alcohol and digest again for three days, then strain and add tincture to the first lot. Add another 10 oz. alcohol to the residue and repeat the operations. The weak tincture made with this third extraction is in place of alcohol for extracting a fresh batch.

Another method is to grind together 1 oz. musk in grain, 2 oz. sugar; then add 2 quarts alcohol, 1 oz. pearl-ash. Allow to stand for a week, shaking at intervals, then filter, when the tincture will be ready for use. This will be rather weaker than the above.

ARTIFICIAL MUSK.—Under the name of "Musk Baur" there has been introduced into commerce, since about 1890, a white powder, which has a strong odour of musk, and it has been largely employed in imparting a musk odour to soaps. The production of this has been patented (No. 4963, 1889) by the discoverer, Albert Baur. There can be isolated from rosin spirit a hydrocarbon, butyl toluene, which has the formula $C_6H_4(CH_3)(C_4H_9)$. The simplest method for making artificial musk from this is to allow the hydrocarbon butyl toluene to drop slowly into five times its weight of a mixture of one part of nitric acid of 1·5 specific gravity, and two parts of fuming sulphuric acid, containing 15 per cent. of anhydride, and heating the mixture on a water bath for eight or nine hours. On pouring the mass into water a crystalline mass of impure nitro compound is obtained. This is renitrated, and the product recrystallised from alcohol.

Musk Baur, the trinitro-iso-butyl-toluene, occurs in the form of a creamy crystalline powder, which is insoluble in water, but is easily soluble in alcohol, ether, chloroform, petroleum spirit, benzine. It melts at 96° to 97° C. It has a most intense odour of musk, and may be used in perfuming soaps. Its odour is not quite so pleasant as that of true musk. It may be added direct to the soap or preferably in the form of a solution in methylated spirit.

Although Musk Baur is at present the only form of artificial musk to be met with in commerce, yet other compounds, mostly trinitro derivatives of aromatic organic compounds, are known, which have a musk-like odour, and will probably be sooner or later placed on the market.

MYRBANE.—This product is largely used in the scenting of soaps and other products which require a cheap scenting material, owing to its pleasant odour of almonds, while it is a strong agent for perfuming soaps, etc. Chemically it is nitrobenzene, having the formula $C_6H_5NO_2$, and is manufactured in large quantities by treating benzene, the benzol of the coal-tar distiller, with a mixture of nitric and sulphuric acids. The crude product is mixed with water to free it from excess of acids when distilled. Myrbane, or nitrobenzene, is a pale straw-coloured liquid having an odour of almonds; its specific gravity is 1·209, so that it is heavier than water, in which it is almost insoluble. It mixes freely with oils, fats, spirits, etc. It boils at 207° C., while it can be cooled down until it forms a solid, having a melting point of 4° C. It is capable of being distilled in a current of steam, a property which may be taken advantage of to free the crude nitrobenzene from unchanged benzene or other hydrocarbons. A valuation of the commercial product may be made by determining its specific gravity, which ought to be exact. When treated with a mixture of zinc and hydrochloric acid it ought to yield nothing but aniline, while no hydrocarbons should be left behind on distilling some in a retort with steam. In the soap trade myrbane is very largely used for scenting soaps. Being very strong, it takes but little to develop a pleasant almond odour, while it mixes well with other perfumes. It retains its odour for a long period.

CHAPTER V.

WATER AS A SOAP MATERIAL.

WATER is such a ubiquitous substance and finds so many applications in industrial and domestic uses that much may be written about it of a very interesting character so as to appeal to almost every reader; however, here it is simply proposed to consider it as the most valuable chemical compound which is known.

Water is a compound of the two gaseous, non-metallic elements, oxygen and hydrogen, in the proportion of 16 parts by weight of the former to 2 parts by weight of the latter; its chemical formula is H_2O. Under ordinary conditions it is a colourless liquid, perfectly neutral in all its properties. When heated to a temperature of 212° F. (100° C.) it boils, and passes off in the form of an invisible gas. The temperature at which water boils is found to be a constant one and hence is taken as one point in the graduation of the thermometers, the boiling point, 212° on the Fahrenheit scale, 100° on the Centigrade scale, and 80° on the Reaumur scale. When water is cooled down it solidifies into a solid white ice; the temperature at which it solidifies is also a constant one, and is taken as the zero or starting point on the Centigrade and the Reaumur scales, 0°, and is 32° on the Fahrenheit scale. Water is taken as the standard of specific gravity of solids and liquids; this is on account of the fact that it can be obtained anywhere in a state of purity; its specific gravity is 1·000. Ice is lighter than water, having a specific gravity of 0·9; it will therefore float upon water, a property of immense natural importance. When water is transformed into vapour it expands some 1500 times in volume. When water is changed from solid ice it absorbs heat which is rendered latent or imperceptible, not being capable of measurement by the thermometer: the latent heat of water is 142½ units of heat. In a similar manner when liquid water is converted by heating into gas it also takes up and renders latent a large quantity of heat, the latent heat of water gas being 966 units. When water gas is converted back into liquid water, this latent heat is given out, a property on which depends the employment of steam for heating soap pans, evaporating liquids, drying stoves, etc., and when liquid water is changed to solid ice its latent heat is dissipated. These properties have a very important bearing in relation to water as a motive power; it is, however, not the intention to discuss this point more fully here. When pure water is exposed to the atmosphere or heated it is converted into vapour and passes away without leaving any residue behind.

One English imperial gallon of water weighs 10 lb., while one United States gallon of water weighs 8·33 lb.; one cubic foot of water weighs 62·3 lb.

When water is viewed in large masses, as in deep tanks and lakes, it has a blue colour, and the purer the water the deeper and brighter is this colour.

The most important feature about water is its great solvent properties; there are few substances indeed which will not dissolve in this liquid. There is, however, much variation in the degree of solubility; there are some substances which will dissolve in their own weight of water, such as calcium chloride, caustic soda, while there are a few which will form a solution with less than their own weight; on the other hand some bodies, such as calcium sulphate, strontium sulphate, ammonium oxalate, are but sparingly soluble. Temperature has an important influence upon the degree of solubility, the rule being that with an increase of temperature there is an increase in the quantity of substances dissolved; this is notably the case with such bodies as ammonium oxalate, potassium bichromate, boiling water dissolving much more than cold water; on cooling hot solutions of these bodies the salt crystallises out. When a solution contains as much of a substance dissolved in it as the water will dissolve, it is said to be a saturated solution; from such solutions the substance will crystallise out on cooling to be re-dissolved again on the original temperature being regained. The following table gives the strength of a saturated solution of some important substances:—

TABLE OF SATURATED SOLUTIONS AT 15° C. (60° F.).

	Per cent. of Substance.	Specific Gravity.	Degrees Twaddell.	Degrees Beaume.
Ammonium chloride .	26·3	1·0776	15·5	10
,, sulphate .	50·000	1·2890	57·8	32·3
Barium chloride . .	25·97	1·2827	56·5	31·7
Calcium chloride . .	40·66	1·4110	82·2	42·1
Magnesium sulphate .	25·25	1·2880	57·6	32·3
Potassium chloride .	24·90	1·1723	31·4	19·5
,, carbonate .	52·02	1·25708	114	52·4
,, nitrate . .	21·07	1·1441	28·8	18·2
,, sulphate .	9·92	1·0831	16·1	10·7
Sodium chloride . .	26·39	1·2043	40·8	24·5
,, carbonate. .	14·35	1·1535	30·7	19·1
,, nitrate . .	46·25	1·3804	76	39·8
,, sulphate . .	11·95	1·1117	22·3	14·5
Caustic soda . . .	54·92	1·500	100	48·1

Water plays a very important part in the manufacture of soap; it forms the medium through whose agency the fat on the one hand and the alkali on the other are enabled to unite and form soap; without water this combination or union cannot take place. In addition to thus being the medium there can be no doubt that water has other influences in soap-making due entirely to its great solvent properties. It is a well-known fact that the grains or textures of soaps made in different works from the same materials and by the same process often differ in a rather unaccountable manner; this difference is most likely to be caused by a difference in the character of the water which is used in the various works.

There is no such thing as pure water in nature. The purest is rain water, but this always contains some gases dissolved in it, derived from the atmosphere during its passage through that medium; the next purest is spring water, then come river waters, and, lastly, the most impure natural water is sea water.

Spring, river, and sea waters contain dissolved in them varying amounts of inorganic or mineral and organic matters derived from the rocks over which or through which they may have flowed. It may be inferred that on this account such waters will vary considerably in the character and extent of the matters which are contained in them. For our present purpose we may leave sea water entirely out of consideration as it is not used in making soap, and simply deal with spring and river waters. Now it is found that waters that are derived from a district in which the rocks consist chiefly of granite or other silicious rock contain but small quantities of matter dissolved in them, perhaps not more than 4 to 5 grains per gallon, and these chiefly of an alkaline character. Waters which flow through a region where limestone or magnesian rocks predominate are liable to contain more lime or magnesia in solution, sometimes in rather large proportion. The presence of these bodies imparts a quality known as hardness to the water, a quality which is more easily demonstrated than described ; at all events such waters are very difficult to wash with. Besides lime and magnesia, water often, in fact nearly always, contains small quantities of salt, iron, silica, etc. It is not needful here to discuss in detail all that may be found in water.

Lime and magnesia exist in water in two forms, carbonate and sulphate; the carbonates of these are almost insoluble bodies, and will not dissolve in pure water to any appreciable extent; on the other hand they are soluble in water which contains carbonic acid in solution, in the form of the bicarbonate, and as all natural waters contain more or less carbonic acid it follows that such waters will take up the carbonates of lime and magnesia from rocks and soils. By boiling such waters the carbonic acid is driven off and consequently the lime and magnesia which are held in solution will be thrown down out of the water. The latter having lost its lime becomes "softened"; any hardness which is due to the carbonates of the two metals in question is therefore said to be "temporary hardness". The sulphates of lime and magnesia are soluble in water of their own inherent properties; they therefore are not thrown down when water is boiled; hence any hardness which is due to them is known as "permanent hardness".

Now it is these lime and magnesia compounds which are present in water which will exert the greatest amount of influence in the manufacture of soap. This is due to the fact that they have the property of entering into action with the soap and forming therewith insoluble lime and magnesia soaps; a very small amount of these substances in water will react with a large proportion of soap; it is no uncommon thing to find waters containing 30 grains per gallon of lime carbonate and sulphate.

Now according to the equation

$$\underset{\substack{\text{Calcium}\\\text{Carbonate}}}{CaCO_3} + \underset{\text{Soap}}{2NaC_{18}H_{35}O_2} = \underset{\substack{\text{Sodium}\\\text{Carbonate}}}{Na_2CO_3} + \underset{\text{Lime Soap}}{Ca(C_{18}H_{35}O_2)_2}$$

we see that 100 parts of calcium carbonate will react with 612 parts of soap to form 606 parts of an insoluble lime soap; this latter is the curdy masses which form when soap is mixed with limey water. Now supposing we have water that contains 30 grains per gallon of lime, then each gallon of that water will cause the formation of 183 grains of lime soap, and if in a boiling of soap we are dealing with 6000 to 7000 gallons of water then the lime in that water will result in the formation of 16 to 17 lb. of lime soap, which getting into the finished soap must have some influence on the texture of the soap.

For all practical purposes the sulphate may be considered to have the same action as the carbonate.

The soap-maker will desire to use a water which contains as little lime and magnesia as he can get. In some cases he cannot help himself, but must take the water as it comes to him. He can, however, adopt some method of softening or otherwise removing the lime, etc., from the water. For this purpose several methods and appliances are available. The original Clerk process may be adopted, which consists in first determining the temporary hardness of the water and then adding so much quick-lime as will combine with the carbonic acid in the water, when both the carbonate of lime or of magnesia originally present in the water and the lime added will precipitate out, and on allowing the precipitate to settle in tanks the water becomes clear and is softened. A modification of this plan, which is tedious, is the Porter-Clark process, where the water and lime are mixed together in proper proportions and the mixture sent through a filtering apparatus. A better method is the Archbutt-Deeley process, in which the water is mixed in a tank with the requisite amount of a mixture of carbonate of soda and lime, and the mixture blown with air for a short time, after which the precipitate is allowed to settle and the clear liquor drawn off. This process works well; it will reduce the hardness of a water from 16° to 17° down to 3° with ease and rapidity. Other methods have also been devised for softening water, and it would be worth while for the soap-maker if he is working with a very hard water to soften it before using. It does not cost much, while the operation of making the soap would be easier and a better quality of soap would be turned out. Then where the water is also used in the steam-boiler for raising steam another advantage would accrue, and that is the reduction of scale in the boiler and a necessary reduction in the coal bill.

CHAPTER VI.

SOAP MACHINERY.

The plan on which the present chapter is based will be that of following the materials, the fats and oils and alkalies, used in soap-making, through the various operations needful to their transformation into a bar of soap, and describing the various machines they pass through during that process. Incidentally, a little may be said about soap-making, but it is not intended to describe the operation of soap-making or the process of making any kind of soap in any detail, reserving that portion of the subject for a subsequent chapter. Care will be taken to point out the principles on which the working of the machinery is based, and to show the best methods of working.

It is a difficult matter to give general advice on the construction of a soap factory, so much depends upon local features, such as site, relations to railways and waterways, proportion of floor area to vertical height, all of which have a material influence on the planning of efficient soap works. It is always best to have as much floor area as possible, so that the great majority of the factory buildings shall be one storey in height. One little point should be kept in mind, and that is to so plan the various portions of the works that as the operation of making fats and alkalies into soap progresses they will travel from room to room in a steady way, without having to traverse any ground previously gone over. Another point is to use the power of gravity as much as possible in the transference of oils, fats, and alkalies from one place to another; it comes much cheaper than labour in carrying about.

The Alkalies.—The soap-maker receives his caustic potash or caustic soda in large iron drums, containing the alkali in a solid form; this it is needful to reduce to a liquid form by dissolving it in water. In many soap works this is done by breaking out the caustic from the drum, which by-the-by is a most unpleasant operation for the workmen engaged, and throwing the lumps into an iron tank, usually placed somewhere on the ground floor; water is run in and the mass boiled with the aid of steam. This is by no means the best method of working. Another defect which is sometimes met with in old soap works, is having the top of the tank level or nearly so with the floor. This is a bad fault, as there is great liability for accidents to happen in the way of operatives falling into the lye with disastrous results. In the usual plan of dissolving the caustic, one of source of trouble is met with, that of the caustic forming into a solid cake at the bottom of the tank and refusing to dissolve, the lye thereby being weaker than it would otherwise be.

The best method of making the soda or potash lyes is to provide a tank in a room or place above the soap-boiling kettles; part of this tank may be placed below the floor; a swing syphon tube should be placed in the tank for the purpose of running off the lye. For this purpose a syphon tube has many advantages over a simple or fixed tap placed on the side of the tank. A grating should be fixed in the top of the tank just below the surface of the liquor contained in the tank; this grating may be placed on supports which extend from side to side of the tank. On this grating the drums of caustic, which have had the ends knocked out, are placed. The water penetrating into the drum gradually dissolves out the caustic; the solution, being heavier than the water, sinks to the bottom of the tank, a constant circulation of fresh water or weak liquor passing through the drum becoming stronger in so doing, which then goes to the bottom of the tank. This goes on until all the caustic in the tank is dissolved. This method of working means less labour in the handling of the caustic, which is of some advantage; there is no undissolved caustic formed at the bottom of the tank, while the operation is done somewhat quicker.

Figure 25 is an illustration of a tank constructed on these principles.

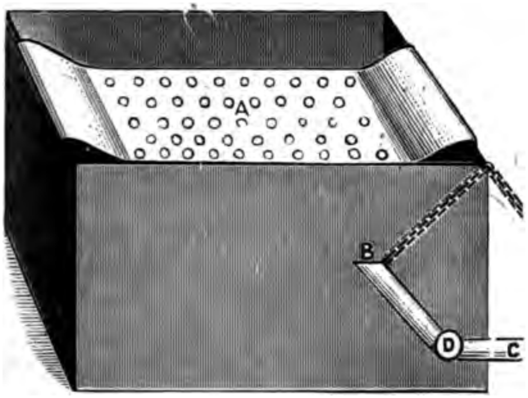


Fig. 25.—Lye Tank.

The following table gives some idea of the most useful sizes of tanks, with their capacities in gallons, when filled to within one foot of the top, and the weight of caustic of 77 per cent. strength contained in the number of gallons of lye of various strengths.

Size of Tanks.			Gallons Capacity.	Weight in Pounds of Solid Caustic 77 per cent. in Lye of			
Depth.	Length.	Width.		10° Tw.	20° Tw.	30° Tw.	50° Tw.
5	5	3	374	171¾	332	615½	1047
5	7½	3	500	243	443	823	1400
8	10	4	1·310	636½	1160½	2156¼	3668
8	12	5	2·620	1273	2321	4312½	7336

Sometimes lye tanks of a cylindrical form, fitted with mechanical stirrers, are used, but there is no advantage in using such over the form just described, and the stirrer absorbs power to drive it, which it is desirable to avoid if possible.

Fat-melting Tanks.—Although it is a custom with some small soap-makers to break open the casks of tallow, oil, or other soap-stock as they receive them, and throw the contents into the soap-kettle as required to make soap, such a course is not to be commended, as the fats, etc., may contain much dirt, all of which goes into the soap-kettle. Then, again, the casks are liable to be broken up in getting out such solids as tallow and rosin. The best course to pursue is to provide a shallow trough about the width of the length of a cask and sufficiently long to accommodate a number of barrels. Along the top of this trough are placed two stout wooden supports, on which the barrels are held in position over the trough, bunghole downwards. Into each barrel, through the bunghole, is run a steam pipe, the steam from which causes the tallow or other soap fat to melt and run into the trough below, from whence the melted fat flows into a large settling tank in which all the dirt, etc., drops out, while the

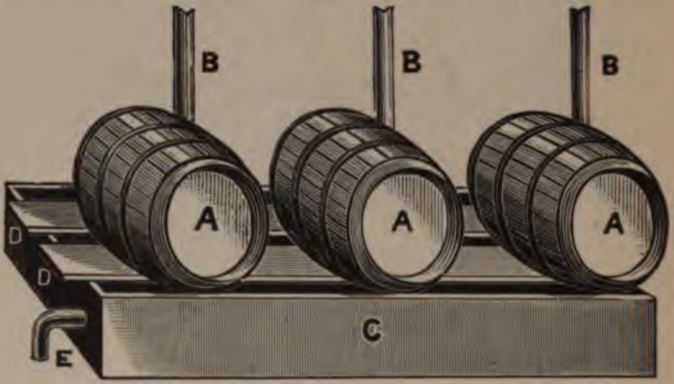


Fig. 26.—Fat Tanks.

clear melted fat is run as required into the soap-kettle. Figure 26 shows this arrangement.

It is best wherever it is possible to place the fat tanks above the soap-kettle, so that the fat can flow by gravity into the kettle. This, however, is not always feasible, and then some means must be found to transfer the melted fat from the tank to the kettle above. This may be done by means of a pump, such as will be found described later on, but in many soap works the transference is effected by means of what is often named a stock-blower.

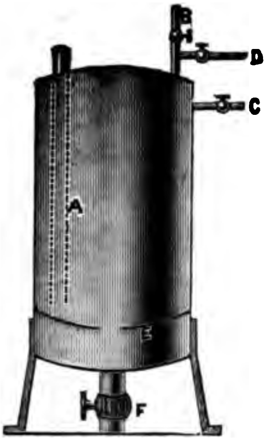


Fig. 27.—Stock-Blower.

The stock-blower is shown in figure 27. It consists of a cylindrical vessel which can be made air-tight and placed upright; a little above the bottom is placed a dished false bottom with a hole in the centre; this is for the purpose of allowing any dirt and water to settle out under the false bottom, which prevents them from getting into the soap-kettle. A pipe passes from the bottom of the vessel to the soap-kettle. A steam pipe passes steam into the top of the vessel, and the pressure of this forces the stock into the soap-kettle.

Soap-boiling Kettles or Pans.—In the manufacture of soap, alkali and fat are commonly boiled together. This is carried out in what are called soap-kettles. These are almost invariably made of iron, although they can be built of other materials. The size can, of course, be proportioned to the quantity of material which has to be made, and something will be said on this point shortly. In olden times these soap-kettles were always heated by fire, but in modern soap works they are heated by steam, sent into the kettle from a steam boiler. This steam may or may not be superheated. Steam heating has many advantages over fire heating. It is cleaner and, besides, less labour is required to keep the materials in the pan well mixed together—the passage of the steam through the mass ensures this. Then in a fire-heated pan there is a risk that those portions of the kettle nearest to or in contact with the fire or hot fire gases will become overheated, and any soap contiguous thereto will become burnt or charred, and the pan of soap thereby discoloured. The great difficulty there is in keeping a pan of pasty soap well stirred up by hand adds to this danger, which

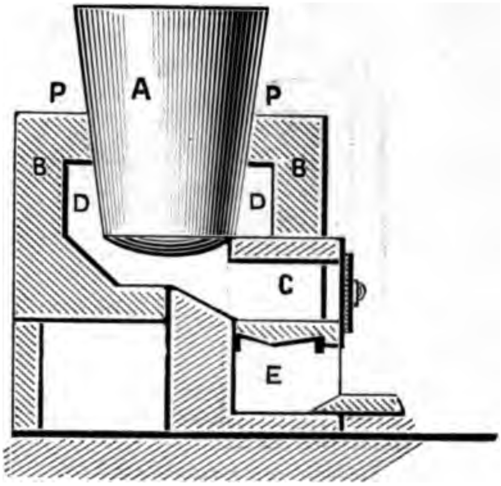


FIG. 28.—Fire-heated Soap Pan.

is quite absent from a steam-heated pan. Then there is another point. Soap is very liable to froth over and fob, the only remedy for which is to draw the fire or shut off steam and allow the kettle and its contents to cool down. In the case of a fire-heated pan this is by no means easy, and should any of the soap materials boil over and get into the fire, there is no telling what might happen. With a steam-heated pan, shutting off the steam is all that need be done.

Figure 28 is a drawing of a fire-heated kettle. The kettle A may be made of any size; it is supported by brickwork B B, the upper portions P P of which are made to serve as the working platform from which the contents of the kettle are manipulated. The fireplace C is at one side, and the heat and gases from the fire pass round the kettle in flues D D; E is the ashpit.

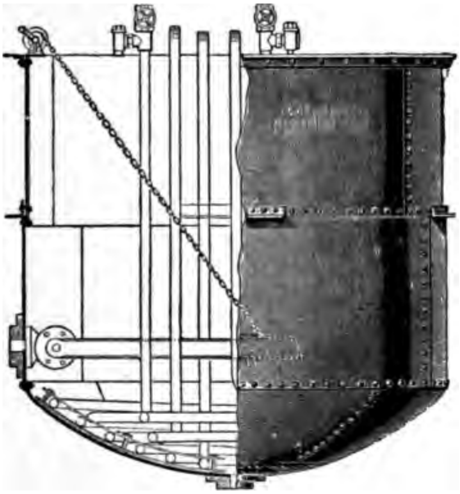


FIG. 29.—Steam-heated Soap-pan.

As fire heating is going out of use in soap-making, it is not needful to describe such kettles in more detail.

Steam is now almost universally used for heating soap-pans, except perhaps in small works. Figure 29 is a drawing of a steam-heated soap-pan, made by Messrs. W. Fraser & Co., which shows the manner in which steam pans are usually constructed.

This pan is, circular in shape, made of stout boiler plates riveted together; a flange running round the pan about its centre serves to act as its support, and for constructing a platform to work the pan from. It is fitted with both open and closed steam coils. This is almost absolutely necessary in soap-pans. The open coil is employed during the first portions of a boil, while the closed coil is used at the last. The pipe fitted with a chain on the left of the figure is a draw-off pipe (the skimmer pipe as it is called) for the finished soap, and is connected with pipes outside the pan, which convey the soap to the flames or crutchers as may be required. The opening at the bottom of the pan is for running off the lyes, and is for that purpose connected with valves and pipes leading to the spent lye tanks.

It is customary with large pans to fix two open and two closed steam coils, so that the degree of boiling can be better regulated and under control than is possible if all the steam were sent through one coil, for it must be obvious that a certain amount of pressure is required to overcome the back pressure of the materials in the pan against that of the steam. If one large coil is turned full on, then the boiling might be too strong; if the steam in such a coil were turned partly off the pressure might not be sufficient to work the materials in the pan, whereas by having one large and one small steam coil, when the valve is turned full on in either, there is certain to be sufficient steam pressure to overcome that of the soap in the pan. With the small coil a gentle boil can be obtained, with the large coil a strong boil. A pressure of 45 to 60 lb. is very good to work at.

It is not customary to enclose the soap-pans in any way, but in one or two soap works a wooden hood has been fitted above the pan in prolongation of its sides; this is continued up to a floor above the pan, while from this floor rises a shaft, passing through to the outside, and in communication with the hood below. This chimney shaft serves the purpose of conveying the steam which rises from the boiling soap away from the pan, and therefore adds to the comfort of the workmen. The hood serves also to prevent boiling over should the soap begin to fob very much.

To prevent the loss of heat from the sides of the pans, these may be coated with a non-conducting composition and with boards. This is not always done, but it is a very desirable addition, and facilitates the separation of the lye from the soap by enabling the latter to retain its heat, and so keep fluid longer.

In some soap works, instead of being made circular, the pans are made square. So far as practical working is concerned there is no material advantage of one form over another.

As regards the size of soap-pans, they may be made of any dimensions to suit the quantity of soap which it is desired to make. Generally large soap-pans are easier to manipulate and deal with than small pans; the yield of soap is usually greater, while it is of better quality and freer from enclosed lye. There is a maximum size, however, a pan of about 30 tons capacity, beyond which it is not wise to go. It may be taken as a general rule that 1 cwt. of fat requires a pan of about 40 gallons capacity to boil to soap, that proportion being required to give room for the aqueous lye which is added, with the necessary room for boiling.

A pan of about 15 feet deep, and of the same diameter, will be large enough to make 26 to 28 tons of soap in at one batch. A pan of 7 feet in diameter and 6½ feet in depth, will be large enough to deal with 1½ tons of fat, giving about 2 to 2½ tons of soap. These are only approximate figures.

The soap-pans should not be placed too far from the boilers supplying the steam, or otherwise there is a great risk of condensation occurring in the connecting pipes, and this condensed water finds its way into the pan and weakens the lyes, while increasing to too great an extent the bulk of the contents. The main objection to the pan as constructed in the manner shown in figure 28 is that the various coils are in the way of the pan being cleaned out. This, however, is not an insuperable objection, and much depends on the manner in which the coils are made and placed in the pan; besides it is not needful to clean out the pan every time it is used, as whatever soap remains adhering to the sides of the pan or on the steam coils goes into the next batch and so is not lost. When a change is made from one soap to another the pan must be cleaned out.

FIG. 30.—Steam Soap Pan.

The steam which is passed through the closed steam coil should be passed through condensers, and the water so obtained again returned to the boiler, or employed in making the caustic lyes.

Steam jacketed soap-pans have been made and are employed in soap-making. Such pans are, however, only suitable in small sizes, say up to 500 gallons capacity; large jacketed pans are much more expensive than a simple pan with a steam coil.

FIG. 31.—Steam Soap Pan.

Figure 30 shows Dopp's seamless steam jacketed pan. This pan has the jacket cast along with the pan proper, and hence is stronger than pans in which the jacket is fastened to the pan with rivets. It is made in all sizes, from 1 to 500 gallons capacity. The stays which join the inner pan with the outer shell materially strengthen the vessel, while they serve as conductors of heat to the inner pan. Thus these pans are more economical in use than plain jacketed pans. They can be fitted with an agitator, as shown in figure 31, and will be found very useful to check fobbing and to mix the soap ingredients together.

One of the troubles of the soap-maker is that of fobbing, as it is called, the tendency of the soap mass at the beginning of operations to froth or boil up. This defect is best remedied by turning off the steam and beating down the froth by means of paddles; better still a whirling wheel may be employed. Such is shown in figure 32. It is attached to the sides of the soap-pan by means of loose brackets and is turned by a handle at one end of the axle. It acts by breaking up the foam, or froth, and so preventing it increasing in quantity. Sometimes a more elaborate form is employed, consisting of a pair of paddles revolving in opposite directions; these are suspended at a suitable point in the soap-pan, and by their revolution the froth is broken up and prevented from increasing. The paddles are held in a Y-shaped support, the legs of the Y forming the bearing for the paddles, a pulley connected with suitable gearing overhead communicating motion to the paddles. Although more elaborate it is doubtful whether they are more effective than the reel described above.

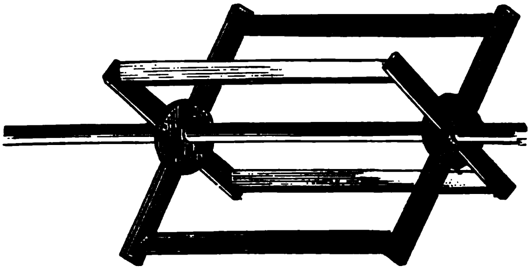


FIG. 32.—Soap Whirl.

A great deal of soap is now being made under pressure in a suitable boiler.

Messrs. W. Fraser & Co. make a high-pressure soap-boiler, which is shown in figure 33. This boiler is 4 feet in diameter and 8 feet high and is made of steel boiler plate; it is fitted with steel manhole and cover. The fittings usually attached are charging pipe and valve, outlet pipe and valve shown at the bottom of the illustration, thermometer tube and thermometer, a safety valve which is usually set to blow off at 65 or 70 lb. pressure. The boiler is set in a brickwork fireplace, the fire playing at the bottom and a portion of the side. The brackets which are fitted on the side of the boiler are for supporting it on the brickwork.

FIG. 33.—Pressure Soap Boiler.

These pans are worked by putting in the charge of fat, the right quantity of alkali and water, then heating and maintaining the pressure at 60 to 65 lb. for about four to five hours, when as a rule the saponification will be complete. The soap may next be run off into crutchers, the scent, etc., mixed with it, and then it is framed. The pan is ready for a new charge, which is run in immediately the old one is run off. Two batches of soap may thus be made in one pan in the course of a day. The weight of the charge is 1 ton.

The soap as made in this manner contains the whole of the ingredients added; there is no salting out nor are there any lyes to run away. A great deal of the success of making soap by this high-pressure system depends upon employing the right proportion of alkali to fat and the proper quantity of water; if too much be used the soap comes out too soft.

An analysis of a sample of soap made by the high-pressure system by the author showed it to contain:—

20·70 per cent. of water.
5·65 per cent. of combined sodium.
·36 per cent. of free alkali.
68·00 per cent. of combined fat.
·20 per cent. of free fat.
5·09 per cent. of glycerine, saline bodies.

The sample was firm and of excellent quality, which shows that the high-pressure system can make as good soap as the low-pressure system commonly in use, while a larger quantity of soap can be turned out in a given time.

Some other forms of apparatus for saponifying under high pressure have been devised, some of which practically consist of a boiler fitted with agitators; these have in practice become obsolete, as the agitators made the boilers difficult to clean out and were of no material advantage.

SOAP FRAMES.

The next kind of soap plant which merits description is the soap frames as they are called. It is astonishing how old names still adhere to modern forms of machinery, however much they may differ from the original form to which their first name was due. Soap frames are a case in point.

In the early days, they were a frame-like structure, in which the soap was allowed to cool. Now they take a box-like form, and a more appropriate name would be soap coolers.

Figure 34 shows an old wooden soap frame such as was used in the old time when an excise duty had to be paid on soap. These frames are made 45 in. long by 15 in. wide. A number of them were placed one on top of another, pegs in one fitted into holes in the other, or rods were passed through the lot to form one large box of about 45 in. deep holding 9 to 11 cwts. of soap. The dimensions here given were fixed by law. These wooden soap frames are now only employed in a limited manner, chiefly for making mottled soaps, or soaps by the cold process.

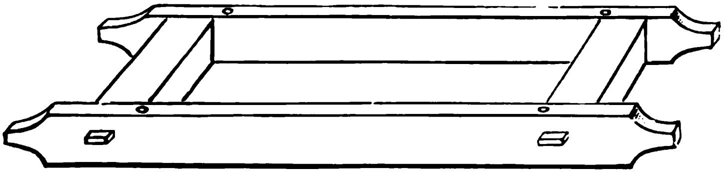


FIG. 34.—Wooden Soap Frame.

The modern soap frame usually consists of a wooden base board, placed on small wheels so that it may be moved from place to place as may be convenient. Upon this base board is built four sides of wrought or cast iron so as to form a box; these sides are fastened together by bolts and nuts, so that they can be taken apart whenever required.

Figure 35 is the drawing of a soap frame as made by Messrs. E. Forshaw & Son, the sides of which are made of cast iron and have diagonal strengthening bars cast on them. The mode of fastening the sides of the frame together differs in different makes of the frames; sometimes portions of the sides are prolonged into lugs containing holes through which rods pass, binding the ends of the frames against the sides, the ends of the rods being secured by screw nuts. The ends of the frame are generally made to fit into grooves in the sides so as to make as tight a joint as possible, thus preventing the leakage of soap. In the frame illustrated the ends fit into groves which are planed into the sides. All edges and bottoms are planed so as to ensure the frame being perfectly tight when fitted together. The bolts which fasten the frame together have square threads. It can be swivelled round on the two centre wheels and moved in any direction. These soap frames are made to hold from 5 to 10 cwts. of soap; small sized frames allow the soap to cool quicker and are thus more advantageous than large frames, in which the cooling is much slower. In the making of mottled soaps and sundry other special kinds, slow cooling is a desideratum, and therefore it is worth while to employ large frames.

FIG. 35.—Iron Soap Frame.

The thickness of the metal of which the sides are made has also a material influence on the rapidity of cooling. If the metal be thick the rate of cooling is slow; it is, however, necessary to have the metal of a certain thickness to withstand the pressure of the soap in the frame.

Figure 36 represents Whitaker's patent soap frame. This frame is made with a wooden bottom and sheet-iron sides, which being thin allow the heat to pass away quickly, and so the soap gets cold quicker than in frames with thick iron plates. To give the necessary rigidity to the sides ribs of corrugated iron are fastened to them as shown in the drawing. The ends are made of wooden planks and are tightened against the sides by means of clamps, which are easily worked, and permit the frame to be built up or opened out in a few minutes. In such frames soap cools sufficiently in from thirty-five to forty-eight hours, according to the time of year, to strip and slab. A good frame may be made as follows: The sides are made of steel plate of about ⅛ in. thick, the ends are made of wood of 1⅓ in. thick, along the ends of the sides are placed 1½ in. angle irons, the web that projects being tapered from the top to the bottom, so that when the frame is built up, the bent clamp forced down, the tapered irons press the sides and ends together. Close to the top and along the sides are fastened angle irons, which project

Fig. 36.—Whitaker's Soap Frame.

beyond, these projections serving as handles to manipulate the sides with in building up or taking apart the frame; besides these, two other longitudinal angle irons are fixed to the sides for the purpose of strengthening them. The bottom of the frame is made of a piece of wood of about 1½ to 2 in. thick; in the centre of this is fixed an axle carrying a pair of 9 in. wheels, on which the frame can be moved at will; near each end and in the centre are fixed a pair of 4½ in. wheels, arranged to move on a swivel like a caster wheel; these small end wheels much facilitate the moving to and fro of the frame and turning it round if desired. Such a

FIG. 37.—Morgan's Soap Frame.

frame 55 in. in length, by 40 in. in depth and 15 in. wide, these measurements being inside, will hold about 10 cwts. of soap.

Figure 37 is a drawing of a soap frame made by Mr. H. D. Morgan, of wrought steel, which is patented in this country and in the United States. This frame is made of special mild steel plates hammered flat, and stiffened at the upper edge by flanging, and along the sides by a beaded flange to prevent warping. The beaded flange is so formed that, should any soap escape past the joint between the end and side, it is cooled in the cavity before it can get away, thus preventing leakage. The sides and ends fit into a cast-iron base iron plate grooved to receive them.

Bolts and nuts are entirely dispensed with. The clamping bars are so shaped that they both bind the sides against the ends and pull the ends tightly against the beaded flanges.

It is a good plan to have two bottoms to each pair of sides and ends. Then while one bottom is in use and the soap on it is being slabbed and barred, the other bottom is being fitted to the sides and ends and made into a frame to be filled with soap.

In some factories there are tracks of rails to which the wheels of the frame fit so that they can be more easily moved about.

All iron frames should be coated inside with lime to prevent rusting, which would discolour the soap. This defect of iron frames is absent with wood ones; these gradually get their pores filled up with soap and the sides become smooth, which aids much in the stripping of the soap, while leaving the sides of the soap smooth and glossy. Iron frames made from enamelled iron would be found of service in soap-making; there would be no tendency to rust, while the smooth sides of the enamelled iron would impart a gloss to the soap, besides allowing stripping to be done more easily.

In framing soaps it will be found an advantage if when the soap has been run into the frames and has set on the top, a board which just fits the frame be placed on the top of the soap and then weighted; thereby the soap is pressed and becomes of a better grain. This weighting of the soap is not always done.

SLABBING SOAP.

After the soap has been framed and it has become sufficiently cool for the purpose, the next proceeding is to cut it up into slabs of about 2 inches thick, or as may be required for the particular size of tablets which the soap-maker proposes to send out.

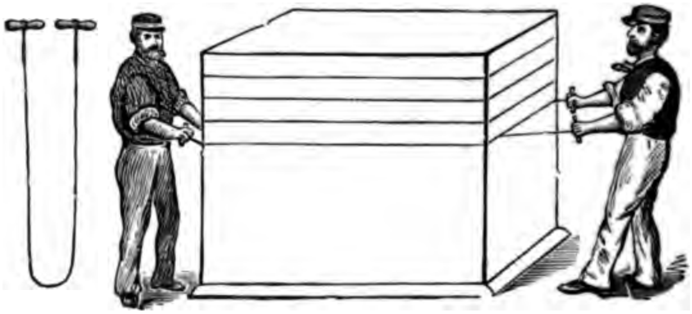


FIG. 38.—Slabbing Soap.

Slabbing may be carried out either by hand or by machine. Figure 38 is a drawing showing the method of slabbing soap by hand. The block of soap has its sides marked by means of a scribe along the lines of which it has to be cut; this scribe is a wooden rod containing iron points at the proper distance apart. The workman is provided with a long piece of steel wire, the ends of which are sometimes fastened to two handles, or in some instances to one. This wire is fitted to the mark made by the scribe, and then drawn through, thereby dividing a slab of soap from the main block. This operation is repeated until the whole block has been so slabbed. This method of working is very simple but effective; it is still largely employed in preference to using machines.

Ralston's slabbing machine is represented in the diagrammatic sketch which shows the principle of the machine (see figure 39). It is a portable machine, and can be wheeled about from place to place as occasion may demand. It consists of four pillars, one at each corner, at such distances apart that a block of soap can be placed between them, or rather that the machine can be placed round the block. At one end is a block of wood which takes up the pressure on the block of soap while it is being cut. The cutting arrangement consists of a frame carrying horizontal wires placed at the proper distance apart; this is so made that it can by means of chains and windlass be drawn along the machine, and thus the wires cut the soap up into slabs. The action of the machine is fairly quick, and it is capable of doing a large amount of work. Another form of slabbing machine

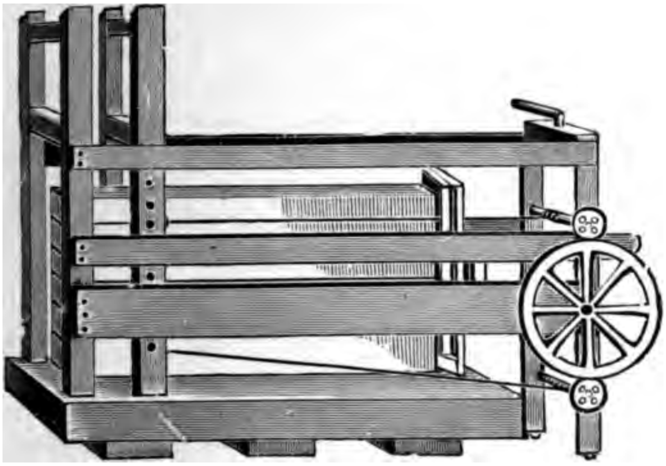


FIG. 39.—Slabbing Machine.

sold by Messrs A. Saalfeld & Co. consists of two parallel beams of wood supported on tressels; on this runs a trolley provided with wheels, on this trolley being placed the block of soap. In the centre of the machine is stretched a wire, the height of which above the trolley can be regulated so that slabs of various thicknesses can be cut. The block of soap on the trolley is pushed first in one direction, and then after raising the wire to the right extent the direction of the machine is reversed and another slab cut. These operations are repeated until the block of soap is cut into slabs.

A similar machine to Ralston's has been made and sold by some other firms of soap machinists. The construction of this machine may be briefly described. There is a bed formed of grooved girders, in which an upright frame, carrying wires, travels backwards and forwards.

At the opposite end is fixed a triangular arrangement formed of an upright block, against which the soap is pressed during the working of the machine. There is a windlass with attached chains that, passing over pulleys, draw the wire frame through the block of soap, and so divide it into slabs. The working of this machine is simple. The block of soap from the frame is placed on the bed of the machine, then the triangular winding gear is placed in position, the chains properly adjusted, and the windlass turned. When the soap has been slabbed the windlass and chains are removed, the slabs of soap taken away to be barred, when the machine is ready for another block of soap.

Another machine which is sold by Messrs. Adolphe Saalfeld & Co. is constructed to cut a block of soap up into bars in one operation. It consists of a table near one end of which is a frame carrying two sets of wires, one vertical, the other horizontal. At the other end of the table is a rack and pinion, which on being worked causes a block of soap which may be put on the table to be forced against the wires, and so cut into bars. Such a machine is not, as a rule, found to be well adapted for large blocks of soap, as the power required is then too great for hand labour.

In all modern slabbing machines the wires are made movable, so that they may be set at any gauge apart to cut up soap into slabs or bars of any convenient size. It is important that these wires should be tightly stretched, so that when they come into contact with the soap they will not sag or bend in any way, as such bending if it occurs spoils the slab for cutting into bars or tablets. Stout piano wire is the best material to make wires of.

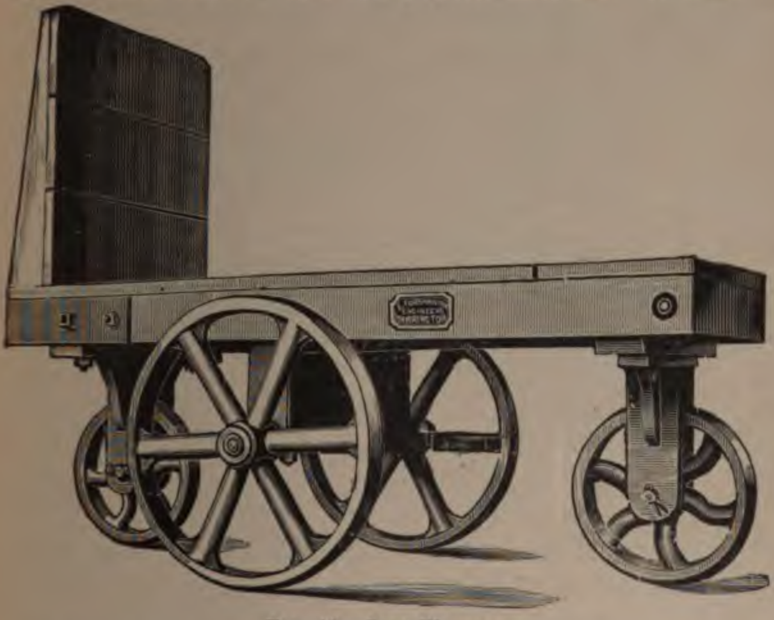


FIG. 40.—Soap Waggon.

Figure 40 shows a soap waggon for wheeling the slabs of soap to the bar-cutting machines. The wheels are so arranged that the truck swivels round on the two large wheels in the middle, and allows easy movement in any direction, a feature of no little importance in the construction of soap waggons.

BARRING MACHINES.

After the soap is cut into slabs, the next proceeding is to cut these into bars. The variety of machines which have been devised to carry out this operation is fairly great; generally hand-power machines are used, but mechanical ones are also made.

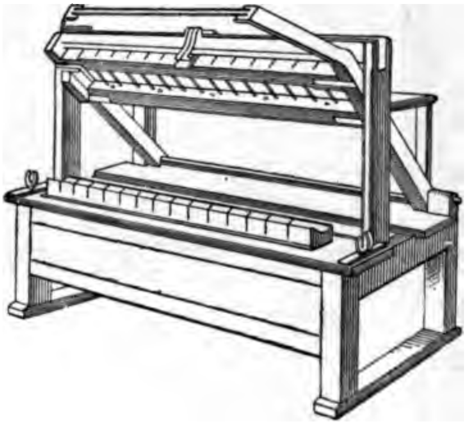


FIG. 41.—Soap Barring Machine.

Figures 41 and 42 show different makes of what is perhaps the most common form of barring machine in use in soap works. Figure 41 is the form made by Messrs. W. J. Fraser & Co., while figure 42 is that made by Messrs. William Neill & Son. This machine consists of a table carrying an upright frame; on the table near the front is the long rest with notches at about 2 inches apart, that being the usual thickness that a bar is made. From the back of the machine springs another framework, which is hinged to the table; this in its normal position rests against the upright frame previously referred to, forming, as it were, the hypotenuse of a triangle. The slab of soap is placed with one edge on the rest at the front of the table, and the other against the wires. The cutting frame is now released from the hook or catch which keeps it up, and pressed down through the soap, whereby the latter is cut into bars. These bars fall upon a rest which is fixed to the back of the cutting frame, and when the latter is returned to its normal position are removed while another slab is being placed in position.

FIG. 42.—Soap Barring Machine.

Generally these machines are provided with a drawer placed under the table to receive the scraps of soap which are always made in cutting up soap. These scraps are afterwards thrown into the next boiling of soap.

These machines work very well and are not very expensive, and being simple in construction are not liable to get out of order.

A London firm supplies a barring machine in which the wire frame is made to travel to and fro, so that when a slab of soap is placed in front of the frame, and has been cut up into bars, these may be removed and another slab put in their place. Then the wire frame is moved back again and cuts this second slab into bars. This machine saves a great deal of labour, and is of comparatively simple structure.

A barring machine which is in use in some soap works not only cuts the slab up into bars, but separates them from one another afterwards, thus facilitating their removal. This is effected by having the cutting wires fixed in the centre of a table. On one half, the slab to be cut is placed; by means of a wheel and chain the slab is forced against the wires and cut. The bars are received on the other half of the table, which is made up of wooden bars of the width of a bar of soap. These are connected together by webbing. While receiving the soap they are close together, but when the soap is in position the webbing is stretched, and so the bars are separated.

After being cut into bars, the soap is often cut into tablets; this operation is carried out in the barring machines described, which are adapted for the purpose, the distance between the wires being altered.

Figure 43 represents a machine worked by power, which cuts slabs of soap up into bars and tablets. It wil be noticed that it has two sets of wires placed at right angles to one another; these wires are made movable so that their distance apart, and therefore the size of the bars and tablets, may be regulated as required. A slab of soap is placed at one end of the machine and forced against the barring wires; when it has travelled to the full length of the machine in that direction the bars of soap are forced against the tablet-cutting wires by mechanism working at right angles. By the time the tablets have been cut the machine is ready to receive another slab. This machine is capable of turning out a very large quantity of soap, something like 15 tons per day, and saves a great deal of trouble.

Other forms of tablet-cutting machines have been devised, but the above will be found very efficient machines and it is not needful to describe any other forms.

FIG. 43.—Soap Cutting Machine.

SOAP-STAMPING MACHINERY.

Time was when soap was sold by the makers to the retailer in the form of bars, in boxes of 1 or 2 cwt., and the retailer cut the bars up into pound pieces and sold them either in that form or in the bar form in which he received it. Often the consumer did not know the name of the maker of the soap he used. Now, however, matters have altered in this respect, for while a good trade is still done in bar soap, and those consumers who are able will find it the best to buy the soap in this way, the custom has now grown of selling in packets, or tablets, and these are invariably stamped with the name of the maker of the soap, although some large retailers by arrangement with the maker have their own names stamped on the soap. This stamping of soaps has led to a great increase in the use of stamping machines, and these will now be described.

Even now, as at first, a great deal of soap is stamped by a hand stamp, this being usually made like a brass box with a handle. The letters are formed of separate pieces, and are fastened in the box in the required order by means of thumb screws. This system is a slow one, although an expert stamper will get through a large number of tablets if he adopts a good system of working. But where very large quantities of soap have to be dealt with it is imperative to employ a mechanical stamper, of which there are many makes to be bought; some work by hand, others by steam power, and others are constructed to work by steam direct. A brief *résumé* of such machines will be given.

One of the most important parts of the stamping press, so far at any rate as the appearance of the finished tablet is concerned, is the mould or die in which the soap is pressed. In most machines this takes the form of two pieces, to form the upper and lower surfaces of the soap tablet, together with a loose ring which serves to form the body of the tablet. By altering the shape of the ring, and the shape of the upper and lower dies, the shape of the tablet which is formed can be altered to any extent. This form of mould with loose ring is perhaps not the best that could be devised; the soap tends to stick in the ring. This is overcome by moistening it with a little salt water from time to time. The delay, however, caused by having to remove the soap tablets from them reduces the working output of the presses. This is avoided by making the ring and bottom die in one piece and fitting the press with an automatic lifting apparatus which presses the tablet out of the mould during the upstroke of the press. This lifting apparatus will be shown later on.

With some presses the tablet moulds are in separate pieces and the sides are hinged on to the bottom piece. The action of the press on this is to press all the sides up, and so form a mould for the soap. When the tablet has been formed and the press returned, the sides fall down leaving the tablet to be removed. With moulds made in this way a much larger output of tablets per machine is obtained.

FIG. 44.—Soap Stamping Machine.

Hand Soap Presses.—Several forms of hand soap presses are made by various firms. The principal forms will be here noted. Figure 44 shows a form of press made by Messrs. William Neill & Son. The action of this machine can be grasped by an inspection of the drawing. A plunger carrying the upper surface die and the ring or mould for the sides of the tablet is connected with a pair of weighted levers, the pulling down of which on the piece of soap placed on the bottom die presses the tablet. With this machine a large quantity of soap may be got through by a boy, who works the press with one hand, while with the other he places the soap in position and removes it when stamped. In this machine there is no arrangement for automatically removing the tablet of soap from the press or mould, and, as stated, the tablets sometimes stick.

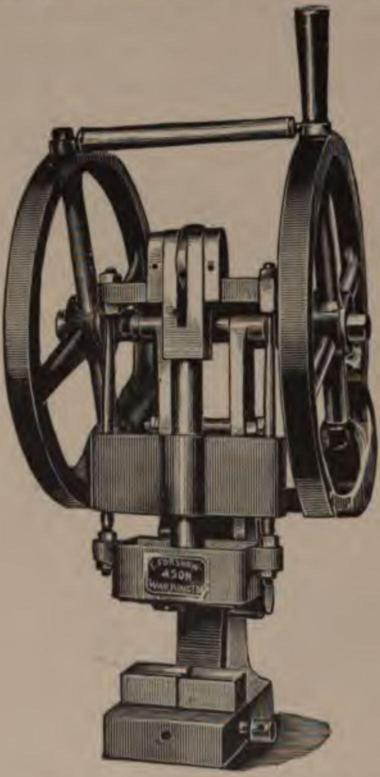


FIG. 45.—Soap Stamping Machine.

Messrs. E. Forshaw & Son make the soap press shown in figure 45. In it the levers are replaced by a pair of fly-wheels, the use of which enables a greater pressure to be brought to bear upon the soap during the pressing. With this machine a fairly large output can be obtained. It is easy and light to work. This is a favourite form of soap-stamping press. In some makes an arrangement is provided for lifting the tablets out of the moulds after stamping.

The presses hitherto described have been worked by hand, but presses are also made which work by a foot lever. Figure 46 shows such a press made by Messrs. H. Wm. Dopp & Son, the general construction of which can be readily gleaned from the drawing. The pressure of the foot on the lever brings down the die on the cake of soap on the mould, thereby stamping it, while on releasing the pressure the die rises and at the same time a cam comes into action and forces the soap cake out of the mould, this action being noiseless. Since it was first introduced this machine has undergone some improvement in design; the working parts have been strengthened, and the operation of the machine perfected.

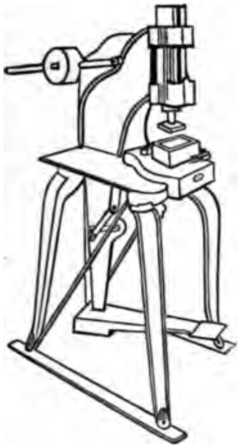


FIG. 46.—Soap Stamping Machine.

The same firms make a press which is capable of taking a bar of soap 14 in. long.

We now come to those stamping presses which are worked by steam power. Such presses are coming more into vogue than formerly, but for reasons which have just been pointed out, it is doubtful whether they will supersede manual presses. Of steam stamping presses there are at least two types: there is one in which the steam is applied direct, while in the other the power is carried through a band and pulley. Of these two types the latter will probably be the one which will be most largely adopted; not that

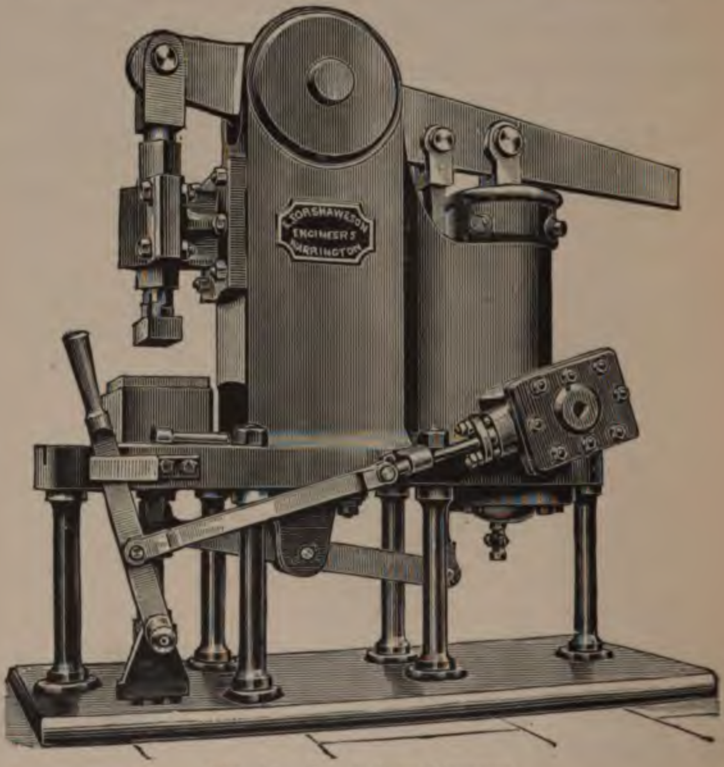


FIG. 47.—Steam Soap Stamper.

it is capable of doing more or better work than can be done with a direct driven press, but that the necessary presence of steam pipes, and the possibility of these having to be carried for some distance, make the former rather objectionable from many points of view. Over long distances of piping there is a considerable loss of power through condensation, a great deal of water being formed in the pipes, which interferes sadly with the efficient working of the presses.

One of the best of the steam presses now being made is that of Messrs. E. Forshaw & Son, and shown in figure 47. It is very well constructed and works automatically. It requires only two boys to work it; one boy places the plain tablet on the table of the machine, the other boy removes it as it comes from the machine stamped. The machine feeds and discharges itself, it works noiselessly and smoothly, and is capable of turning out 1500 tablets of soap per hour. Any kind of moulds may be used and they can be changed very readily. The machine is rigidly constructed, and has been adopted by many large soap manufacturers, who speak favourably of it.

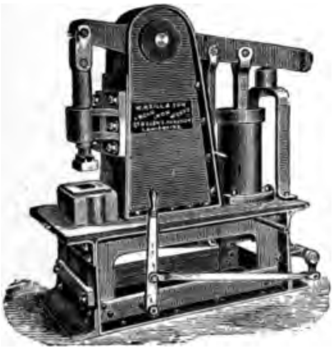


FIG. 48.—Soap Stamping Machine.

Figure 48 shows a steam soap stamper made by Messrs. Neill & Son, which is of most substantial construction.

It works automatically, only needing the plain tablets to be placed on a feeding table, and it discharges at the back of the machine. This machine is capable of turning out a large quantity of work, forty to fifty tablets per minute being the rate of speed.

Figure 49 shows a belt-driven revolving soap stamper made by Messrs. W. Neill & Son. The soap is delivered to this machine at the front by an automatic feeding apparatus, passes through the dies or moulds, and is delivered at the back stamped. It is easy to work and turns out a large quantity of tablets.

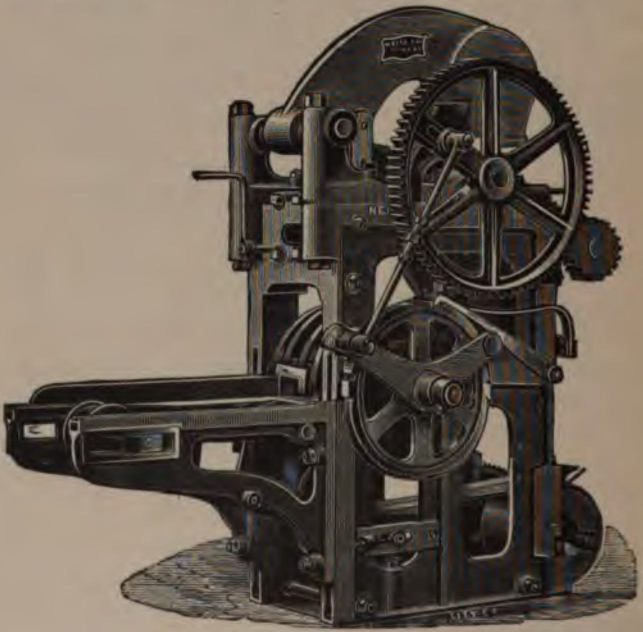


FIG. 49.—Revolving Soap Stamper.

Moulds used in stamping soap are made in great variety of shapes and sizes and to produce designs of all kinds. Some are made with loose sides which fall down after the stamping and permit the soap tablet to be readily removed;

the most common are solid, and the tablet is forced out of them by a suitable contrivance.

Some other forms of presses are made, but the above will be sufficient to serve as types.

TOILET-SOAP MACHINERY.

Time was when all kinds of soap, whether for toilet, ordinary domestic or industrial uses, were produced solely by the aid of such machinery as has hitherto been described. Now, however, a great deal of the best quality of toilet soaps is produced by the aid of elaborate machinery, the main principle underlying which seems to be a grinding or milling of the soap, so as to produce a more homogeneous mass, thereby obtaining a harder and more durable soap and completing the saponification of the fats so that a more neutral soap is formed at the same time.

This system of milling soaps was first developed in France, where it is largely applied, and where the construction of the necessary machinery has been brought to a great perfection. It was early introduced into England. The writer remembers seeing a soap-milling machine at one of the early London Exhibitions, but until lately it never obtained a great footing in this country; soap-makers are, however, beginning to give more attention to the system. In America this system has been largely used.

The milling system starts with a ready-made soap. It need hardly be pointed out that the soap should be, nay, must be, of good quality, for it can scarcely be expected that first-class toilet soap can be made by its means from a poor quality of soap, although the process much improves it. Further on some particulars will be given as to the preparation of soaps for milling.

The first operation is to cut the soap bars up into shavings. To effect this a cutting machine is used, one form of which is shown in figure 50 and which is sold by Messrs. Wm. Neill & Son. The working portion of this cutter consists of a disc carrying six steel blades placed against radial slits in the disc; the bar of soap presses against the disc by its own weight, the bars being fed in the two troughs which are seen on each side of the machine.

The shavings are next dried; this may be done by placing them on trays in a room heated by steam pipes, the room being filled with racks on which to place the trays of soap shavings. In this room the soap is left until it gets sufficiently dry. The amount of water left in should be about 10 per cent.; at all events it ought not to exceed 15 per cent.

FIG. 50.—Soap Cutter.

Messrs. Beyer Frères make a continuous automatic drying machine. This consists of a closed chamber heated by steam pipes. On the top of the machine at one end is fitted a mill with two or more cylinders revolving at different speeds, and above which is a hopper. Into the hopper is fed the soap. The revolutions of the cylinders cause the deposition of the soap in fine shavings into the drying chamber below. Here it is received on endless bands, placed one above the other and extending the full width of the machine. These bands continuously travel from one end of the machine to the other, the motion being in opposite directions in each pair of bands. The soap shavings drop on the topmost band, and are carried by it to the opposite end of the drying chamber, where they drop off on to the band below, by which they are carried to the other end of the machine. From band number two they fall to band number three, and so on until the last band is reached, when they will have become dry enough for the subsequent operations. This machine works very well, and needs little attention; its capacity being one ton of toilet soap per day, requiring the attendance of one man and an assistant. The

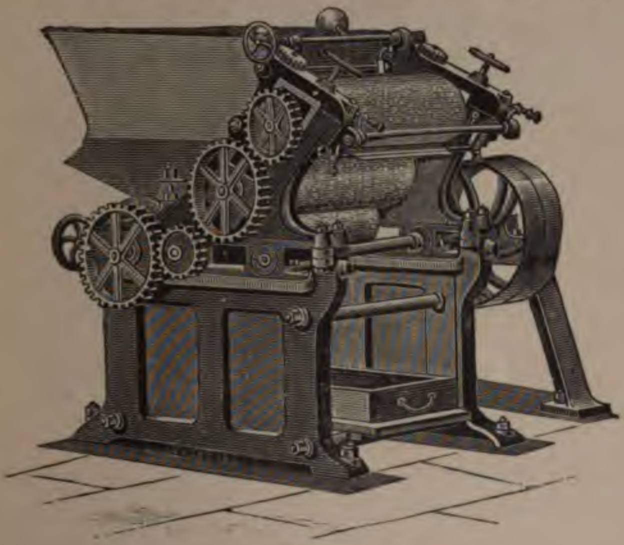


FIG. 51.—Soap Crushing Machine.

machine is rather costly. M. Wallois also makes a similar machine.

The dried soap is next transferred to the crushing mills, where it is passed between a number of granite rollers; such a machine is shown in figure 51, that being the form sold by Messrs. Wm. Neill & Son. This machine has four granite rollers and two hoppers divided by a slide. The dried soap shavings are thrown into the bottom hopper, and travel over the four rollers and fall automatically into the top hopper, a steel comb which scrapes off the top roller; by drawing the slide the soap is allowed to fall into the bottom hopper and again through the rollers. When the soap has thus passed twice through the rollers, colour and perfume are added to the mass in the bottom hopper and the soap, etc., worked three or four times through the mill to thoroughly amalgamate the materials and obtain a homogeneous mass of soap. One cwt. of soap requires ten minutes to run through this machine. The operation may be repeated as often as required. The drawing shows the gearing-wheel uncovered, but the machine is provided with a cover to prevent accidents. The machine runs almost noiselessly.

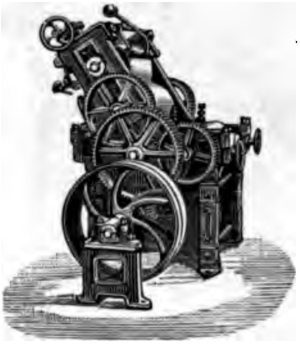


FIG. 52.—Soap Crushing Machine.

Figure 52 is a large soap-crushing mill made by M.

Wallois with four granite rollers of 13 to 16 inches in diameter and two hoppers; from 1¼ to 1½ cwt. of soap can be dealt with at one time. A ton of soap per day can be turned out with such a crushing machine.

When the soap has been thoroughly worked in this crushing mill a new scraper is caused to come into action, which transfers the soap in thin shavings down a tin-lined shoot (the tin lining being for the purpose of keeping the soap clean) into the hopper of a squeezing, or, as it is often called, a plodding machine, which is shown in figure 53. The plodding machine is provided with an archimedean screw whereby the soap is gradually driven forward and at the same time subjected to a considerable degree of compression, the soap being thus consolidated and made firm, the parabolic form of the compression cylinder bringing about this pressure. The cylinder of the machine is at first double, thus forming a jacket in which cold water circulates

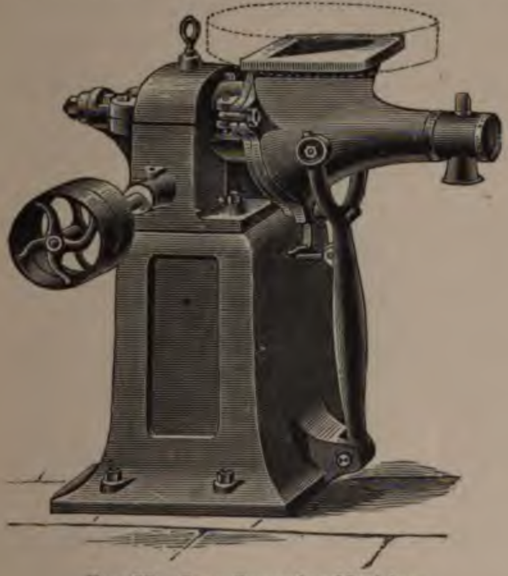


FIG. 53.—Soap Squeezing Machine.

for the purpose of keeping the soap cold, the friction and pressure causing a great deal of heat to be generated; this heat might if allowed to accumulate cause a loss of perfume and colour in the soap. The end of the machine is commonly known as the cannon, as from it the soap is discharged. The mouthpiece is kept hot by means of a gas jet, which is usually supplied with each machine, the purpose of heating being to impart a gloss and finish to the soap. The soap travels very fast through this machine, about 5 cwt. per hour being the output of such a one as is shown in figure 53, which is made by Messrs. William Neill & Son.

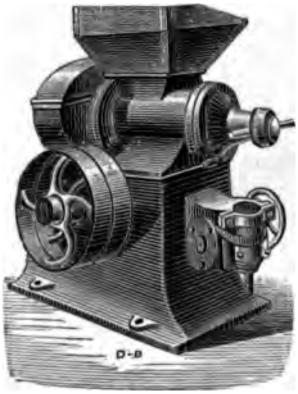


FIG. 54.—Soap Squeezing Machine.

Figure 54 is a large plodding or squeezing mill made by M. Wallois which will turn out 5 cwt. of soap per hour.

As long as soap is supplied to the plodder through the hopper it will issue from the mouthpiece of the cannon in the shape of a continuous rope, the form of which may be varied—round, oval or square—by using various shaped dies or moulds fixed in the mouthpiece. This enables tablets of any shape to be formed with the minimum of trouble. Further, by means of an apparatus and gauge fitted to the stand placed in front of the cannon to receive the soap, the rope can be cut into convenient lengths for tablets, which are next stamped by the stamping press, various forms of which have already been described.

When the plodder has stopped working some soap will remain in the cone. To remove this a small piece of apparatus is turned into the mouthpiece that forces out all that is left. In some forms of these machines the cone is made to turn down so as to facilitate cleaning it and freeing it from any adhering soap.

Combinations of the crushing and plodding machines are constructed, so that no labour need be expended in transferring the crushed soap from one machine to another.

FIG. 55.—Crutching Machine.

CRUTCHING MACHINERY.

In the manufacture of many varieties of soaps, notably in filling the common soaps with silicate of soda and in perfuming and colouring toilet soaps, there are used what are known as crutching machines, the object of which is to mix the various ingredients of the soap thoroughly together. In the early days of soap-making this was an operation usually performed by hand, with an instrument known as the crutch, the operation being termed crutching, and the name has come down to modern times, although now-a-days the operation is done by machinery. The commonest form is a circular vessel, made of wrought iron or boiler plate. In the centre of this is fixed a mixing apparatus, which usually consists of a central shaft which is made to revolve by suitable gearing, this shaft carrying arms and in some cases a chain, the motion of which through the mass of soap causes it to become mixed and form a homogeneous mass.

Figure 55 is a drawing of a pair of soap-crutching machines made by Messrs. Wm. Neill & Son. These are driven by means of a donkey engine fixed on the side of one of the machines, this being in connection with an overhead shaft on which are bevel wheels working the central shaft of the crutchers. An opening in the bottom of the machine, which is ordinarily kept closed by a valve, allows the soap to run into the frames when it is properly mixed.

FIG. 56.—Crutching Machine.

Figure 56 is a drawing of a pair of crutchers made by Messrs. E. Forshaw & Son. These are fitted with a special driving engine, friction crutches for throwing the agitators in and out of gear, outlet valves, etc. Generally, crutching machines are made without steam jackets, but, occasionally, such are desirable to keep the soap warm and enable it to mix easily.

Crutching is a very simple operation and purely mechanical, and there should be no trouble in crutching soap; the only thing is to allow the machine plenty of time to do its work.

Sometimes this operation is carried on in conjunction with that of remelting, and a good many makes of modern mixing machines are really combined remelting and crutching machines.

DOPP'S REMELTING AND CRUTCHING MACHINE.

This consists of a steam jacketed pan. The firm, Messrs. H. Wm. Dopp & Sons, have a special method of casting the pan and jacket in one piece. The steam pipes for supplying the jacket are fixed to the front side of the machine, while there are also suitable outlet pipes for exhaust steam and condense water. The mixing arrangement consists of an archimedean screw working in a cylinder, the action being to draw the soap up through this central cylinder and cause it to flow over the top and back into the main body again; this is a most effectual manner of working. The driving gear for the screw is on the top of the machine, and is so arranged that the direction of motion of the screw can be reversed, and in place of the soap moving up it moves down, this arrangement also bringing about a more perfect admixture of the soap. There is another feature of this machine, which is that it may be used for remelting old scraps of soap, and, the screw working in conjunction with the cylinder (which, it may be remarked, has open sides), it acts as a cutting apparatus, and so easily reduces the soap to fragments, and thus facilitates the remelting and mixing of the soap.

Another form of crutcher which is sometimes made with a steam jacket, and at others without, according to the requirements of the users, has the cylinder horizontal; the central shaft is in the centre, and is also horizontal. From it extend a number of arms which are arranged spirally, their action as they revolve being to mix up the soap and at the same time to cause it to travel towards one end of the crutcher, whence it flows back to the other end, when it is thoroughly mixed by opening a valve at one end of the machine. The soap is forced by the working of the arms out into the frames which are placed ready to receive it.

Crutchers require to be strongly made, as the material they have to deal with is very stiff and by no means easy to stir; they require some power to drive, say about two-horse, but of course this will vary according to the size of the machine. Some makers fix an eight-horse engine to the larger machines; the power thus supplied is rather in excess of actual requirements, and that excess may be employed in other directions if needful.

REMELTING MACHINES.

In preparing toilet soaps it is a common plan to prepare them from soap of various kinds already made, melting them by heat and then mixing in the perfume and other ingredients which may be required.

A very convenient form of remelter consists of a jacketed pan in which the soap, which has been previously cut into thin shavings, has been put. The pan should be provided with a stirring arrangement so that the soaps, etc., can be thoroughly mixed together. Soap is, however, a bad conductor of heat, and in a steam jacketed pan, unless the contents are kept well stirred, the outer portions might be melted while the inner portions are still cold and solid. It is advisable, therefore, to bring the heat as soon as possible to the whole mass of soap. This is effected in one form of remelter by having a number of upright steam pipes or tubes fixed in the machine; the heat is thus brought very quickly to the very centre of the mass of soap, and so the operation is soon done.

The time it takes to remelt a batch of soap depends upon the state of dryness of the soap; the more water there is in it the quicker is the operation over. Should the soap be too dry it is often advantageous to send in a current of open steam, whereby both heat and moisture are supplied at the same time.

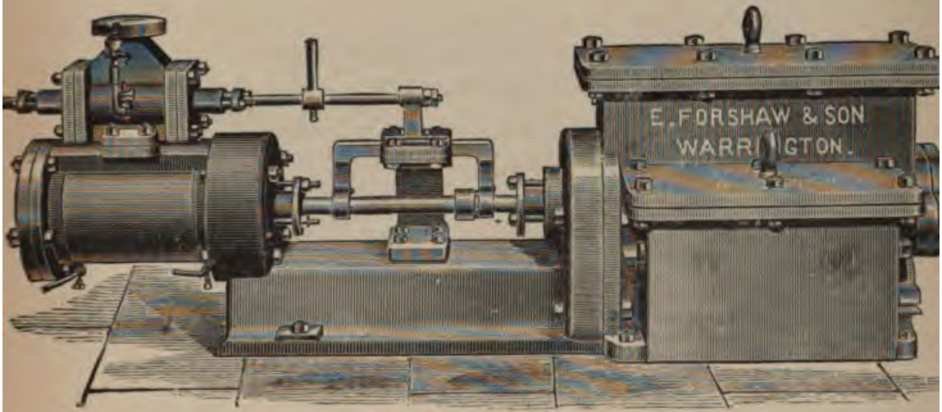


FIG. 57.—Soap Pump.

SOAP PUMPS.

For the purpose of transferring the soap from one place to another, as, for instance, from the soap pan or crutcher to the frames, the best plan is to take advantage of gravity and run the soap into the place where it is required to go. But this is not always possible, inasmuch as it necessitates the placing of the plant or machines one above the other, and this cannot always be done. Where the machines are on a level it is necessary to employ some mechanical means for conveying the soap from one machine to the other; this may be done by hand labour, using ladles or scoops, but such a plan is tedious and costly, and in large soap works is inadmissible. The best method is to use pumps which are made specially for the purpose.

Soap pumps are of the ordinary direct acting plunger type such as is shown in figure 57, which represents a soap-pumping engine made by Messrs. E. Forshaw & Son. This is a very convenient form, and quite satisfactory in use.

Another form of soap pump, which is largely adopted because it does not necessitate the employment of a separate engine, but may be attached to the ordinary shafting of the works, is of the type known as rotary pumps. The feature of this form of pump is a circular cast-iron box with an inlet and outlet. In the box rotates a blade of a spiral form, which, catching the soap as it flows in by the inlet, forces it out by the outlet pipe and so as to place it where it is required.

FIG 58.—Soap Drying Machine.

In making toilet soap it is found very desirable that the tablets should be dried a little before stamping, as then a better impression is obtained, an important feature in connection with tablets having fancy designs on them. Then for other reasons tablets may have to be dried before being sent out. A very convenient machine for this purpose is one shown in figure 58, made by Messrs. W. J. Fraser & Co. Its construction is well shown in the drawing. It consists of a number of shallow trays or drawers placed in a drying chamber. At one end is a heating chamber through which, by means of a fan, air is drawn from the surrounding atmosphere and sent into the drying chamber where the drawers are. In its passage through the heating chamber the air gets warm, and its capacity for holding water being thereby increased it takes up water from the soap and dries it during its passage through the drying chamber. This machine may be used for drying all kinds of soap, in tablets, bars or shavings.

So far has been described all the different forms of machines employed in the manufacture of soap. Of course the machines by different makers will vary from one another in minor details, although the forms bear a close resemblance. It is practically impossible to describe in detail the machines of every maker, so what has been done is to mention those that may be regarded as types.

CHAPTER VII.

THE TECHNOLOGY OF SOAP-MAKING.

A WIDE and yet only sufficient classification of soaps would be into:—

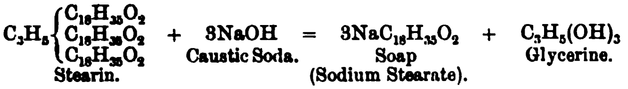
A. Domestic soaps.
B. Toilet soaps.
C. Industrial soaps.
D. Special soaps.

Domestic soaps are those used in the house for washing, scouring, etc. Toilet soaps—those better qualities of soaps which are employed solely in the toilet. Industrial soaps—those employed in certain trades, as in wool washing, calico printing, etc. Special soaps—those used for specific purposes, as for medical purposes, shaving purposes, etc. Each of these classes may be even further divided, but the writer does not believe in systems of classification into a great variety, as has been done by some writers on soaps.

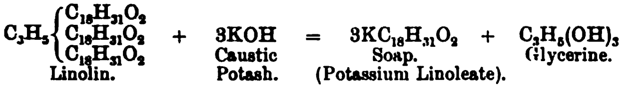
A. DOMESTIC SOAPS.

Soap is prepared by causing an alkali and a fat or fats to enter into chemical combination; the alkalies used are solely soda and potash. Ammonia has but little action on fats, while lime is of no use, because the soap it forms is insoluble in water.

When a fat or oil is brought into contact with a solution of either caustic soda or caustic potash (the carbonates of these alkalies have but a weak action and cannot be used in the ordinary process of soap-making) then saponification begins to take place; the acid constituent of the oil enters into combination with the alkali to form the soap, while the basic constituent, glycerine, is set free. This reaction is shown in the following equations, which gives the action of both caustic soda and caustic potash on typical oils :—



$$\underset{\text{Stearin.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{35}O_2\\C_{18}H_{35}O_2\\C_{18}H_{35}O_2\end{matrix}\right.} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\substack{\text{Soap}\\\text{(Sodium Stearate).}}}{3NaC_{18}H_{35}O_2} + \underset{\text{Glycerine.}}{C_3H_5(OH)_3}$$



$$\underset{\text{Linolin.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{31}O_2\\C_{18}H_{31}O_2\\C_{18}H_{31}O_2\end{matrix}\right.} + \underset{\substack{\text{Caustic}\\\text{Potash.}}}{3KOH} = \underset{\substack{\text{Soap.}\\\text{(Potassium Linoleate).}}}{3KC_{18}H_{31}O_2} + \underset{\text{Glycerine.}}{C_3H_5(OH)_3}$$

The first one represents the action of caustic soda on tallow, the principal constituent of which is stearin, while the second one shows the action of caustic potash on linseed oil, the principal constituent of which is linolin. If these equations are studied they will be found to be built upon common lines, and further that there is an exchange of constituents between the bodies which take part in the reaction; the acid portion of the fat takes the basic metal of the alkali to form the soap, while the basic constituent of the fat, the glyceryl, C_3H_5, takes the hydroxyl, HO, of the alkali to form the glycerine, or, as the chemist prefers to speak of it, the glycerol, which is set free.

The reaction between the fat and the alkali is a chemical one, and like all chemical reactions takes place in definite proportions; that is, a certain quantity of fat will always take a certain quantity of caustic soda or caustic potash to saponify it; and as oils differ from one another in their composition, one oil or fat will take a different proportion of alkali than another, thus, for instance, castor oil takes 18 per cent. of caustic potash to saponify it, while tallow takes 19 per cent., and coconut oil 26 per cent. It unfortunately happens, however, as is always the case with natural products, that the same oil varies in the amount of alkali it requires with different samples, although the amount of variation is small. The following table compiled from several sources gives the percentage of caustic potash and of caustic soda required to saponify various oils and fats ;

Oil.	Per cent. of Caustic Potash, KOH.	Per cent. of Caustic Soda, NaOH.
Lard	19·1 to 19·6	13·6 to 14
Almond	19·5 ,, 19·6	13·9 ,, 14
Sesame	19 ,, 19·4	13·5 ,, 13·7
Rape	17·1 ,, 17·9	12·2 ,, 12·8
Poppy seed	19·3 ,, 19·5	13·8 ,, 14
Niger seed	18·9 ,, 19·1	13·5 ,, 13·6
Cod	18·5 ,, 21·3	13·2 ,, 15·2
Whale	18·8 ,, 22·4	13·4 ,, 16
Butter	22·1 ,, 23·2	15·8 ,, 16·5
Palm nut	22 ,, 24·7	15·7 ,, 17·7
Tallow	19·3 ,, 19·8	13·7 ,, 14·1
Palm	19·6 ,, 20·2	14 ,, 14·4
Sperm	12·3 ,, 14	8·8 ,, 10
Olive kernel	18·8	13·4
Olive	19·1 ,, 19·6	13·6 ,, 14
Arachis	19·1 ,, 19·6	13·6 ,, 14
Cottonseed	19·1 ,, 19·6	13·6 ,, 14
Linseed	18·7 ,, 19·5	13·3 ,, 14
Hemp seed	19·3	13·8
Walnut	19·6	14
Seal	18·9 ,, 19·6	13·5 ,, 14
Porpoise	21·6	15·5
Coconut	24·6 ,, 26·8	17·5 ,, 17·7
Lard	19·2 ,, 16·6	13·7 ,, 14
Dripping	19·6 ,, 19·7	14 ,, 14·1
Bone fat	19·1 ,, 19·7	13·6 ,, 14
Castor	17·6 ,, 18·1	12·5 ,, 13
Rosin	17 ,, 19·3	12·1 ,, 14

As regards the quantity of glycerine which is formed during the reaction, Allen in his *Commercial Organic Analysis*, vol. ii., gives the following figures as to the proportion of glycerine which may be obtained from various oils:—

Bottlenose sperm oil	3·10	per cent.
Northern whale oil	11·96	,,
Porpoise oil	11·09	,,
Menhaden oil	11·10	,,
Lard	10·83	,,
Tallow	10·00	,,
Butter fat	11·06	,,
Olive oil	11·40	,,
Rape oil	9·82	,,
Sesame oil	9·94	,,
Cottonseed oil	9·50	,,
Linseed oil	9·39	,,
Castor oil	9·13	,,
Coconut oil	12·11	,,
Palmnut oil	11·70	,,
Palm oil	9·71	,,

It will be seen that the proportion of glycerine which can be obtained from those fats and oils commonly used in soap-making is from 10 to 12 per cent.

The methods employed in the manufacture of soap of any kind may be divided into three groups:—

1. Boiling the fats and alkalies together under ordinary atmospheric pressure in open boilers—the ordinary process of soap-boiling.

2. Boiling the fats and alkalies together under pressure in closed boilers.

3. By mixing the alkalies and fats at ordinary temperatures—the so-called cold process.

The first method is by far the oldest and most commonly employed. In this method the soap is boiled with a solution of the alkali (caustic soda for hard soaps, caustic potash for soft soaps) until it is saponified; then, in the case of hard soaps, salt is added, which throws out the soap in the form of curds, which are collected and allowed to set into the form with which the public is familiar. There is also obtained what is known as "spent lye," an aqueous liquor containing the salt used, any excess of alkali that may have been used, and also the glycerine which was formed during the process of saponification. Formerly this was thrown away, but now it is treated for the recovery of the glycerine it contains.

In the second method the fat and alkali are boiled together under pressure in a closed vessel or boiler, and when saponification is complete the soap is set on one side to cool and when cold it is ready for sale.

In the third method the fat is just melted and then mixed with the alkali in the form of a strong solution, the mixture being placed on one side for some time to allow the saponfication to become complete, when the soap is ready for use.

In both the second and third methods there is no salting out, while the glycerine that is formed remains behind in the soap.

Each of these three methods will be discussed in detail.

Hard Soap.—It is extremely difficult to attempt any classification of hard soaps; the varieties are numerous, and many are produced by simple modifications of the process of making and of the materials employed. Then again some kinds of soap, grain or curd soaps for instance, can only be made by one—the boiling—process. It will therefore be best to describe in detail the processes employed in the manufacture of the various grades of domestic soaps, and indicate the various kinds of soap for which they are best adapted.

SOAP-MAKING BY THE BOILING PROCESS.

Probably 90 per cent. of the soap which is made in this country is made by the boiling process in open pans, such as have been described in the last chapter, heated by fire or by steam, the latter being the most modern plan. In this method of boiling the fat and alkali are brought together in the presence of water in such proportions as experience has shown will enable them to make soap, but the quantities are not definitely proportioned one to the other; the boiling brings about the saponification of the fats and forms the soap, which can then be finished in any way that is desirable. There are three chief varieties of hard soap produced in this way dependent upon certain modifications in the finishing operations; these are known as "curd," "fitted," or, in America, "settled," and "run" soaps. These of course are independent of varieties of soaps produced by varying the materials used.

In starting a soap boil it is advisable to see that the pan is quite clean, while the inside should be well white-washed or lime-washed; this prevents the iron of the pan from affecting the soap in any way and prevents its corrosion. Then a small quantity of weak lye of about 2° Tw. is run in, filling up the pan to about one-tenth of its depth; this is heated by means of the closed steam coil to near the boil, and then there is run in a portion of the fats which are to be saponified, this fat having been previously melted in separate tanks; the quantity is not of much consequence, but about one-third of the total charge is a fair proportion. There is then run in soda lye at 10° Tw.; a stronger lye than this should not be used. One of the difficulties in soap-boiling is to start the saponification of the fat; if the lye be too strong this starting does not take place readily enough, and other difficulties are introduced. By using weak lye, however, there is little if any difficulty experienced; about 15 gallons may be allowed to every 5 cwt. of tallow run into the pan. The steam is turned on to bring the mass to the boil. The material may rise up in the form of froth very considerably, this proceeding being known to soap-makers as fobbing. This occurs only at the starting of a boil, or when running in more fat or alkali; if it happens the steam must be turned off, the mass of fob beaten down by the hand paddle or beater and the pan left to itself for a few hours, when the boiling may be resumed. It will probably be found that the boiling will now proceed very quietly and without further trouble; during the time the pan has been standing the fat and alkali have been reacting and entering into combination with one another. It is this liability to fob that renders it undesirable that a soap pan should be fully charged to start with. Sometimes there appears very little difficulty in starting the saponification, at other times there appears great difficulty. Much will depend on the condition of the fat; if this be very neutral then it will not be easy to start its saponifying; on the other hand if it contain some free acid this will at once enter into combination with the alkali and form soap, which by increasing an emulsifying tendency of the fat enables the alkali and fat to more thoroughly amalgamate together, and therefore facilitate the process of soap formation. With a view of imitating this action it is the custom of many soap-makers (and it is a custom worth following) to throw into the pan on its being first charged all the scraps of soap which they may have about; such scraps dissolving in the weak lye help forward the saponifying of the fat to a great extent There are always plenty of soap scraps produced in cutting the blocks of soap up into slabs and bars; these should always be placed on one side and sent into the soap-boiling house for this particular purpose.

When the first lot of fat and lye appears to have been thoroughly amalgamated together, there may be run in a ton of oil; afterwards, or better simultaneously, lye; this may now be used stronger, say 17° to 18° Tw., than was first employed, and of it 200 gallons will be required for one ton of fat. This lot is now boiled up for two hours. Fobbing will rarely occur at this stage. At the end of the time given the rest of the charge may be run in and the boiling continued. It is advisable to keep it well stirred so as to bring the fat and alkali into intimate union. If the boiling be done with open steam, then the steam itself passing through the soap is almost sufficient to do this. In this case, however, there will be some considerable condensation of the steam in the pan; this must be allowed for, and rather stronger alkali, 23° to 25° Tw., employed in the last stages. If a closed steam coil be employed, then the soap must be kept stirred by means of the hand paddle or mechanical stirrers. At the end of the boil very little stirring will be required; the soap will boil up very nicely and gently in what are known as roses and this gentle boil is a sign that the end is approaching. Soap-boiling is one of those things that cannot be taught by books owing to the difficulty of describing all the changes in appearance of a charge of soap during the process of boiling it up. The length of time a pan of soap takes to finish depends entirely on the weight of soap being treated and may vary from five hours for a small charge to twelve or fifteen hours for a large one. The end of the operation is ascertained by taking out samples from time to time by means of the paddle and examining them. They should have a firm consistency, be free from any oil or fat, which would show that more alkali is required, and when tasted have only a faint biting sensation on the tongue; this would show that the alkali was in slight excess, as it should be. Then again the appearance of the soap is some guide. When properly saponified it will have a homogeneous and semi-transparent look, smooth and glossy, and fall off the paddle in clear flakes; on the other hand if it be opaque and rather granular in appearance, this is an indication that there is either an excess of fat or an excess of alkali, which will be shown by the other tests previously alluded to. Sometimes there are signs that there are free alkali and free fat present in the soap-pan at the same time, which shows that the saponification of the fat has not been properly conducted; the remedy in such a case is to add some water and proceed with the boiling.

It may be stated here that roughly 100 lb. of fat require 100 lb. of lye at 32° Tw. to complete saponification; coconut oil takes about one-fourth more.

Salting Out.—The next operation is that of salting out, or, as it is sometimes called, "graining" the soap; this is done by throwing into the pan either common salt or a strong brine liquor. This throws the soap out of solution in the form of grains or curds and thus separates the soap from the water employed in the operation of boiling and from the excess of alkali used, and from the glycerine formed during the process of saponification. This property of salt of throwing out the soap from the solution in which it exists in the soap-pan depends upon the fact that while soap is soluble in water yet it is insoluble in solutions of alkaline salts; when therefore such are added to a solution of soap the latter is thrown out of solution. Some soap-makers prefer to use brine, but ordinary common salt is what is commonly used. The salt is thrown into the pan in small quantities at a time until the soap forms in small grains and a quantity of lye is clearly visible when the paddle is placed in the soap and then lifted out. A very little practice soon shows the soap-maker when this point is reached. Care must however be taken not to add the salt in too large a quantity at a time and to allow each portion to dissolve before adding another portion, otherwise there is a liability to get an excess of salt in, and this is undesirable for two reasons—because it is not economical to use more material than is necessary to do the required work, and second, excess of salt introduces difficulties to be overcome in subsequent operations. The soap in the pan loses its smoothness and transparency, becomes more opaque and grainy; the boiling also becomes rather irregular, and tends to occur in bursts, and sometimes there is a tendency to boil over.

When sufficient salt has been added and the contents of the pan separate out on the paddle into a grainy soap and clear lye, the steam is shut off and the pan allowed to remain at rest for four to five hours according to the size of the batch. It may be mentioned here that it is impossible to state definitely the quantity of salt which may be required to salt out any given batch of soap. This will be found to vary and is dependent upon the action of several factors—the strength of lye used in the saponification, whether there has been much or little condensation of water from the steam in the pan, whether any coconut oil or palmnut oil has been used in making the soap; and as all these factors are liable to vary with every batch of soap it is not possible to state any definite quantities of salt for salting out.

On standing for four to five hours the mass in the pan separates into two layers or portions ; the upper one consists of the soap holding perhaps about 40 per cent. of water, while the lower layer is a liquid known as the "spent lye". This is more or less dark in colour according to the character of the fat used in making the soap; it contains any excess of caustic soda which may have been used, the salt added to separate out the soap, sodium carbonate, any impurities which may have been present in the original caustic soda and in the fat, together with the glycerine which has been formed during the saponification of the fat. This lye is now run off from the soap into storage tanks so as to be ready for subsequent treatment with a view to the recovery of the glycerine and salt it contains.

This concludes the first stage in the preparation of all soaps, and it is from this point that differences of treatment arise to produce various kinds of soap. The operation of soap-boiling requires to be conducted with care and attention, and every effort should be made to see that the boiling is complete. This makes a considerable demand on the skill and experience of the soap-boiler. Too strong an alkali should not be used, or, as stated above, it will be difficult to start the saponification, and yet different fats will require different strengths of lye or will saponify with different strengths. Thus while tallow, palm oil, cottonseed oil and some others will not work with lye stronger than 10° to 12° Tw., coconut oil and palmnut oil will take lye up to 20° Tw., indeed saponifying best with the strong lye; linseed and olive oils usually work best with a lye of intermediate strength. Then of course some fats take more alkali than others, and this must be allowed for or imperfect saponification will take place ; a little excess of alkali should be used, but too much should be avoided, as such excess tends to retard saponification rather than assist it.

Boiling on Strength or Clear Boiling.—The soap from the salting-out operation is now run into the pan and then a small quantity of caustic lye at 20° Tw. run in and the soap boiled on this for three to four hours. During this boil the soap should remain open and a clear lye always visible; if it does not thus present itself, then a little stronger lye should be added. Some soap-makers give a preliminary boil with a little water and thereby close up the soap before they add the caustic to open it again, and there can be no doubt but that this is the preferable course. The object of this boil on strength is to complete the saponification and to ensure that the soap is quite free from any unsaponified fat. For this purpose it is not advisable to use any stronger lye than is absolutely necessary for the purpose of just opening the soap; any excess is harmful rather than otherwise, as it tends to retard rather than assist the reaction, while the soap exhibits a tendency to be rather caustic. Some attention should be paid to this boil, as it has a material influence on the grain and quality of the finished soap.

After boiling for three to five hours, according to the size of the batch of soap being made, the steam is shut off, and the pan of soap covered up and left to settle; this takes from thirty-six hours to three days, according to the amount of soap in the pan. At the end of this time the contents of the pan will have divided into two portions—one of soap at the top, the other of lye, "half-spent lye" it is called. This still contains some caustic soda, although possibly it may have a dark colour, especially if poor fats have been used in making the soap. It should be stored in a separate tank and used in the first boil of a new batch of soap.

The soap is taken away from the lye by any convenient means and placed in the frames to cool and set, which will take from three days to a week according to the season of the year and the relative coolness of the frame room.

The soap as so made is known as "curd soap" (see p. 241). It may be made from a number of fats, but what is sold as "curd soap" is generally made from tallow.

Curd soap, while it possesses excellent detergent properties, is apt to be rather alkaline and sharp and therefore does not suit everybody as a toilet soap.

Fitted Soaps.—In the manufacture of the most common kinds of domestic soaps, the soap, after undergoing the process of boiling on strength and salting out, undergoes a further treatment, the extent of which may be varied according to special requirements and the ideas of the soap-maker. The first treatment consists in giving what is known as a cleansing boil; this is done by running the soap into a pan and adding some water and sending steam through; there is then run in a strong brine liquor in just sufficient amount to open the soap, and the boiling continued with either close or open steam for three to four hours or even longer according to the size of the batch of soap, after which the pan is allowed to settle for about twelve hours, when the soap will be found on the top and the brine below, this being run off when the soap is ready for the finishing operation. The cleansing boil helps in the completion of the saponification, and therefore in the production of a more perfect soap, while it tends to wash out any excess of alkali that the curd soap may hold from the "boiling on strength," and so make a more neutral soap. Some soap-makers will, with their best qualities, give even a second cleansing boil. The brine liquor may be used several times, according to the quality of the soap which is being made. If from good, clean fats the liquor may be used several times; if from poor, dirty fats it cannot be used more than once or twice, as it becomes too highly charged with dirt to work satisfactorily.

The next proceeding is to close up the soap again. This is done by placing the soap in the pan, sprinkling on to it a little water and heating by the close steam coil; soon the soap loses its granular appearance and becomes more transparent and homogeneous. When this happens, the boiling is discontinued and the pan allowed to cool, or the soap may be run into the frames to set, after which it is cut up into slabs and bars and tablets, ready for sale to the public.

Such is a general description of the ordinary process of soap-boiling. It is subject to a little modification here and there, according to the fancy of the soap-maker, the kind of soap being made, and the fats used.

We may now proceed to discuss the methods of making various kinds of domestic soap.

Common Pale Soap.—The soap which is made in this country in the largest quantity is one made from tallow and rosin, and is variously known as "pale soap," "XX pale soap," etc. In making this soap the soap-boiler has a choice of several methods of procedure which we will briefly indicate. First, however, a few words as to the tallow and rosin used. For this kind of soap the tallow need not be of the best quality and the cost of the soap may be reduced to some extent by employing a cheaper grade of tallow. A medium quality of rosin may be employed. Too dark a rosin should not be used, as, although most of the colour comes out in the process, yet the soap is apt to come out of a dark colour.

The tallow is saponified in the manner just described and salted out. The soap, after running off the spent lye, is now ready for the rosin; this is added to the soap pan along with fresh alkali, and the boiling continued as before until the rosin becomes saponified. Rosin practically takes as much lye to saponify it as does tallow; it is, however, more easily saponified.

This boil is known as "the rosin boil"; when it is finished the soap is salted out as before. In this case the spent lye does not contain any glycerine; it will be of a dark colour, for it will contain much of the colouring matter of the rosin; it may be thrown away. Plenty of time should be allowed for it to settle out, so that the lye may be as free as possible from any particles of fat, rosin, or soap. When making soap from rosin, and after salting out, the contents of the pan usually separate into three layers, sometimes four, as follows: a layer of light, frothy soap on the top—this is collected and sent into the next boiling of soap; second, a layer of good soap, which is finished as usual; third, under this a layer of a dark-coloured curdy mass, the "nigre," as it is called—this varies very much in colour, consistency and extent according to the quality of the rosin and fats used in making the soap. It is rather a troublesome product to deal with; if not too strongly coloured it may be left in the pan and worked up into the next batch of soap, for it consists largely of soapy matter; if it be too dark then it may be used along with other dark fats in making brown soap. The lowest layer consists of the spent lye; this is dealt with as mentioned above.

After the rosin boil, the soap is finished by boiling on strength and fitting as previously described. In all these operations the nigre will be met with; in running off the "neat soap" or the spent lye it is important not to run any of the nigre into them, as it would affect the grain of the finished soap or interfere with the treatment of the lye.

Some soap-makers saponify the rosin with lye before they add it to the tallow soap. Unless they are working with poor grades of rosin and desire to purify it somewhat before mixing with the other constituents, there is no advantage in this course of procedure.

Although the rosin and the tallow may be saponified together, yet it is not advisable to do so, as thereby the spent lye is increased in bulk without increasing its actual contents of glycerine, and this increase in bulk leads to extra cost of boiling down; then again the colouring matters and impurities of the rosin getting into the lye add to the difficulties of refining and extracting the glycerine, and it is desirable that these difficulties be minimised as much as possible.

The following are some recipes for making this class of soap:—

White Castile.

1.	4 cwt.	olive oil.	3.	3 cwt.	olive oil
	6 ,,	tallow.		3 ,,	cotton oil.
2.	3 ,,	olive oil.		4 ,,	tallow.
	3 ,,	lard.	4.	5 ,,	bleached palm oil.
	4 ,,	palmnut oil.		2 ,,	sesame oil.
				3 ,,	tallow.

Golden Pale Soap.

15 cwt.	mutton tallow.	5 cwt.	bleached palm oil.
5 ,,	coconut oil.	6 ,,	window glass rosin.

Golden Pale Soap.

20 cwt.	tallow.	7 cwt.	bleached palm oil.

7 cwt. window glass rosin.

Crown Pale Soap.

10 cwt.	beef tallow.	5 cwt.	palmnut oil.
10 ,,	bone tallow.	5 ,,	bleached palm oil.

7½ cwt. rosin.

Primrose Soap.

10 cwt.	beef tallow.	10 cwt.	mutton tallow.

6 cwt rosin.

Golden Primrose Soap or Castile Soap.

10 cwt.	beef tallow.	5 cwt.	bleached palm oil.
10 ,,	mutton tallow.	1 ,,	palm oil.

Cottonseed oil is now coming largely to the front for making pale soaps for ordinary household use, the great improvements which have been made of late years in refining the oil having rendered this possible. Cotton oil is fairly easily saponifiable; it is not so easily salted out as tallow is, but on the other hand it produces a soap which lathers easily. The following are some recipes for its use:—

XX Crown Pale Soap.

10 cwt. cottonseed oil.
5 ,, tallow.
1 cwt. palm oil.
4 ,, rosin.

Golden Soap.

1½ cwt. cotton oil
18 lb. tallow.
75 lb. best rosin.
3 ,, palm oil.

Common Soap.

1 cwt. cotton oil.
1 ,, bone grease.
½ cwt. rosin.
¼ ,, palm oil.

Brown Soaps.

1. 7 cwt. tallow.
3 ,, cotton oil.
6 ,, rosin.
½ ,, palm oil.

2. 4 cwt. tallow.
4 ,, palmnut oil.
2 ,, cotton oil.
6 ,, rosin.
½ ,, palm oil.

These recipes will probably be sufficient for the ordinary makes of household soaps; the practical soap-maker will know how to vary them to suit his special requirements.

Mottled Soaps.—There are two kinds of mottled soaps known. One is a very old kind, having a faint grey mottle scattered through its substance; this mottle was originally obtained by using rather impure fats and alkalies. A more modern kind of mottled soap is that having a prominent mottle or grain of a blue, red or other colour, which is artificially produced. We will speak of the grey kind first.

The mottle is produced in the following manner: The fats and alkalies used in the early days were often largely contaminated with earthy matters and metallic impurities; these acting upon the fats formed metallic soaps, differing in colour from the main body of soap which was formed by the alkali. These earthy or metallic soaps became entangled in the soap as it cooled down in the frame and imparted to it a mottled appearance, the character and extent of which depended upon the character and amount of the impurities present.

To produce mottled soap of a good grain requires some experience in soap-boiling. The method usually followed is to make a soap out of bone grease, kitchen grease, bleached palm oil or common tallows, using low grades of caustic and adding it in large excess. The soap is well boiled, and then it is well boiled down with some lye until it begins to curd out; it is at once run into the frames, and these are covered over with cloths to keep the heat in. During the cooling the metallic soaps tend to aggregate together and so produce the mottle. One of the chief arts in making a mottled soap lies in the boiling; if boiled too long it sets too soon and the mottling has not time to form properly, while if not boiled long enough, then it is apt to contain an excess of lye, and the mottling settles out too quickly.

It sometimes happens that the soap will not mottle properly on account of the fact that there are not sufficient impurities present. In such a case the soap-maker imitates the mottle by adding for a grey mottle a little animal black, or even black oxide of manganese. What is known as Castle soap, and some makes of the Marseilles soaps have a green mottle, which turns red on exposure to the air; this is produced by adding near to the end of the boiling a little copperas (ferrous sulphate), ¼ lb. to 200 lb. of soap will be sufficient; this produces in the soap a deposit of green hydroxide of iron. So long as this remains unexposed to the air it keeps its green colour, but when exposed by cutting fresh surfaces of the soap it turns red, which remains permanent. It may also be added that in making these soaps green olive oils form the chief basis for them, with occasionally the use of hemp seed, poppy seed, niger and sesame oils.

Common Blue Mottled Soap.—Of more recent introduction than the blue mottled soaps just described is a soap with a large blue mottle, much used in households for scrubbing floors and other rough cleaning purposes. These soaps are very strongly detergent, and contain silicate of soda; they will be described later on.

Curd Soaps.—Curd soaps are chiefly made from tallow, with or without the addition of olive or other oils, which are employed to tone down the hard and difficultly lathering properties of a tallow soap. For a curd soap the fats are melted in the soap-pan and saponified with lye of 10° to 12° Tw. strong, using small quantities at a time; considerable care is to be taken to produce what is known as "close" soap, which is a homogeneous, pasty mass, free from any indications of fatty matter or separated lye. At this stage there is formed a soap containing a little free fat in an emulsified condition. The soap is next "grained" or "cut" by salt, and the "grain soap" is allowed to settle. The curding forms the final operation. The grain soap is first boiled up with a little weak alkali and wet steam, so as to again "close" it and complete the saponification, after which stronger lye is added and the mass heated with dry steam, when the soap opens and the curd is formed. From time to time some of the soap paste is taken out and cooled, and when it sets properly the steam is turned off, the curd allowed to settle out, and then run into the frames. Curd soaps are made from any kind of fats, and the only difference between them and other soaps lies simply in the method of boiling and curding out.

Paraffin Soaps, Petroleum Soaps.—These soaps are made by crutching into a soap paste 10 to 20 per cent. of petroleum oil. The addition of these products to a laundry soap appears to increase its detergent effect, and greasy clothes in particular are more readily washed with a paraffin soap than with an ordinary soap. Some makers of this class of soap do not use the oils, but a soft, low-class, and somewhat oily paraffin wax, on account of the odour being less.

Filled and Sophisticated Soaps.—Several varieties of soaps are made which sell at a low price. These are produced by adding to the common but pure grades of soaps previously described certain bodies which cheapen their cost of production, while not altering the appearance of the soap. It is obvious that these fillers, whatever their nature may be, must answer a few requirements before they can be used. In the first place they should not materially interfere with the solidity, appearance, or keeping properties of the soap, although some do not answer all these requirements; then they should not interfere with the uses of the soap in any way. Among fillers there have been, or are used, such bodies as silicate of soda, silicate of potash, starch, French chalk, kieselguhr, silicious substances, petroleum jelly, or, as it is called in America, mineral soap stock, Glauber's salt, soda crystals. Silicate of soda is very largely used; it does not detract from the detergent properties of the soap, if even it does not increase them; it can only be used in the very cheapest of domestic soaps on account of the fact that it makes them strongly caustic; it also makes the soaps rather wasteful in water. Too much cannot be used, or the soap is liable to be too thin. Starch has been added to soaps; it forms with water and in the presence of alkali a stiff gelatinous mass which is freely soluble in water. It can therefore be added to soap without altering its appearance. The detergent properties are reduced by the employment of starch.

The addition of such mineral substances as French chalk, silicious matters, kieselguhr, is not now practised in this country, as such a sophistication is readily detected in the appearance and use of the soap. These bodies do not add to the cleansing properties of the soap in any respect, while they tend to break the grain of the soap, make it more wasteful in use and sometimes unpleasant to wash with.

Glauber's salt and soda crystals are sometimes added to soaps to make them harder, which they do by their property of crystallising. The former reduces the detergent properties of the soap, the latter tends to increase them. One defect they have is that they are liable to bring about the formation of a white saline efflorescence on the surface of the soap which is not at all desirable, while further they make the soaps very wasteful in use.

Mineral soap stock, which is a kind of impure vaseline or petroleum jelly, affects the soap simply by making it more pasty in consistency and more greasy to work with. It is rarely if ever used in this country, but in America, where they seem to have a particular *penchant* for sophisticated soaps, it is often added to common soaps.

Having thus briefly discussed the various filling agents which are used, we may proceed to describe the methods of using them.

Silicated Soaps.—These are frequently known as run soaps and the silicate of soda or potash as "runnings". Their introduction is due to Thomas & Sons, Limited; Gossage & Sons, Limited, have also made this class of soap very largely.

Silicate of soda is sold usually in the form of a viscous liquid having a specific gravity of 100° Tw., although some grades reach 140° Tw. The method of mixing and the quantity used vary very greatly with different soapmakers. There are some who make but little use of "runnings"; there are others who make great use of them, all their common grades of soap containing silicate of soda in more or less quantity.

The method of using this material is very simple. The soap to be filled is run into a crutcher, heated by steam until it is pasty, and then the silicate is added.

A good grade of silicated soap is made by taking a neat soap made from rosin, cottonseed oil and tallow in the usual manner, and adding to it in the crutcher 1 cwt. of silicate at 100° Tw. to each ton of soap. Such a soap will be stiffer and harder after the filling than before and is a good quality for ordinary use.

When it is desired to make a very weak soap, then 1 ton of neat soap is taken and 5 cwt. of silicate at 32° Tw. is crutched in. This soap will be thin and soft and very wasteful in use. A more limited use is to add 1½ cwt. per ton of soap of silicate at 10° Tw. A few makers use 2 cwt. of silicate at 120° Tw. per ton of soap.

Usually silicated soaps are sold as "pale," "primrose," "XX," etc., household soaps.

To make silicated soaps appear harder, they are often put into a drying oven and dried quickly for a few hours; the outside thereby becomes covered with a skin which makes the soap keep better. Another plan of obtaining the same effect is to soak the soap in a strong solution of soda crystals or of Glauber's salt. One fault of such methods is that the soaps tend to become covered with a powdery coat; this gives it an unpleasant appearance which the customer does not like to see, as he takes it as an indication of an inferior make of soap.

Some analyses of silicated soaps will be given later on.

We may now devote a few words to other methods which have been employed for filling soaps.

Starch is sometimes added when highly watered and rather caustic soaps are to be made. It has the property when boiled with caustic soda of forming a thick glutinous mass which, when present in soap, acts as a binding material and helps to keep the soap together. It dissolves freely in water, and, while it does not add to the detergent properties of the soap in any way, detracts but little from them. Two per cent. is a fair quantity to use.

French chalk or ground talc, a silicate of magnesia, may be added to the extent of 5 to 10 per cent. without being readily detected by simple inspection. At one time it was largely used for this purpose, but now it is rarely met with. It has no binding property and simply acts mechanically in filling the soap.

Soda crystals—washing soda. This salt is often added to soap, to the extent of 5 per cent. of the soap; a larger quantity cannot be used, as it would cause much efflorescence on the soap. This material both cheapens the cost of production and adds to the detergent properties of the soap.

One feature in connection with the use of soda crystals in soap, is that it softens hard water, and when this is used for laundry purposes there is thus a saving of soap.

Glauber's salt—sulphate of soda. This substance has a hardening action on soap. It does not add to its detergent properties nor does it soften hard water.

Borax may be used as a filling, but it is rather an expensive one and therefore cannot be used to cheapen soaps. It is an excellent addition to soaps, as it possesses good detergent properties, while it exercises slight bleaching effects on the clothes washed with it.

Pearlash—carbonate of potash. This substance is sometimes added to soaps first for the purpose of hardening them, second for giving them a finer texture. This latter is brought about by double decomposition between the soap and the pearlash, resulting in the formation of a potash soap and sodium carbonate; the former improves the texture of the soap, rendering it smoother and more transparent, while the latter tends to harden it. Too much pearlash should not be used or the soap will become too soft and pasty.

SOAP-MAKING BY SPECIAL PROCESSES AND FROM SPECIAL MATERIALS.

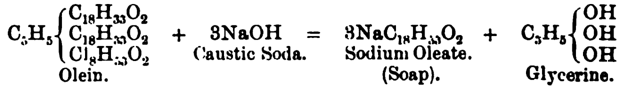
Cold process and pressure process.

In these two processes an attempt is made, at all events in theory if not in practice, to employ the fats and alkalies in the proportions in which they combine to form soap ; the glycerine which is formed is not separated out but remains in the finished soap. The cold process has been in use for many years, and, being a comparatively simple process, requiring no special plant, is much employed by small users of soap who desire to make their own soap. The pressure process is of more modern introduction and requires special plant for it to be carried out.

We may, before describing the practical operations devote some attention to the theory of the processes, the employment of which has been greatly facilitated by the improvement which has taken place of late years in the manufacture of caustic soda.

The idea of the process, whether it be cold or pressure process, is to bring the fat into contact with just the amount of alkali that will ensure complete saponification and produce a neutral soap, although by using a slight excess of alkali an alkaline soap may be made if so desired.

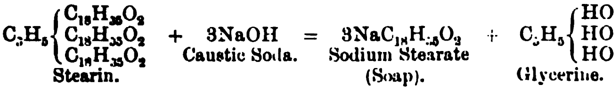
Although equations showing the reaction which takes place during the saponification of fats have been given previously, yet to save reference it may be well to repeat them here. The first equation shows the action of caustic soda on the triglyceride, olein, which is chiefly found in oils.



$$\underset{\text{Olein.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{33}O_2\\C_{18}H_{33}O_2\\C_{18}H_{33}O_2\end{matrix}\right.} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\substack{\text{Sodium Oleate.}\\\text{(Soap).}}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerine.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.}$$

From this equation it is easy to calculate the proportions of olein and alkali which take part in the reaction. These are 884 parts of olein to 120 parts of caustic soda, the ratio being 7·4 to 1, while there are formed 912 parts of sodium oleate (soap) and 92 parts of glycerine.

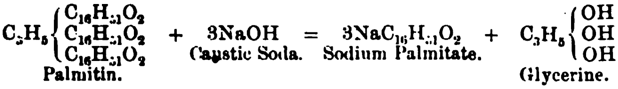
In the case of stearin, the solid constituent of tallow and many other fats, the equation becomes :—



$$\underset{\text{Stearin.}}{C_3H_5\left\{\begin{matrix}C_{18}H_{35}O_2\\C_{18}H_{35}O_2\\C_{18}H_{35}O_2\end{matrix}\right.} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\substack{\text{Sodium Stearate}\\\text{(Soap).}}}{3NaC_{18}H_{35}O_2} + \underset{\text{Glycerine.}}{C_3H_5\left\{\begin{matrix}HO\\HO\\HO\end{matrix}\right.}$$

From this equation we can calculate that 890 parts by weight of the glyceride require 120 parts of caustic soda to saponify it, and produce 918 parts of soap and 92 parts of glycerine.

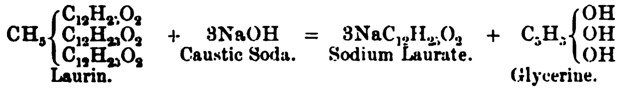
Palmitin, the glyceride of palm oil, saponifies with caustic soda, as shown in the equation:—



$$\underset{\text{Palmitin.}}{C_3H_5\left\{\begin{matrix}C_{16}H_{31}O_2\\C_{16}H_{31}O_2\\C_{16}H_{31}O_2\end{matrix}\right.} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\text{Sodium Palmitate.}}{3NaC_{16}H_{31}O_2} + \underset{\text{Glycerine.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.}$$

From which it may be calculated that 806 parts of the glyceride require 120 parts of caustic soda, and there will be produced 834 parts of soap and 92 parts of glycerine.

Laurin, the principal glyceride of coconut oil, is saponified as shown in the equation:—



$$\underset{\text{Laurin.}}{CH_5\left\{\begin{matrix}C_{12}H_{23}O_2\\C_{12}H_{23}O_2\\C_{12}H_{23}O_2\end{matrix}\right.} + \underset{\text{Caustic Soda.}}{3NaOH} = \underset{\text{Sodium Laurate.}}{3NaC_{12}H_{23}O_2} + \underset{\text{Glycerine.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.}$$

638 parts of laurin require 120 parts of caustic soda, and produce 666 parts of soap and 92 parts of glycerine.

If all fats and oils were composed simply of one glyceride it would be an easy matter to make the manufacture of soap a truly scientific proceeding, but unfortunately the oils and fats have not the simple composition which has been assumed above, they being mixtures in various proportions of two or more different glycerides. Thus tallow contains both stearin and olein; palm oil, palmitin, stearin and olein; coconut oil is even more complex, it contains laurin, caproin, caprin, caprylin, olein, stearin, etc. Then again the proportions of these various constituents vary from time to time hence the soap-maker cannot assume that his fats will always have a constant composition, and base his method of working on that assumption.

As the process of soap-making under the cold and pressure systems must, or should be, carried on in such a way that an excess of alkali be avoided, the soap-maker ought to be placed in a position to ascertain the amount of alkali, caustic soda or caustic potash any lot or parcel of fat he is using will take; this he can do by ascertaining by means of the Koettstorfer test the proportion of alkali required to saponify any given fat or oil. The method of carring out this test we will now describe.

The Koettstorfer Test.—To carry out this test there is needed first a wide-mouthed glass flask of about 4 to 6 oz. capacity, fitted with a cork, through which passes a piece of glass tube about 3 feet long and ½ inch wide. There will also be required a water bath heated by a bunsen burner for the purpose of heating up the flask when in use. A burette, 25 c.c. pipette and balance and weights are also necessary. The chemicals required are a solution of 30 grammes of pure caustic potash in 1000 c.c. of alcohol and a standard solution of sulphuric acid, or better what is known as seminormal strength, that is, containing 24·5 grammes of pure sulphuric acid per litre.

Weigh into the flask 2 grammes of the oil or fat to be tested, add 25 c.c. of the alcoholic solution of caustic potash and heat on the water bath for half an hour, shaking up at intervals. At the end of the time stated the fat will have been completely saponified, and it is only necessary to determine the excess of the alkali used. This is done by diluting the test solution with a little water, adding a few drops of an alcoholic solution of phenol phthalein, which will impart a red coloration, then adding carefully from the burette the standard acid until this red colour disappears, noting the number of c.c.'s of acid required. The flask is

KOH 28 .028 KOH
NaOH 20 .02
H 49 = 56
1.cc ,, ,, ,,

next well rinsed out and a blank test made by measuring into it 25 c.c. of the potash solution, boiling up on the water bath as before, then diluting with water, adding the phenol phthalein solution and titrating from the burette with the standard acid. The object of making this blank test is to standardise the potash solution in terms of the acid solution, and this is best done in the manner just described, as then any error which may be caused by impurities in the alcohol used acting on the alkali during the boiling is eliminated.

To calculate the percentage of caustic potash required to saponify the fat from the data obtained, the number of c.c.'s of acid used in the test with the oil is subtracted from the number used in the blank test; the difference multiplied by 0·028 gives the weight of alkali, KOH, required to saponify the 2 grammes of fat taken, and this multiplied by 50 gives the percentage. To take a concrete example: 2 grammes of tallow were taken and treated as described, the number of c.c.'s of acid used being 8·2, the blank test taking 22·1. Then we have:—

Blank test	22·1
Oil test	8·2
Difference	13·9

13·9 × 0·028 = 0·3892.

0·3892 is the weight of KOH required to saponify 2 grammes of tallow. Multiplying this by 50 we have 19·46, the percentage of caustic potash, KOH, required to saponify tallow.

Should it be desired to ascertain the quantity of caustic soda required, then the difference in the standard acid use is multiplied by 0·02. In the above case we should have 13·9 × 0·02 = 0·278. 0·278 × 50 gives 13·9 as the percentage of caustic soda required to saponify tallow.

In the same way the Koettstorfer value or saponification equivalent of other fats and oils may be obtained, and having got these, and knowing the actual strength in real caustic of the sample of commercial caustic soda he is using, the soap-maker will be in a position to calculate the quantity of caustic soda or of caustic potash he must use to convert a given quantity of fat or mixture of fats into soap by either the cold process or the pressure process.

Thus supposing the soap-maker wishes to make a soap from:—

1 cwt. kitchen fat having a Koettstorfer value of 13·5,
2 cwt. of tallow with a Koettstorfer value of 13·9,
2 cwt. of coconut oil with a Koettstorfer value of 18·4;

and is using 74 per cent. commercial caustic which contains 95·5 per cent. of real caustic soda; then we shall have to make the following calculations:—

The kitchen fat will take:—

100 : 13·5 : : 112 : 15·12 lb. of caustic soda.

The tallow will take:—

100 : 13·19 : : 112 : 15·56 lb. of caustic soda.

The coconut oil will take:—

100 : 18·4 : : 224 : 40·21 lb. of caustic soda.

Then we have:—

15·12
15·56
40·21

A total of 70·89 lb. of caustic soda required to saponify the weight of fats given.

Next we have to calculate the quantity of commercial soda to be used. For this we have the proportion 95·5 : 100 : : 70·89 : 74·3. There will therefore be required 74·3 lb. of 74 per cent. caustic soda to saponify the fats taken.

In a similar way calculations may be made concerning other mixtures of fats and oils.

The Koettstorfer values or saponification equivalents of various oils have already been given; these may be taken without much error, but the soap-maker is recommended to test separately each fresh batch of fats that he may be using, as they often vary considerably. The method of testing commercial caustics for their real strength has been given when dealing with alkalies.

There is another point which requires attention in making soaps by either of the two processes under consideration, and that is the proportion of water they must contain when finished; for it must be borne in mind that whatever water is added during the process of manufacture remains in the soap and cannot be conveniently removed if an excess has been used, or increased if too little has been employed.

The soap-maker must, therefore, if he desires to produce a soap with a given proportion of water, use only that quantity which will give him this result, and this of course he adds along with his caustic in the form of lye. Thus supposing that in working up the fats given in the example above he wishes to produce a soap with 30 per cent. of water, he would add the weight of fat employed to that of caustic used and then work the proportion sum—

$$70 : 30 : : 446 + 74{\cdot}3 : 223{\cdot}9$$

he will therefore have to add 223·9 lb. of water in making his soap. This water he will of course add to the caustic soda.

THE COLD PROCESS OF SOAP-MAKING.

The process now to be considered is perhaps the simplest of all processes of making soap. It consists essentially in just heating the fats from which the soap is to be made sufficiently to melt them, then thoroughly mixing the melted fat with strong caustic lye, and then allowing the mixture to stand for a few days. The saponification of the fats proceeds, and at the end of the time stated is fairly complete, and the soap is made. The plant required is of a simple character, and this is probably the reason for the process having come into use.

The advantages of the "cold process" of soap-making may thus be summed up. It is very simple and easily carried out, requiring little labour and plant. Small quantities can be made by its means, which is not the case with the boiling process. The soap too has a better appearance than a boiled soap; further it keeps its form better and does not crack so readily as a boiled soap. It is therefore better adapted for making tablets of toilet soap, for which purpose the cold process is chiefly employed. The yield of soap from any given weight of fat is larger on account of the fact that all the material used in making the soap remains in.

The disadvantage of the cold-process soap is that it is difficult, indeed impossible, to secure complete saponification of the whole of the fat used. There always is present in these soaps a small but variable quantity of free fat. Then they also contain a little free alkali, which causes the soap to work harsh and feel sharp to many skins. The presence of the free fat may sometimes lead to the soap becoming rancid. Cold-process soaps when exposed to the air are rather liable to sweat and they dry up more easily than a boiled soap; it therefore does not look well when old. It however dissolves more freely in water and therefore lathers better; for hard waters it is better suited than a boiled soap.

As all the ingredients which are used remain in the soap, it is evident that all the materials used should be of the best quality if a good grade of soap is to be made.

The fat most used and best adapted for making soap by this process is coconut oil. At one time it was considered that a cold-process soap could not be made without this oil forming fully one half of the fats used. This however was at the time when highly causticised lyes were not made and when caustics of high strength were unknown. Now however any kind of fat may be employed, but coconut oil remains the chief one used. Its merit lies in the fact that it saponifies more readily with strong alkalies such as have to be used than any other fat. It yields a soap of a fine colour, it dissolves easily in cold water and lathers very freely; on the other hand it is apt to be harsh and feel sharp to delicate skins.

Tallow is also very largely used for cold soaps, giving good white soaps of a firm texture, durable in use.

Palm oil, too, is largely used, as is also castor oil. The soap-maker may indeed use any fat or admixture of fats according as he wishes to produce a soap having particular properties.

Whatever fats are used they should be of a good quality, free from any foreign matter and be fresh. It is advisable to subject them to a clarifying process before using them; this process may take the form of melting and allowing to settle, or the fat may be melted over a salt lye of about 10° Tw., and in each case using only the clear fat which rises to the top. It is of great importance to use fresh fats and fats free from any great proportion of free fatty acid, as such tends to the formation of soap which is not uniform in grain, the free fatty acids, when the alkali is mixed with the fat, immediately combining with it to form soap which separates from the rest of the mass in the form of grains and curds; the presence of which destroys the homogeneous character of the soap. If it be suspected that any particular batch of fat contains too much free fatty acid, such may be removed by heating the fat to just about its melting point, then thoroughly mixing it with a little weak lye made from soda ash of about 2° to 3° Tw. strong; the alkali takes out the acid in the form of soap, which dissolves in lye. By keeping the mass at 130° to 150° F. the purified fat will rise to the top and may be skimmed off and used. If any difficulty be experienced in separating the clear fat a little brine added will remove it. It pays to use only the best grades of fat.

The alkali used must be the highest grade of caustic that can be bought, either the 77 per cent. solid caustic soda or the 100° Tw. liquid caustic soda. The strength of lye most commonly used is 70° to 72° Tw. and containing 32 to 33 per cent. of actual caustic. The alkaline lye should be made with as soft a water as can be got. Low grades of caustic are not suitable for making soap by the cold process, inasmuch as the foreign salts and impurities they contain interfere with the complete saponification of the fat and lead to the production of a soap which contains a large proportion of free fat and free alkali; then again if a very low grade caustic were used the impurities and salts would be liable to efflorescence on the surface and spoil the appearance of the soap and of any wrappers in which it may be placed.

As regards the quantity of lye used and the proper strength at which to use it, this necessarily varies with the kind of fat employed. Coconut oil, for instance, will require more lye, and a stronger one may be used than is the case with tallow.

It has been found that coconut oil and cotton oil saponify best with a lye at 72° Tw., while for tallow, palm oil and most other fats the saponification proceeds best at 66° Tw. Too strong a lye should be avoided, as then the soap is made rather curdy in texture and the saponification but imperfect, the soap being hard and rough. It is better to use a lye one or two degrees weaker than stronger.

As regards the quantity of lye to be used, coconut oil, as before mentioned, takes the most, 100 lb. of the oil taking 50 lb. of lye at 72° Tw. made from 77 per cent. caustic soda. With a lower grade of caustic, say 70 per cent., then the lye may be made stronger, say 77° Tw., and the same quantity used.

Tallow, cotton oil, palm oil, and other fats do not require so much alkali; in their case it is best to use a lye of 66° Tw., and of this 50 lb. will be required for each 100 lb. of fat.

Using the fats and oils and lyes in the proportions and strengths given, the finished soaps will contain about 25 per cent. of water, which is a fair average quantity. If a soap containing more water be desired, then a weaker lye may be used, while if a stronger soap is wanted, then a stronger lye must be employed.

It may again be stated that in the cold process the saponification is never complete; there is always in the finished soap a little free fat and a little free alkali. In making a toilet soap it is advisable to so proportion the fats and alkalies and the strength of the lye used as to leave as little free alkali as possible.

Having so far dealt with the materials and principles of the cold process of soap-making, we may now proceed to describe in detail the operation itself.

Working of the Cold Process.—The fats and oils which are to be used are placed in a pan, which ought to be fitted with a mixing arrangement. The fats are melted by heat in any convenient way, either by steam or fire. A suitable pan for this purpose is that made by Dopp of New York and already illustrated, (Fig. 31, page 187). The temperature should not be too high, simply that which is sufficient to melt the fats. When coconut oil is used this will be 80° to 90° F., with a mixture of coconut oil and tallow about 100° F., with tallow and other greases from 110° to 120° F. When melted the lye is run in with constant stirring, which is continued until the mass of fat and lye begins to thicken and flow from a paddle in a uniform sluggish stream. The temperature of the lye may be that of an average summer heat, 70° to 80° F. There is no need to heat or warm it in summer, but in winter it may be advisable to heat the lye to 80° F. before mixing it with the oil. After the lye and oil have been mixed and it begins to thicken the soap mass is run into the frames, which are then covered over with sacking to keep the heat in as much as possible, and left for from three days to a week for the soap to form fully, after which it may be cut up in the usual way.

Although comparatively simple, yet, as with all processes of soap-making, the cold process must be conducted with care and attention to some points of detail, otherwise the product will not be quite right. Some of these points have already been mentioned, others may now be briefly referred to. To ensure a perfectly good product, the fats must be of good quality and free from free fatty acid, or otherwise the soap is liable to turn out curdy and not homogeneous in structure. The fats should be at the right temperature, not too cold, or otherwise they might set on adding the lye, nor too hot, or then the saponification of portions may take place too rapidly and a curdy or grainy soap be produced. The strength of the lye has already been dealt with and does not need repeating here. The mixing or crutching of the fat and lye together should be thorough but not too prolonged. It is not desirable that any actual saponification should take place during the mixing operation, but only in the frames afterwards. It is found in practice that, if the crutching be too prolonged, there is a tendency for the materials to separate out in the frames, and an indifferent quality of soap produced, with which only one thing can be done and that is to throw the materials into the soap-boiler and boil them up.

The frames into which the soap is run from the crutchers should not be too large; those holding from 2 to 2½ cwt. are best, and it is preferable that these should be low and broad rather than narrow and high. The latter shape of frames retains the heat too long, and the soap does not set properly, while with the low flat frames covered with sacking the heat is retained, sufficient to ensure the proper saponification taking place. Too much heat should be avoided, as then there is a risk of oil separating out. In summer time this is a risk specially to be guarded against.

Filling Cold-process Soaps.—The cold process adapts itself very well to the perfuming, colouring, and filling of the soaps made by it.

As regards perfuming any kind of perfume may be added, and recipes for such perfumes will be found described under the head of Toilet Soaps. The perfumes should be added after the stock has been mixed in the crutchers and before the crutching is finished, so that the perfume has time to get intimately mixed with the whole of the soap stock.

Cold-process soaps may be coloured to any extent and with any kind of colouring material. In the case of employing such bodies as vermilion, ultramarine, chrome green, etc., which are insoluble in water, they may be added to the fats before adding the alkali, when they will get thoroughly incorporated with the soap. Of course care must be taken not to employ any colouring matter, like Prussian blue, which is acted upon by the alkali. As regards soluble colouring matters like annatto, safranine, eosine, and the coal-tar dyes in general, the best plan is to dissolve these in water, straining the solution to free it from any undissolved particles which might lead to the production of specks in the soap, and add the solution to the lye, using this rather stronger, perhaps, to allow for the dye solution weakening it, although when there is but a small quantity of dye stuff being used this point does not need much attention.

Filling materials such as silicate of soda, starch, sulphate of soda, salt, sugar, etc., or combinations of these, may be added towards the last while in the crutchers to any required extent. They are best added just before framing, although the practice of soap-makers varies very considerably on this point.

In the chapter on Toilet Soaps will be found a number of recipes for making these soaps by the cold process; we shall here confine attention to domestic soaps.

Hard White Soap.—100 lb. good white tallow, 50 lb. caustic soda lye at 68° Tw.

White Hard Water Soap.—100 lb. coconut oil, 50 lb. caustic soda lye at 72° Tw.

White Soap.—50 lb. tallow, 50 lb. coconut oil, 50 lb. caustic soda lye at 70° Tw.

Domestic Soap, Yellow.—50 lb. coconut oil, 30 lb. tallow, 20 lb. palm oil, 50 lb. caustic soda lye at 70° Tw.

Pale Soap.—50 lb. coconut oil, 25 lb. tallow, 25 lb. palm oil, 25 lb. castor oil, 63 lb. caustic soda lye at 70° Tw.

The replacement of a portion of the soda lye, say one-fourth, by caustic potash of the same strength, much improves both the appearance and quality of these soaps. Soap-makers working from the above recipes can easily reckon on the respective quantities of soda and potash.

SOAP-MAKING UNDER PRESSURE.

During recent years there has been introduced a system of making soap under pressure, and in the chapter on Soap Machinery there has been described a plant which is used for this purpose. The materials employed are those used in the ordinary cold process, and any recipe which has been given under that head may be employed for making soaps under pressure.

For a good yellow soap there may be used a charge of 7 cwt. of tallow oil, 3 cwt. of rosin, 3 cwt. of palm oil and 140 gallons of caustic soda lye at 34° Tw.; or there may be used 7 cwt. tallow, 2 cwt. palm oil, 4 cwt. rosin, with 140 gallons caustic soda lye at 42° Tw. This will make a drier soap than the last formula.

The plant is made sufficiently large to hold 1 ton of charge, but may however be built larger to take 2 tons in one charge. The method is simple; the apparatus is charged through the manhole provided for the purpose, which is then closed, and the fire is lighted and maintained to such a degree that the pressure in the boiler stands at 50 to 60 lb., as indicated by the steam jet provided for the purpose. The length of time allowed is from five to six hours, at the end of which time the finished soap is run into the crutchers and mixed with any colouring matter or scent that may be required, after which it is run into the frames to set. It is quite possible when working a high pressure system to use two charges a day. The soap made is generally excellent in quality and quite equal to that made by the ordinary processes. Like the cold-process soap it will retain all the glycerine and other materials which have been added in the process of making. (See also Bennet and Gibbs' process farther on.)

Oleic Acid Soap.—Oleic acid is prepared in fairly large quantities as a by-product in the manufacture of stearic acid for candle-making, and is used for a variety of purposes among which that of soap-making may be included. It is sold in two principal products, pale oleic acid of a light straw colour, and brown oleic acid which has a reddish amber colour, both varieties having a peculiar odour which is rather characteristic. The composition of oleic acid varies somewhat from time to time, according to the processes by means of which it is made. Its chief constituent is, of course, oleic acid, but it contains in addition small traces of hydrocarbon matter, and traces of fatty oil which has escaped saponification. The following are analyses, recently made by the writer, of two samples of commercial oleic acid, from which the average composition of the commercial article can be readily gleaned. The specific gravity is also given at 60° F., and the temperature at which it begins to set.

	"Pale."	"Brown."
Oleic acid	93·06	87·70
Oil	6·04	9·41
Hydrocarbon	·90	2·89
Specific gravity	0·897	0·904
Turbid at	42° F.	38° F.

There will be required the proportion of oleic acid actually present, together with the amount of saponifiable oil; these may be ascertained by the usual methods. Taking as a concrete example the analysis of the brown oleic acid given above, and assuming that a charge of 1 ton of oleic acid is going to be worked, and that 77 per cent. caustic soda is to be used, we shall have the following:—

282 : 40 : : 87·7
100 : 2240

which gives 257 lb. of 77 per cent. caustic as being required to saponify one ton of this brown oleic acid. As there is 9·41 per cent. of saponifiable oil in the sample, the additional quantity of caustic to saponify this may be calculated thus, allowing 14 lb. of caustic for 100 lb. of the oil:—

100 : 14 : : 9·41
100 : 2240

which gives 29·5 lb. as the additional quantity to add.

Oleic acid combines immediately or almost immediately in the cold with caustic soda and caustic potash, and it will react also with the carbonates of soda and potash; in the latter case a considerable evolution of carbonic acid taking place.

Soap may be made from oleic acid by using either caustic soda or carbonate of soda for hard soaps, or by using caustic potash or carbonate of potash if soft soaps are required. A good sample of oleic acid takes half its weight of

282 : 56
acid KOH
100 : 19.85%

add 1.5 gms
Total KOH 20.357 = 23.39 gms 87%
in H2O 68 cc.

caustic soda at 66° Tw. for its complete saponification. The two substances may be brought together either in the cold or boiling; when brought together heated, the combination is apt to take place so rapidly that the soap separates out in the form of grains which are apt to contain unsaponified oleic acid. In a somewhat lesser degree this is also apt to occur when using it cold. The best method of working is to run the fatty acid into the steam-jacketed pan, which is fitted with an agitator. There is then added the required quantity of caustic soda at 66° Tw. with agitation. At the same time the heat is turned on so as to heat the mass. The heating and agitating are continued until a uniform pasty mass is obtained. To this may be added any required scent or colouring matter, after which it is run into frames to set. The same plan may be adopted if caustic potash be employed in the place of caustic soda.

30%

The theoretical equivalents between oleic acid and the alkalies are: 282 of oleic acid to 40 of caustic soda, or 56 of caustic potash, these being parts by weight. The soap-maker will find it as well to ascertain by chemical analysis the exact strength of the oleic acid, and to calculate from these proportions the quantity of caustic soda or caustic potash which he will combine with any given charge of oleic acid. As commercial oleic acid generally contains a small percentage of unsaponifiable oil a slight excess of alkali may be added; this will ensure complete saponification of the fatty matter. In place of employing the caustic alkalies, the cheaper carbonates may be used; but in this case the soap-maker is troubled with a considerable amount of frothing, owing to the formation of carbonic acid gas, which necessitates the employment of very large vessels for the production of the soap, which is in many cases rather inconvenient. The proportion of soda ash of 52 per cent. to oleic acid may be taken as 19 lb. of soda to 100 lb. of oleic acid, and 3¼

acid KOH
100 gms : 21.2

gallons of water will be required to dissolve that quantity of soda ash. If needful the better qualities of alkalies may be employed, when a proportionately less quantity will be used. Theoretically 282 lb. of oleic acid require 53 lb. of sodium carbonate or 69 lb. of potassium carbonate for saponification. There is no difficulty in making a good soap from oleic acid, and the carbonates should be used warm and the solution of the soda ash added, allowing time for the subsidence of the frothing, by which means the process can be carried on with more effective control. After all the alkali has been added the mass of soap should be kept heated until it assumes the form of a smooth, homogeneous paste, when it is ready for running into the frames for cooling.

If thought desirable the oleic acid may be combined with other fats or rosin. A good proportion would be 3 cwt. of oleic acid and 1 cwt. of rosin, or 3 cwt. of oleic acid, 1 cwt. of palm oil, and 1 cwt. of rosin. When these fats are used the mixture requires boiling rather longer than when oleic acid is used by itself. The soaps thus made are rather better in taste and sweeter in odour than soaps made from oleic acid alone. It may be noted that the soap made from brown oleic acid tends to become darker in colour by keeping; with pale oleic acid this defect is not met with.

HYDRATED SOAPS.

A similar plan of working is one which has been especially followed in making what are generally known as marine soaps; it is practically a modification of the cold process, but employed at the boil, the soap not being salted out afterwards. The method of working is as follows:—

The fat is melted in the pan in the usual way; the alkali of the required degree of strength is run in, but not in sufficient amount to completely saponify all the fat. The mixture is thoroughly boiled, and when saponification is as nearly complete as possible more lye is added and the boiling continued, and fresh lye added until there is just a faint taste of alkali. The soap is then run into the frames for cooling. Any kind of fat may be used for this purpose, and it is known as marine soap. Each kind of fat requires a certain particular strength of alkali to ensure the best results; thus, tallow is best saponified at 16° Tw., coconut oil at 32° Tw., palm oil at 28° Tw., olive oil at 25° Tw. The quantities are given in the following table:—

100 lb. of tallow take 231 lb. of lye at 16° Tw.
100 lb. of coconut oil take 130 lb. of lye at 32° Tw.
100 lb. of palm oil take 114 lb. of lye at 28° Tw.
100 lb. of olive oil take 120 lb. of lye at 25° Tw.

Hydrated soaps are not made to any great extent now, on account of the fact that they contain the glycerine formed during the process, and it does not pay to leave glycerine in the soap. Hydrated soaps which are made from cheap greases are sometimes hardened by crutching in soda crystals or Glauber's salt, which makes them very much harder, and in some cases increases their detergent value.

SAPONIFICATION UNDER PRESSURE.

(Bennet & Gibbs' Process.)

Many attempts have been made to produce soap by other than the ordinary boiling and cold processes before described, and in which agitation of the materials performs the preliminary stage of the operation. Messrs. Bennet & Gibbs of New York obtained a patent in 1865 for a mechanical process which is said to possess the following advantages: 1, Rapidity of manufacture; 2, improvement in quality; 3, increased quantity of soap produced; 4, economy in labour; 5, saving in fuel; 6, the use of cheaper materials; 7, saponification of all grease; 8, saving of all the glycerine which enters into the soap. The last may have been thought an advantage thirty years ago, but to-day when glycerine is so valuable it is rather a disadvantage. The following is a description of the process:—

Their process consists in agitating the saponifiable materials with caustic or carbonated alkalies in solution in water in a closed vessel, while under heat and pressure, in such a manner as to cause a thorough mixing of the fats with the alkaline solution and producing an instantaneous combination of the fatty acids with the base of the alkaline solutions. If a quantity of fatty matter be enclosed in a vessel with a solution of carbonate of soda in water, and heat applied to produce a pressure of 220 to 280 lb. per square inch and a temperature of 350° to 400° F., a combination between the fatty acids and the soda of the solution will take place only at the upper surface of the solution when in contact with the under surface of the grease, the heavy lye occupying the lower part of the vessel, and soap will be produced where the fat and alkali unite.

If the mass be agitated in such a manner as to stir together and thoroughly mix the contents of the vessel, the whole will be instantly converted into a homogeneous and even quality of soap. It is advisable to use no more water than is wanted in the soap. The process is carried on in a boiler or cylinder similar to a plain cylinder steam boiler resting horizontally, and heated in any convenient manner. One or both heads of the cylinder are made so as to be conveniently removable, and are the full size of the inner diameter of the cylinder, so as to admit of the insertion of a revolving shaft, which should be as long as the cylinder itself. The shaft, which is in the centre of this cylinder, is carried through both ends and works in stuffing boxes; power is applied to revolve the shaft. On the shaft are fastened arms with floats or stirrers, extending nearly to the sides of the cylinder; the arms, floats or agitators on one side of the shaft when revolved carrying the fat down into the alkali, while the agitators on the other side carry the alkali up into the fat, thus, while under heat and pressure, thoroughly mixing the whole, causing the conversion of the whole contents of the vessel instantly into a uniform, even, and good quality of soap.

At one end of the cylinder are placed two safety valves, one at the top of the cylinder, the other on an outlet pipe inserted in the head of the cylinder. There is also a mercury bath of about 4 inches in length of gas-pipe which is screwed into the boiler or cylinder in any convenient place for the insertion of the thermometer bulb. At the opposite end of the cylinder is an opening for the insertion of a supply pipe; at the other end is also an opening for the insertion of a second outlet pipe, and which is intended to be used only when it is desired to draw off the whole contents of the vessel. When the machine is first put into operation, if carbonate of soda is used, it is necessary to allow some carbonic acid to escape by one of the safety valves, in order to prevent undue pressure by the liberation of the carbonic acid when combination of the fatty acids with the alkali takes place. If any of the liquids be allowed to escape before the temperature reaches 325° to 375° they should be returned to the cylinder.

The safety valve on the outlet pipe may be so loaded as to allow an escape of soap at a pressure of 250 to 270 lb. A quantity of lye and oil may be pumped in at the opposite ends, the agitation being kept up; a continual stream of soap flows out at the other end. The product may then be prepared for the market by cooling, moulding (framing), and cutting processes in ordinary use. By this process the soap is made in less than one hour from the time the ingredients are introduced into the boiler, but a uniform thorough saponification is obtained at the instant that the heat and pressure arrive at the required degree, be the time long or short; if this degree is reached in five minutes the soap is made.

The proportions employed are as follows: carbonate of soda at 48° 27 lb., water 100 lb., lard, tallow or oil 100 lb. 27 lb. of carbonate of soda will, it is said, make a neutral soap for soft water; the quantity obtained by the above process is 200 lb. of soap for every 100 lb. of grease employed.

The process is stated to be applicable to making any kind of soap, including soft soap, which is prepared with the same rapidity, without requiring the use of so much potash as in the ordinary process.

Although the original inventors recommend carbonate of soda it would be better to work with caustic soda, as the annoyance and trouble caused by the evolution of carbonic acid would thereby be avoided.

B. Toilet Soaps.

The variety of name, shape, perfume, colour, in toilet soaps is great, while the price at which they are offered to the public ranges from one penny to half a crown the tablet. Needless to say the former is that of a poor class of toilet soap—and yet it is wonderful what a fair class of soap may be turned out for the democratic penny—while the higher price is asked for a soap of superb quality, packed up in a very artistic manner, and which appeals strongly to the aristocracy for support.

Toilet soaps are of two kinds—the ordinary opaque kind and transparent soaps.

Toilet soaps are made by two processes, those known to the soap-makers as the boiling and the cold process. Again we may draw a further distinction between those which are milled, and those which are made by crutching or remelting. The boiling process of soap-making has been described in the first part of this chapter. Practically, it is the same for all kinds of soap; if there be any difference at all it is that it is more carefully worked when the better qualities of soap are being made. The cold process is fairly well known and is much used; it has been described. In the preparation of toilet soaps the maker really starts with a ready-made soap, whether this has been made by the boiling or the cold process is immaterial, and by carrying out certain finishing operations he converts his soap into a toilet soap.

Common Toilet Soap.—A great deal of the common toilet soaps are very simply made. An ordinary soap is taken when just hot, and before it is framed it is put into a crutcher; there is then added a small quantity of palm oil or of coconut oil, according as a coloured or white soap is being made, the object of this addition being to neutralise the last traces of alkali which may be contained in the soap. There is then added a little scenting material, some colouring matter if needful; the soap is then framed, allowed to cool, then cut up into slabs and bars, stacked until it gets fairly firm, then cut up into tablets and stamped. The scenting materials usually employed are mirbane or artificial oil of almonds, citronelle and oil of caraway. The most common colouring matters to add are Bismarck brown, chrysoidine or soap yellow. As an example to work upon, the following recipe for a

Brown Windsor soap made in this way may be taken:—

75 lb. of soap made from a mixture of tallow and palm oil.
2 lb. of palm oil.
1 lb. of mirbane.
1 ounce of Bismarck brown.

A white Windsor soap can be made from:—

75 lb. of a white soap made from tallow and coconut oil.
3 lb. of coconut oil.
1 lb. of citronelle.

The recipes to be found further on will also give the manufacturer some idea of how to make other qualities of soap in this way.

Toilet Soaps by Remelting and Crutching.—A large quantity of toilet soaps are made in this country from stock soaps by remelting and then subjecting them to a mixing with the perfume and colouring matter. This method is carried out in the following manner: The soap or soaps which are employed are cut up into shavings, which are then put into a remelter, which may take any form. The best is however a steam-jacketed pan fitted with an agitator, which serves to keep the soap in motion and mix the other ingredients with it. As just hinted there are often used several kinds of soap; the toilet soap-maker will find it convenient to make his stock soaps from tallow, coconut oil, palm-nut oil, palm oil, castor oil. These should be carefully made, as free from excess of caustic alkali as possible, and contain little or no salt. The soap should not be too dry—about 25 per cent. of water is a good proportion for it to contain—the operation of remelting results in the soap losing some of its water. In the case of using dry soap it may be advisable to send a little open steam into the remelter to give the soap the necessary degree of moisture.

If the remelter is fitted with an agitator, when the soap is melted the other ingredients, colouring matter and perfume, may be added, and when all are mixed, the soap is run into the frames to set. It will be found best to turn off the steam from the remelter while carrying out the last operation so as to avoid as little loss of perfume as possible. If the remelter is not fitted with an agitator, then the soap when melted is run into a crutcher and the perfume, etc., mixed with it there before running into the frames to set.

The following recipes for making several kinds of toilet soaps will be found useful, but of course an intelligent soap-maker may use them as guides, and concoct a recipe of his own, using any particular perfume his fancy may direct and any colour he likes. The recipes are adapted for soaps to be made by remelting, as described in the last section.

Brown Windsor Soap.

Tallow soap	75 lb.
Coconut oil soap	25 „
Palm oil soap	25 „
Oleic acid soap	25 „
Oil of thyme	2 oz.
Oil of cassia	2 „
Oil of lavender	2 „
Bismarck brown	3 „

If a darker shade be required it is best to add a little new blue.

Heliotrope Soap.

Tallow soap	40 lb.
Oil of almonds	1 oz.
Oil of neroli	2 „
Benzoin	3 „

Bouquet Soap.

Tallow soap	40 lb.
Coconut oil soap	20 „
Oil of bergamot	3 oz.
Oil of rose geranium	1 „
Oil of caraway	¾ „
Oil of citronelle	¾ „
Oil of lavender	½ „

Santal Soap.

Tallow soap	25 lb.
Santal oil	1 „
Bergamot oil	5 oz.

Citron Soap.

Tallow soap	16 lb.
Palm oil soap	4 „
Bergamot oil	1 oz.
Oil of lemon	1 „

Almond Soap.

Tallow soap	75 lb.
Coconut oil soap	25 „
Oil of bitter almonds	12 oz.
Citronelle	2 „

Brown Windsor Soap.

Tallow soap	50 lb.
Coconut oil soap	25 „
Palm oil soap	25 „
Oil of cinnamon	4 oz.
Oil of cloves	2 „
Oil of caraway	1 „
Oil of sassafras	2 „
Oil of bergamot	4 „
Bismarck brown	8 „

Honey Soap.

Tallow soap	75 lb.
Palm oil soap	25 „
Oil of verbena	6 oz.
Oil of lemon grass	6 „

Another formula is:—

Tallow soap	50 lb.
Palm oil soap	25 „
Olive oil soap	25 „
Oil of verbena	6 oz.
Oil of bergamot	6 „
Oil of citronelle	5 „
Tincture of musk	½ „

These will be found sufficient recipes, but others will be presently given under another head which the soap-maker may utilise for this process if he thinks fit.

Toilet Soaps by the Cold Process.—The cold process may be employed for making some of the cheaper grades of toilet soaps. The details of this process will be found described in another place; here will be given simply some formulæ which may be used. It may be pointed out that it is not every perfume which may be employed, on account of the presence of alkali in the materials during the process of manufacture. Still, the soap-maker may use a large number of formulæ and produce a great variety of toilet soaps by the cold process.

White Windsor Soap.

Coconut oil	50 lb.
White tallow	50 „
Caustic soda lye at 70° Tw.	50 „

Stir the fats which have been previously melted together with the alkali; when well mixed add the perfumes as follows:—

Oil of caraway	6 oz.
Oil of lavender	4 ,,
Oil of thyme	2½ ,,

Brown Windsor Soap.

Coconut oil	45 lb.
Tallow	45 ,,
Palm oil	10 ,,
Caustic soda lye at 70° Tw	50 ,,
Oil of lavender	2½ oz.
Oil of cassia	6 ,,
Oil of caraway	1½ ,,
Oil of neroli	¾ ,,
Bismarck brown	3 ,,

Violet Soap.

Coconut oil	40 lb.
Tallow	10 ,,
Caustic soda lye at 70° Tw.	25 ,,
Dried orange peel	1½ ,,
Violet root	2½ ,,
Tincture of musk	1½ oz.
Oil of bergamot	1 ,,
Oil of citron	1 ,,
Oil of cassia	1½ ,,
Oil of neroli	¾ ,,
Peru balsam	½ ,,
Tolu balsam	¼ ,,

Another formula is:—

Coconut oil	40 lb.
Tallow	10 ,,
Caustic soda lye at 70° Tw.	25 ,,
Oil of lavender	1 oz.
Oil of bergamot	2 ,,
Oil of cassia	1 ,,
Tincture of benzoin	2 ,,
Balsam of Peru	1 ,,

Almond Soap.

Coconut oil	40 lb.
Tallow	60 ,,
Caustic soda lye	50 ,,
Mirbane	½ ,,
Oil of bergamot	½ ,,

Rose Soap.

Coconut oil	100 lb.
Caustic soda lye at 70° Tw.	50 ,,
Oil of rose geranium	5 oz.
Oil of bergamot	5 ,,
Tincture of musk	½ ,,
Eosine	1 ,,

Glycerine Soap.

Coconut oil	50 lb.
Caustic soda lye at 70° Tw.	50 ,,
Glycerine	4 ,,
Oil of rase geranium	1½ ,,
Oil of sassafras	¾ ,,
Oil of thyme	¾ ,,

Another formula for glycerine soap is:—

Coconut oil	48 lb.
Palm oil	2 ,,
Caustic soda lye at 70° Tw.	25 ,,
Glycerine	4 ,,
Orange peel	½ ,,
Violet root	1 ,,
Caramel	7 oz.
Oil of lavender	1½ ,,
Oil of bergamot	¾ ,,
Oil of cassia	¼ ,,
Oil of sassafras	¼ ,,

Lemon Soap.

Coconut oil	50 lb.
Tallow	50 ,,
Caustic soda lye at 70° Tw.	50 ,,
Oil of lemon	¾ ,,
Oil of bergamot	5 oz.
Oil of lemon grass	6 ,,
Oil of cloves	2½ ,,

Honey Soap.

Coconut oil	50 lb.
Tallow	40 ,,
Palm oil	10 ,,
Oil of citronelle	1 ,,
Oil of bergamot	½ ,,
Oil of caraway	1 ,,
Caustic soda lye at 70° Tw.	50 ,,

Bouquet Soap.

Coconut oil	50 lb.
Tallow	40 „
Bleached palm oil	10 „
Oil of bergamot	12 oz.
Oil of sassafras	4 „
Oil of cloves	4 „
Oil of thyme	4 „
Oil of neroli	2 „
Caustic soda lye at 70° Tw.	50 lb.

Orange Soap.

Coconut oil	50 lb.
Tallow	25 „
Palm oil	25 „
Oil of orange peel	12 oz.
Oil of cinnamon	1 „
Oil of thyme	2½ „
Caustic soda lye at 70° Tw.	50 lb.

If it be desired to produce coloured soaps by the cold process, the soap-maker will find a wide range of the coal tar colours open to him. Eosine will give him a variety of tints from the faintest blush rose to a deep pink. Acid green may be used for green tints, acid blue for blue tints, acid violet for lavender to violet shades, Bismarck brown for browns, acid yellow for yellow. With these by combining them together a variety of pleasing effects may be obtained. (See farther on as to colouring soaps.)

Milled Toilet Soaps.—We may now proceed to consider in some detail the production of toilet soaps by a process of comparatively modern origin, but which promises in the future to almost, if not quite, entirely replace the older methods of preparing toilet soaps. The milling system had its origin in France, where more attention has been paid to toilet soaps than in any other country; from there it has gradually spread to other countries. It is to the credit of the French that the best machines for carrying out the milling system are of French invention.

There is no question of the superiority of milled soaps over other soaps. Weight for weight they are of more value, because they contain less water, while it is an acknowledged fact that the reworking to which the soaps are subjected improves their quality. Then again, milled soaps are usually prepared from the best materials, as it is hardly worth while to put the extra work and expense involved in milling into a soap made from crude materials. Milled soaps are superior to other soaps in use on account of the fact that their small proportion of water and their dense texture cause them to waste away less rapidly than ordinary soap. The appearance, too, of milled soap is much superior to a toilet soap made by other processes.

The process of milling is a merely mechanical one to which a well-boiled soap is subjected, and it is carried out in special machinery, which has been previously described in the chapter on Soap Machinery (see p. 211). We shall not repeat these descriptions here, but simply speak of the process itself, pointing out its special features, and emphasising the points which require attention from the soap-maker.

The principal machines employed in the milling of toilet soaps are, according to the order in which they are used: (1) Cutting machine, (2) drying machine, (3) crushing mill with four granite rollers, (4) continuous squeezing machine, or, as it is sometimes known, the plodding machine, (5) steam-stamping process.

The soap which is to be treated is first cut into strips by means of the cutting machine, from which they are transferred to the drying machine. The degree of fineness of cutting the soap has some influence on the speed of drying it, fine chips drying quicker than coarse chips. In some cases the drying machine is so constructed that this preliminary cutting can be dispensed with, and the soap dealt with as it comes from the soap-kettles. This is done in the case of using the continuous automatic drying machine; the soap paste, drawn from a soap-pan, is fed into the hopper of a mill at one end of the machine with two or three cylinders and receivers, one or two millings, according to the number of cylinders, and at last falls in extremely thin shavings into the chamber which forms the real drying machine; the shavings are received on endless linen bands which are so arranged that they are one over the other and occupy the full width of the chamber. These linen bands are put into motion and are arranged so that the soap falls at one end on the topmost band of the machine, and is carried along to the other end, whence it drops on the next linen band; this in turn passes it to the third one, and so on until it comes to the last one, or the lowest, which carries the soap out of the apparatus. In the lower part of the drying machine is a hot-air stove which is preferably heated by steam. The stove is furnished with apparatus for drawing the heated air at a temperature of about 60° C. through the chamber. This hot air meets the soap shavings as they travel on the bands, gets saturated with the moisture they contain, and then escapes through the top of the apparatus by the ventilator, while the soap, dried to the desired extent, passes out at the bottom of the drying stove. This stove which dries the soap paste in an automatic and continuous manner, securing a good profit to the soap-maker who uses it, has an area about 45 feet square and can be manipulated by one workman and one assistant; it gives a yield of more than one ton of dried soap. The motive powe required is about two horse power, and the expense for heating is small.

Making Coloured Soaps.—All colouring matters which are proof against heat—mineral colours among others—can be mixed with the liquid soap when it comes out of the boiler, but when soft and delicate shades of fine soaps are wanted, shades that can only be got from delicate colours, it is better to incorporate the colour after the soap shavings have been dried, and in the crushing mill.

Regarding the incorporation of perfumes into the soap in a liquid state, as is necessary with the remelted soaps, this method is faulty. First of all the soap paste is heated to a temperature of 100° C., which effects a change in the perfumes, and secondly a considerable portion of the latter is wasted by evaporation during the treatment in the drying stove; the perfumes are better added to the soap in either the crushing or the plodding mill.

To ensure the most perfect working of the succeeding machines it is essential that the drying of the stock soap should be done to a proper degree. The soap must not be too dry or too damp; if the latter, then the soap works pasty in the crushing or plodding machines, while if too dry, then a soap of good texture cannot be made. Generally the dried soap should contain from 10 to 15 per cent. of water. It will be found that in this respect much will depend on the make of the mill; some work best with a dry soap, while others require a soap with a moderate amount of water left in.

The crushing machines, resting on a cast-iron frame in one piece, are composed of granite rollers of progressive diameter, two of which lie underneath horizontally, the other two being placed above them, the former supporting the latter. The dried soap with any perfume and the colouring matter is fed into the hopper of the crushing mill which has two compartments, and is passed out from the lower ones and carried round by the cylinders. These by revolving at different velocities cause the soap to undergo a real progressive milling, carrying it from the bottom to the top and passing it into the upper part of the hopper, from whence it undergoes the same process until the soap is entirely milled and perfectly amalgamated with the perfumes and the colour. The triple crushing caused by the passage through the four cylinders requires only five minutes for about 66 lb. It can be repeated two or three times, as may be required, the soap not leaving the crushing mill until a perfectly homogeneous mass is obtained.

The pressure between the rollers may be increased as the soap passes through the mill so as to increase the efficiency and turn out a better soap.

The plodding mill is made so that the soap is forced at a considerable pressure through a narrow opening, whereby it is made very dense in texture, while the friction which takes place between the soap and a mouthpiece imparts a gloss to the soap which gives it a fine appearance. By varying the form of the nozzle from which the soap flows the bar of soap may be made of any desired form ready to cut up into cakes.

Continuous working of the plodder, with the friction which occurs as the soap passes through the mouthpiece, tends to the heating of the latter. This is rather detrimental to the working of the mill. This trouble is avoided by keeping the mouthpiece cool by running cold water round it in a jacket provided for the purpose, or if this is absent, by allowing the mill to rest at intervals to cool down.

The work of the squeezing machine, or plodding machine, is to collect the material prepared by the crushing mill, to press it into a solid mass, and bring it out in uniform, compressed, and glossy bars.

The heating of the mouthpiece, especially in the extreme end of the nozzle, is good, as it increases the gloss of the soap. Too much heat will, however, cause the soap to become too soft to take a polish, and the surface tends to become streaky. In any case, it is advisable that the first portions of the soap which come from the machine be returned to it, as these are not sufficiently compressed and are then liable to crack.

If the soap goes into the plodder too dry, then it is wanting in pliancy. This may be remedied by adding a little glycerine or fresh stock soap.

After coming from the plodder the bar of soap is cut up into cakes, and these are then passed on to the stamping press for the final stamping.

Having described the process of milling soaps, we may now give some recipes for producing them.

Bouquet Soap.

White soap	100 lb.
Oil of bergamot	6 oz.
Lavender water	1 ,,
Oil of rose geranium	1 ,,
Oil of caraway	1 ,,
Citronelle	1 ,,

Brown Windsor Soap.

Tallow soap	75 lb.
Coconut oil soap	25 ,,
Palm oil soap	25 ,,
Oleic acid soap	25 ,,
Oil of thyme	2 oz.
Oil of cassia	2 ,,
Lavender	2 ,,
Bergamot	2 ,,
Bismarck brown	8 ,,

Santal Soap.

Tallow soap	100 lb.
Santal oil	5 ,,
Oil of bergamot	1½ ,,

Citron Soap.

Tallow soap	100 lb.
Palm soap	25 ,,
Oil of bergamot	6 oz.
Oil of lemon	6 ,,
Oil of citron	4 ,,

Almond Soap.

Tallow soap	100 lb.
Palm oil soap	25 ,,
Mirbane	3 ,,
Bergamot	1 ,,

Violet Soap.

Tallow soap	75 lb.
Palm oil soap	25 ,,
Oil of lavender	½ ,,
Oil of bergamot	¼ ,,
Tincture of benzoin	½ ,,

Honey Soap.

Palm oil soap	50 lb.
Tallow soap	50
Citronelle	2
Oil of sassafras	¼ ,,
Oil of caraway	¼ ,,

2 2
1 ÷
1 4

Rose Soap.

Tallow soap	75 lb.
Coconut oil soap	25 ,,
Oil of geranium	½ ,,
Oil of rose	2 oz.
Eosine	1 ,,
Oil of cinnamon	2 ,,
Oil of bergamot	1 ,,
Oil of cloves	¼ ,,

Orange-flower Soap.

Palm oil soap	75 lb.
Tallow soap	25 ,,
Oil of orange	2 oz.
Oil of neroli.	1½ ,,
Oil of rose	¼ ,,

Millefleur Soap.

Tallow soap	75 lb.
Coconut oil soap	25 ,,
Oil of bergamot	2 oz.
Oil of lavender	1 ,,
Oil of cloves	½ ,,
Oil of nutmeg	½ ,,
Tincture of musk	½ ,,

Shaving Soap.

Tallow oil soap	75 lb.
Palm oil soap	25 ,,
Coconut oil soap	25 ,,
Oil of caraway	6 oz.
Oil of bergamot	6 ,,
Oil of lavender	3 ,,
Oil of thyme	3 ,,
Oil of cloves	1 ..

Elder-flower Soap.

Tallow soap	50 lb.
Palm oil soap	25 ,,
Coconut oil soap	25 ,,
Oil of bergamot	2 ,,
Oil of lavender	½ ,,
Oil of caraway	½ ,,
Oil of peppermint	¼ ,,
Oil of thyme	2 oz.

White Windsor Soap.

Tallow soap	80 lb.
Coconut oil soap	20 ,,
Oil of cassia	1½ ,,
Oil of lavender	1 ,,
Oil of caraway	1½ ,,

Ess.-bouquet Soap.

White soap	50 lb.
Palm oil soap	50 ,,
Lanolin	4 ,,
Farina	1 ,,
Powdered orris root	4 ,,
Musk	30 grains.
Neroli oil	2 oz.
Geranium oil	5 ,,
Palma rosa oil	5 ,,
Citronelle	5 ,,
Bergamot oil	12 ,,

Musk Soap.

White soap	50 lb.
Palm oil soap	50 ,,
Powdered orris root	10 ,,
Musk	30 grains.
Cassia oil	1½ oz.
Lavender oil	1½ ,,
Bergamot oil	4½ ,,
Citronelle	1½ ,,
Vermilion	3 ,,
Soap brown	3 ,,

Flower Soap.

White soap	50 lb.
Palm oil soap	50 ,,
Lanolin	4 ,,
Farina	1 ,,
Powdered orris root	2 ,,
Powdered catechu	⅛ ,,
Musk	15 grains.

Rosewood oil	2 oz.
Citronelle	2 ,,
Lavender oil	2 ,,
Peru balsam	2 ,,
Palma rosa oil	2 ,,
Geranium oil	2 ,,
Bergamot oil	2 ,,
Coumarin	⅛ ,,

These few recipes, which have been selected from a large number, will perhaps be sufficient to show the lines on which the soap-maker can work in making milled soaps ; further the recipes which have already been given for other kinds of toilet soaps may be consulted with advantage.

The stock soaps which are used in making milled soaps should be of good quality, made from fresh and pure fats and oils, well boiled with good caustic so as to be thoroughly saponified. Rancid and discoloured fats and oils should not be used, such tend to rob the perfumes used in making the soap of much of their aroma and delicacy—a thing which is to be avoided. The condition that the fat or oil should be thoroughly saponified has an important bearing on the keeping qualities of the soap. Any unsaponified fat or oil will soon cause the soap to become rancid, thereby spoiling the perfume. A defect of this kind cannot be remedied entirely by the milling process, although there is no doubt that the process completes the saponification of a soap. The soap too must be free from any lye, and too much care cannot be exercised in settling it.

A stock soap to be good in condition for milling should not be too short in texture, and when fresh made ought to adhere together when worked between the fingers.

Tallow makes a good stock soap for milling. Both unbleached and bleached palm oil yield excellent soap for this purpose, although it is important to see that the oil is not rancid and has the agreeable violet-like odour of fresh palm oil to perfection. Coconut oil also makes a good soap ; great care ought to be taken with it to see that it is thoroughly saponified. Cottonseed oil does not make a good stock soap for milling. Castor oil yields a fair soap; other fats and oils are not admissible for various reasons.

Milled soaps may be coloured to any required degree, the best results being obtained by using coal-tar colours. There is such a variety of them that every imaginable tint can be obtained with their aid; while being easily soluble in soap, they do not in any way affect the brightness of that article; further, being soluble, they can be more easily mixed with the soap to get a more uniform diffusion of the colour throughout the soap mass; whereas, with the old mineral colourings, there was always a tendency on the part of the colouring materials to separate from the soap and settle down in the frame in which the soap cools down.

It is not every colouring matter that is available for tinting soap. There are some that are more or less affected or altered in colour by alkalies such, for instance, as Prussian blue, chrome yellow, Alkali blue, Magenta; soap being usually slightly alkaline, such products cannot be used for colouring it with advantage.

The coal-tar colours are used in a very simple manner. The colouring matter is dissolved in water, or in a few cases a mixture of water and alcohol; the solution should be filtered, and then it is poured into the melted soap paste and thoroughly crutched in. The quantity required is very small —½ to ¾ oz. will colour 1 cwt. of soap in some strong tints. In a few instances a little caustic soda may be added to the colour solution.

For yellows there may be used Fluoresceine yellow, Soap yellow, Quinoline yellow (of which there are two kinds—one soluble in water, the other in spirit), and Metanil yellow. The following recipes will give some idea of the quantities to be used. Each is for 1 cwt. of soap.

Sulphur Yellow.—Use ½ oz. Fluorescein yellow dissolved in 5 oz. boiling water, or ½ oz. Quinoline yellow (spirit soluble) dissolved in 5 oz. methylated spirit.

Lemon Yellow.—Use 1¼ oz. Fluoresceine yellow dissolved in 5 oz. boiling water. When used for tinting transparent soap, this yellow shows a fine green fluorescence or bloom.

Yellow.—Use 1 oz. Soap yellow dissolved in ½ pint boiling water, or 1 oz. Metanil yellow dissolved in ½ pint boiling water. Both these yellows give good results in colouring soaps.

Red Colours.—There may be used all the range of Eosine and Erythrosine dyes, which give bright pinks; the Rhodamines, which also give bluish pinks to reds; Ponceaus and Scarlets for roses; Cardinal red for reds.

Bright Rose.—Use 1¾ oz. Brilliant rose dissolved in ½ pint boiling water. By using 3½ oz. a deep shade of rose can be got; 1½ oz. Rhodamine B dissolved in ½ pint water gives a fine rose.

Bluish Pink.—Use ½ oz. Bluish pink N, or ½ oz. Safranine prima dissolved in 3 oz. boiling water.

Deep Pink.—Use 1 oz. Erythrosine B in 5 oz. water.

Red.—Use 2 oz. Cardinal red B dissolved in ½ pint boiling water, or 2 oz. Ponceau 2 R dissolved in ½ pint boiling water.

Salmon.—Use ½ oz. Mandarine G extra dissolved in 5 oz. boiling water. Another shade can be got by using the same quantity of Chrysoidine dissolved in water.

Sea Green.—Use 2 oz. Fast light green dissolved in ½ pint boiling water.

Pea Green.—A fine shade is got from ½ oz. Fast light green and ½ oz. Fluoresceine yellow dissolved in ½ pint boiling water.

Orange.—Use 2 oz. Brilliant orange G dissolved in ½ pint boiling water.

Dark Brown.—Use 5 oz. Soap brown S dissolved in 1 pint boiling water.

Blue.—Use 2 oz. Methylene blue 2 B dissolved in ½ pint boiling water.

Violet.—Use 1 oz. Formyl violet S 4 B dissolved in ½ pint boiling water.

Chestnut Brown.—Use 1 oz. Soudan brown dissolved in ½ pint spirit.

By mixing these different colours together a variety of tints can be obtained. It is impossible, however, to particularly describe them on paper. Thus, by using a mixture of Safranine and Quinoline yellow, a fine bright scarlet rose is obtainable; a mixture of Safranine and Methylene blue will produce violet and lilac shades; Methylene blue and Quinoline yellow greens of various tones; Methylene blue and Chrysoidine bronze green to olive shades, and so on. The soap-maker by experimenting can soon become expert in mixing colours.

It may be pointed out that some of the coal-tar colours change on being mixed with the hot soap paste; thus the Eosines and Rhodamines may turn yellow, or some of the yellows go brown, but on cooling the original colour comes back.

The mineral colours used for tinting soaps are as follows:—

Cadmium yellow for yellow soaps; ½ lb. will colour 1 cwt. of soap a good yellow.

Caramel or burnt sugar is a fine colouring agent for making brown soaps; ½ lb. will colour 1 cwt. of soap.

Ochres have been used in colouring soap yellow; only the best and strongest in staining powers—the so-called gold ochre—should be used for this purpose. Ultramarine green is suitable for colouring soap green, giving with ½ lb. of the pigment a good sea green to 1 cwt. of soap.

Vermilion is useful for making rose-coloured soaps, but it is rather heavy, and therefore tends to settle out unless well crutched in and the soap quickly cooled.

Chrome green is very suitable for colouring soaps green ; it has a fine colour and readily mixes with the soap, and is quite permanent.

Umbers are used for making brown soaps ; ¼ to ½ lb. per cent. is usually sufficient.

Ultramarine is used for making blue mottled soaps ; ½ lb. will colour 1 cwt. of soap.

TRANSPARENT SOAPS.

The manufacture of transparent soaps is very largely carried on both in this country and abroad, such transparent toilet soaps being great favourites with a large number of persons. It is by no means easy to make transparent soaps ; it requires a good deal of practice and experience to enable a soap-maker to turn out a perfect product.

In making transparent soaps there are a few points which require attention ; first in regard to the oils and fats used.

There are some which adapt themselves better than others to the production of transparent soaps. Castor oil in particular gives rise more readily to transparent soaps than any other oil, perhaps next comes coconut oil, then the various liquid oils. Solid fats, like tallow and palm oil, are most difficult to transform into transparent soaps, and they should be sparingly used.

The great bulk of the transparent soaps, especially the better qualities, are made with alcohol or methylated spirits, the use of which of course adds to the cost of production. There are perhaps two reasons for the use of spirit ; the first is, to obtain a perfect transparent soap the saponification of the fats must be complete. As every soap-maker knows, the more perfect a fat is saponified the more transparent it is ; the alcohol promotes this saponification and so helps to bring about transparency of the soap. Then again, alcohol is a more perfect solvent for soap than water, and by its means a clear, transparent solution is obtained, which on evaporation of the spirit leaves the soap behind as a transparent mass.

The addition of glycerine promotes transparency, but it has to be used with care, or otherwise a pasty, sticky soap is obtained which is not at all satisfactory.

Sugar is often added to transparent soaps, as it increases their transparency.

Generally these soaps are coloured, usually red, the best colouring matter which can be used for this purpose being Safranine, of which a half to one pound is required per hundredweight of soap, according to the depth of tint required. For yellow, what is known as Butter yellow or Soap yellow is used. (See Colouring Toilet Soaps, p. 282.)

Any kind of perfume to the fancy of the maker may be employed.

Each maker has possibly his own method of working: those described below will be found very useful.

Transparent Soap by Cold Process.—Take 50 lb. of stearic acid, 110 lb. of coconut oil and 40 lb. of castor oil, heat these together until they are melted, then stir in 100 lb. of caustic soda lye made from the best quality of solid caustic soda, this lye having a strength of 70° Tw. (1·350 specific gravity). The lye is well mixed with the oils, and the mixture allowed to stand for a few days.

Next the soap so made is mixed with 120 lb. methylated spirit, the mixture being heated until a clear transparent liquid is obtained.

For the purpose of saving alcohol it is best to conduct this operation in a still connected with a condenser, so that the alcohol or spirit which is volatilised during the operation can be recovered and used for another batch of soap; generally about two-thirds of the spirit may be thus recovered. During this treatment the saponification of the fats is completed.

When a transparent mass is obtained there is added to the soap about 40 lb. of crystal sugar made into a syrup with 4 gallons of water and 40 lb. of glycerine.

sugar 3
water 3

The mass, when all the ingredients have been incorporated, is ready to be framed; when set it is cut up into tablets; these are placed for some time in a cool dark room, during which time the alcohol gradually passes away, the soap hardens, and the transparency becomes more perfect.

Transparent Soap by Boiling.—The process described above is necessarily a slow one, and many soap-makers would like to have a quicker method. Then the following process may be adopted, the materials used being the same both in kind and quantity.

The oils are melted together at a gentle heat, then the caustic soda lye and the spirit are mixed together and added to the oils after stirring well to ensure thorough admixture; the mass is kept at a gentle heat until the saponification is complete and a transparent mass is obtained; this may take from three to four hours. Then the other ingredients are added and the soap finished as before. Colour and perfume may be added as may be deemed necessary.

The use of glycerine is not absolutely necessary to the production of transparent soap; the following formula shows the materials required for a transparent soap without glycerine:—

Transparent Soap.

Tallow or stearic acid	60 lb.
Coconut oil	50 ,,
Castor oil	40 ,,
Caustic soda lye at 70° Tw.	75 ,,
Methylated spirit	50 ,,
Crystal sugar	20 ,,
Water	20 ,,

The fats are melted, then treated with the alkali, the whole being kept at about 180° F. until the soap is properly formed, when the alcohol is added, then the other ingredients, together with any colouring matter and perfume that are required, when the soap may be finished in the usual manner.

There is just one point that is important in preparing these soaps by heat, and that is, the temperature must not be allowed to be too high, or all the spirit will be volatilised, which is not desirable, for then a transparent soap cannot be obtained.

Transparent Soap without Alcohol.

Provide the following materials :—

Tallow	48 lb.
Coconut oil	40 „
Castor oil	60 „
Caustic soda lye, 70° Tw.	74 „
Crystal sugar	36 „
Water	36 „
Glycerine	6 „
Soda crystals	10 „

Melt the fats, mix with the caustic alkali, allow to stand for twenty-four hours, then boil for three or four hours to complete the saponification, when a clear transparent mass is obtained, the heat is withdrawn, and the soap is allowed to stand for an hour or so until it has a temperature of about 170° F., and is more or less of a jelly in appearance. There are now added with a brisk agitation the glycerine and the sugar made into a syrup with the water, then the soda crystals, then any perfume and colouring matter, after which it is allowed to stand until cold. Exercising all ordinary care a transparent soap will be readily obtained, of a sufficiently good quality for the cheaper classes of these soaps.

By using a rather larger proportion of sugar, transparent soap may be made without either alcohol or glycerine according to the following formula :—

Tallow	54 lb.
Coconut oil	44 „
Castor oil	54 „
Caustic soda lye, 70° Tw.	84 „
Crystal sugar	48 „
Water	26 „

Worked as described above.

It will be sufficient to add that in all processes of making transparent soap without alcohol and glycerine, care must be taken that the saponification of the fats is complete before going on with the finishing processes.

Another plan of making transparent soaps is often adopted in many works. A good ordinary sort of soap prepared properly from good tallow or other oils, best with high grade caustic, is taken, dried and shaved. It is then put into a pan with sufficient alcohol or methylated spirit to dissolve it. The pan may be heated, but the temperature should not be allowed to get too high; from 130° to 160° F. will be found sufficient. The solution is best effected in a still fitted with a condenser as described above, so as to save as much of the alcohol as possible. When all is dissolved, the solution is allowed to stand to allow any insoluble matters, such as salt, carbonate of soda, and sulphate of soda, to settle out. The clear portion is then transferred to a still, where three-fourths of the spirit is distilled off and condensed again for further use. The residual soap is transferred to the frames, coloured and scented if needful, allowed to cool, then cut up into tablets, which are then kept in a warm room to set. At first the tablet is not transparent, but gradually becomes so as the excess of alcohol and water evaporates.

C. INDUSTRIAL SOAPS.

In many trades soap is largely used for the performance of certain operations. The silk manufacturer uses soap to free the raw silk from the gummy matter it naturally contains; the woollen manufacturer finds soap the best thing to use for extracting the dirt and grease from the wool prior to spinning it; the calico printer uses soap for clearing his printed cloths from the thickening he uses and for brightening the colours. To supply the users for the purposes indicated large quantities are annually made.

Generally industrial soaps are not made with the same care as ordinary domestic or household soaps. In many cases the element of price enters into the question of what materials are used and the degree of attention paid to the process of making. The desire on the part of some users for cheapness often leads to many of the grades of these soaps being made from very poor materials. In the following sections we shall indicate those soaps which are most used in manufacturing operations and the best materials to make them from.

Wool Soaps.—Soap is a very useful agent in the manufacture of wool into cloth. The first thing done with the raw wool as it comes into the woollen manufacturer's hands is to extract from it the grease and dirt it contains. It has been found that washing in soap liquors, or in a mixture of soap and soda, is one of the best ways of effecting this operation. The process is known as wool scouring. A rather poor grade of soap is generally used, colour and quality not being of much importance. Bone fat, low grade tallows, cheap palm oils, and oleic acid are used largely. These soaps are always made by the boiling process and are salted and framed at once while hot. The following mixtures are much used:—

1 cwt. bone tallow, ½ cwt. cotton oil, ½ cwt. oleic acid.
1½ cwt. low tallow, ½ cwt. palm oil.
1½ cwt. bone tallow, ½ cwt. cotton oil.

A slight excess of alkali does not matter—in fact is rather beneficial to the scouring qualities of the soap—but too great an excess must be avoided, as it tends to render the wool difficult to bleach in the subsequent operations through which it is passed. Generally these soaps are made to contain 62 to 64 per cent. of fatty matters, 29 to 30 per cent. of water, 6½ to 7 per cent. of combined alkali, with about ½ per cent. each of free fat and free alkali. They should not contain more than one per cent. of the latter ingredient.

The best soaps for this purpose are soft soaps made with potash. They are, however, more expensive than the hard soda soaps, and hence are not made to any extent. Potash soaps leave the wool much softer in feel and more silky in appearance, while they have not the yellowing tendency of soda soaps. It has also greater scouring properties. The same oils and fats are used as in making soda soaps. A good potash soap will contain 50 to 52 per cent. of water, 43 to 44 per cent. of fatty matter, 5 to 6 per cent. of combined alkali, and ½ to ¾ per cent. of free alkali and free fat.

The soap liquors from the raw wool scouring operation are usually collected and treated with acid or other substance to separate out the fatty matter they contain, which is sold under the name of Yorkshire grease.

After being scoured it is necessary, for the purpose of facilitating the spinning and weaving of the wool, to oil it; this is done with various kinds of oil, both fatty and mineral. After being spun and woven, it is needful to extract this oil out of the wool before it can be subjected to the process of dyeing and finishing. This can be done by treatment with a soap, usually the same kind of soap as was employed in the original scouring operation. It is however desirable that a slightly better quality should be used, so that nothing it might contain may interfere with the process of dyeing. The soap which is most used for this purpose is one made from a mixture of equal parts of bone tallow and cottonseed oil ; another favourite soap is made from palm oil and cotton oil. The latter is really the better of the two for the purpose, for the soap made from the bone tallow is liable to contain lime compounds which, if they are left in the cloth, have a tendency to affect the dyeing by forming colour lakes with the dyes, and thereby causing poor shades and dull colours to be obtained. Soaps made from recovered greases are very unsatisfactory for this purpose, as they often contain small quantities of unsaponifiable matter which, getting on the cloth, form grease spots and prevent the dye from going on the cloth properly.

We may remark that, from a strictly scientific point of view, the method of extracting oil from wool by means of soap is not the most correct.

After being dyed the woollen cloth has often to undergo the operation known as milling or fulling, the object of which is to cause the felting together of the fibres and to produce a thicker and fuller cloth, more impervious to the weather and therefore more suitable for making clothes. It is found that this milling is best done in the presence of a soap liquor; in this case the soap has no actual chemical work to do. Milling soaps must, however, be of good quality and well made ; they should not contain any free alkali, as this has a tendency to act upon the dye, causing it to run or bleed, and sometimes it would alter the shade; therefore a milling soap must be well settled and fitted. The soap ought not to contain any free fat, as this would settle on the cloth and form grease spots. The soap should lather freely and be soluble in water. The best materials to use, therefore, will be olive, palm nut, cotton and similar oils. A tallow soap is not sufficiently soluble, nor is a palm oil soap. A good mixture is 50 parts of olive oil, 40 parts of cotton oil, and 10 parts of palmnut oil, thoroughly saponifying the oils and settling well.

A potash soap, if it could be made quite neutral, would be the best, but a sufficient degree of neutrality cannot be obtained in the potash soap without difficulty.

Calico Printer's Soap.—The calico printer makes great use of soap in his works, although the writer has an idea that it is not necessary in all cases. To enable him to print on calico, the calico printer has to mix the various colouring matters and mordants, with gum, dextrine, starch and similar bodies, to thicken them and prevent the colour running when printing on the cloth. The thickening material has subsequently to be removed, and a soap bath has been found to be a convenient and simple means of doing this. In some cases the soap has a further effect in entering into combination with some of the colours, and by so doing making these much brighter.

A calico printer's soap must have the following features: it should be fairly soluble in water and ought to be quite neutral in its reactions, for if it contained any free alkali it might act upon some of the colours and change their tint. The utmost amount of free alkali which is permissible in a calico printer's soap is 0·2 per cent. It should not leave, or have any tendency to leave, any objectionable odour behind it. It is found by experience that the two best materials to make such a soap from are palm oil and olive oil. The use of rosin is not permissible, as rosin soaps are found to react too alkaline for this purpose; a tallow soap is apt to contract an odour, and is scarcely soluble enough. A little tallow may, however, be used in conjunction with the other oils.

Coconut oil, although it makes a very soluble soap, has been found to be rather objectionable, on account of the risk of imparting an odour to the goods, and this statement also applies to castor oil.

The best calico printers never object to pay a good price for their soap, and they find it to be in the end the most economical course to pursue. Some of the smaller printers are, however, tempted to buy cheap grades of soap, which cannot be produced unless low grades of fat be used or by employing rosin.

In making a calico printer's soap, great care must be taken in getting it neutral. This can only be done by careful and complete saponification in the first instance, and thoroughly fitting the soap afterwards, so as to eliminate all the alkali possible.

The best soap is made from bleached palm oil, while many printers prefer an olive oil soap. These soaps are usually made to contain 64 to 65 per cent. of fatty matter.

An analysis of a good make of calico printer's soap made by the writer gave the following figures:—

Fat	64·3	per cent.
Free alkali	0·1	,,
Combined alkali	6·2	,,
Free fat	none	
Water	29·4	,,

Silk Soap.—In the boiling-off of silk to free it from the gummy matter it naturally contains, a strong soap bath, using as much as 20 to 25 per cent. of the weight of the silk, is employed. The soap used for this purpose should be well made, fairly soluble in water, and not too alkaline in character. Alkalinity in this soap is not of so much importance as in calico printer's soap; still, it should not be too strong, and the amount of free alkali ought not to exceed 0·4 per cent. The solubility is of much importance, inasmuch as then a strong and yet liquid soap bath can be got; on this account olive oil is found to be the best material to make silk soap of. Coconut oil would make a good soap for this reason, but it is open to two defects: it is not easy to make a neutral soap from it, and, further, there is the objection to the rancid smell it is liable to leave behind it.

Another feature which makes it needful to have a soluble soap is that it is necessary thoroughly to wash the soap out of the silk after it has been boiled in it.

For a silk soap, olive oil is the best. Ground-nut oil may also be used with good results; a little bleached palm oil may be added. The soap ought to be well made, the principal point being to leave little or no fat.

Another way in which the soap is employed in the silk industry is in dyeing, much of this being done in a bath of soap, a method which seems to the writer to be a relic from other days, and might be abandoned. There is no peculiarity about the soap which is used for this purpose; a good olive oil soap works best—the only point is to avoid the presence of free fat, and have a good soluble soap.

D. Special Soaps.

We may now turn our attention to the production of a class of soaps made for special purposes, or, perhaps, in some cases supposed to be made for some special purpose. These soaps are rather numerous and are sold under a variety of fancy names, and often at equally fancy prices which leave a good margin of profit for the maker.

Medicated Soaps.—A large number of soaps are made which are supposed to be of medicinal value. That some of them are there is no doubt, but whether others have any such value at all is rather an open question. The process of manufacture of these soaps is very simple. First of all there is made an ordinary soap stock in the usual way, and into this is worked by means of the crutcher, or by the milling process (the latter plan, perhaps, giving the best results) the special substance which gives value to the soap. Makers will, of course, differ in the character of the soap stock which they will use for what is normally the same soap, but this is a small point which is of very little moment.

Carbolic Soaps.—Of all the various kinds of medicated soaps, those containing carbolic acid, or, as the chemist calls it, phenol, are perhaps the most important, for they are made in large quantities and are used for common household purposes. For making carbolic soaps almost any good soap stock may be used, bnt this is usually varied according to the quality or grade of the soap. Thus, the lowest grades of carbolic soaps are made from the nigres of pale soaps mixed with fresh soap stock. The best grades of these soaps are made from good pale soaps of tallow, bleached palm oil, and rosin. As carbolic acid has a slight acid reaction, it is a good plan to leave the soap stock slightly alkaline, for, if quite neutral, the acid may cut the soap while being mixed. The usual quantity of carbolic acid is 10 per cent. Occasionally soaps are made containing 5 per cent. This is the minimum quantity which should be added, or the medicinal value of the soap will be reduced to nil.

For pale carbolic soaps the best crystal acid should be used. Before adding to the soap this may be mixed with a small quantity of water to make it liquid. For the commoner class of carbolic soaps, which usually are of a dark brown colour, the crude carbolic acid may be used. The process is simple. The soap stock is made in the ordinary way, and, after being run off and fitted if required, the carbolic acid is crutched in in the crutcher, adding it little by little. After the crutching the soap is framed and allowed to set, after which it may be cut up into bars and stamped in the usual way.

Naphthol Soap.—Another disinfectant soap which is sometimes made is naphthol soap. This is made by crutching 10 lb. of naphthol into 1 cwt. of a good soap and finishing as usual. In place of naphthol, naphthalene may be used.

The makers of special disinfectants, *e.g.*, Germol, Sanitas, Izal, etc., produce them by mixing their products with ordinary soaps in the manner described above.

Sulphur Soap.—A soap containing sulphur is largely used for washing dogs, and also for treating various forms of skin disease. These soaps are very simply made; a good white soap made from tallow and coconut oil is employed, and into it while melted, after it has been fitted, are stirred flowers of sulphur, 10 to 20 lb. to 1 cwt. of soap, a little perfume being added to improve the odour of the soap.

Tar Soap.—A black-coloured tar soap is made and used in fairly large quantities. Either coal-tar, or still better, wood-tar, may be used for it. The latter has rather more medicinal value, and is free from some of the objectionable features of coal-tar. An ordinary soap stock is taken—if slightly alkaline there is no objection—and the tar, in the proportion of about 10 per cent, sometimes a smaller quantity, is crutched in. Wood creosote is also used in making similar soaps, the amount usually added being 5 per cent.

Mercurial Soap.—This is sometimes prepared for treating dogs and other animals, and for preserving skins in taxidermy. It contains corrosive sublimate. One drachm of the latter compound is dissolved in a mortar with 1 oz. of rectified spirit, and 4 oz. of a good soap, cut up into fine shavings, are added. The whole is then incorporated by careful grinding.

Arsenical Soap is also frequently used for washing dogs, cats, and other animals, and in preserving skins. A good formula for making this is to mix in a mortar 4 oz. white soap, 1 oz. white arsenic, 1 oz. soda crystals, and ¼ oz. camphor, grinding the whole together, adding a little water to facilitate the ease of working until a smooth mass is obtained.

Tooth Soap.—Tooth soaps are made by taking a well-made and neutral tallow soap, and adding to it, while in a molten condition, finely sifted pumice powder, prepared chalk and starch. The following quantities may be taken as a guide: 20 lb. of soap, 1 lb. of pumice powder, 2 lb. of chalk, and ½ lb. of starch.

Sand Soaps.—Of late years a class of soap has come largely into use for the purpose of cleaning and polishing metals. They are manufactured by many makers and sent out under a great variety of fancy names. We may, however, include them all here under the name of sand soap. They consist of a soap made in the ordinary way which has been incorporated with fine sand, finely-powdered pumice stone, kieselguhr and similar bodies; the soap is taken while in a melted state, and it should not be too dry. The mineral ingredients are then ground in, to the extent that the fancy of the soap-maker may direct, after which the soap paste is put into moulds and pressed, to consolidate it and form a firm block of soap.

The following formulæ will serve to show of what materials such soaps may be made:—

1.	Tallow soap	20 lb.
	Fine sand	80 ,,
2.	Palm oil soap	20 ,,
	Fine sand	40 ,,
	Ground pumice	40 ,,
3.	Tallow soap	10 ,,
	Coconut oil soap	15 ,,
	Fine pumice	40 ,,
	Kieselguhr	35 ,,
4.	Tallow soap	15 ,,
	Palm oil soap	10 ,,
	Red oxide	5 ,,
	Ground pumice	50 ,,
	Fuller's earth	25 ,,

Shaving Soaps.—Shaving soaps are required to produce a good and persistent lather which, when placed on the face, will remain without drying up. At the same time the soap must not have any action on the skin, however tender that may be. To make such a soap a considerable amount of care is required. The best fats that can be used are tallow and coconut oil, and it is advisable to use both soda and potash in their preparation, as better lathering soaps are then obtained. Shaving soaps can be made either by the ordinary boiling process or by the cold process. In some makes of shaving soap a little gum tragacanth has been added to promote permanence of the lathering qualities. Very little of the gum is required, about 2 lb. to 1½ or 2 cwt. of soap, and it may be added at any convenient point in the process of making.

The following formulæ may be followed in making these soaps:—

Cold-process Shaving Soap.

1. Tallow	100 lb.
Coconut oil	12½ ,,
Soda lye at 72° Tw.	50 ,,
Potash lye at 72° Tw.	6 ,,
2. Tallow	88 ,,
Lard	12½ ,,
Coconut oil	25 ,,
Soda lye at 71° Tw.	55 ,,
Potash lye at 60° Tw.	15 ,,
3. Tallow	100 ,,
Coconut oil	20 ,,
Soda lye at 71° Tw.	52 ,,
Potash lye at 60° Tw.	8 ,,

These soaps may be scented in any way that the maker may approve, and the recipes previously given for scenting toilet soaps may be followed as a guide.

Boiled Shaving Soap.—In making such soap considerable care must be taken to ensure neutrality. If potash be employed along with the soda, as given in the cold process above, then the soap cannot be salted out. Just enough lye should be taken to ensure the soap being made nearly, if not quite, neutral, the soap well boiled so as to free it from excess of water, and then an excess of alkali is killed by the addition of a little stearic acid or coconut oil. The recipes just given may be followed as to the fats employed.

Emollient Soaps.—These are toilet soaps to which is added such bodies as lanolin, vaseline, spermaceti in about 5 to 10 per cent. of the weight of the soap.

Cold-water Soaps.—These are soaps for which it is claimed that they will yield a copious lather with cold water. They are made chiefly from coconut oil or palmnut oil, and are filled with soda crystals. They contain a large proportion of water, 30 to 40 per cent., and they are very wasteful in use.

Antimonial Soap.—Take 1 oz. antimony orange and dissolve in 3 oz. caustic potash lye, then mix with 12 oz. white tallow soap to a smooth paste.

Tannin Soap.—97 lb. good white soap and 3 lb. tannic acid.

Saliacyl Soap.—98 lb. good white soap and 2 lb. salicylic acid.

Thymol Soap.—97 lb. good white soap and 3 lb. thymol.

Benzoic Soap.—98 lb. good white soap and 2 lb. benzoic acid.

Floating Toilet Soap.—The stock soap is remelted and then strongly stirred with an agitator; by this means the soap becomes charged with air bubbles and therefore more or less spongy in texture; it is now framed, cut into bars, dried, which makes it rather lighter, cut into tablets and stamped.

Skin Soaps.—Soaps mixed with bran, oatmeal, cornflour, have been sold under the name of skin soaps.

Liquid Glycerine Soap.—Melt together 274 lb. pale oleic acid, 66 lb. coconut oil, 228 lb. caustic potash lye, 60° Tw., then add, boil up, and when saponified add 20 lb. glycerine and enough methylated spirit to make the liquid clear.

Fuller's Earth Soap. –70 lb. soap and 30 lb. fuller's earth. The fuller's earth is thoroughly dried before adding to the soap, and the latter should not contain less than 25 to 30 per cent. water.

Borax Soap.—90 lb. good soap and 10 lb. borax.

Superfatted Soaps.—Soaps made by the milling process are often sold as "superfatted"; they have added to them small quantities of lanolin, refined wool fat, lard, etc.

The main advantage of such soaps lies in that they are more agreeable to use by persons with tender skins, a fact due to the absence of free alkali.

Iodine Soap.—98 lb. neutral white soap and 2 lb. iodine. This should be made fresh as required as it does not keep, the iodine gradually acting on and combining with the alkali of the soap, thereby losing its medicinal virtues.

Farrier's Soap.—A soft soap made from fish oil, caustic potash and wood-tar.

SOFT SOAP.

Soft soap is a very important article in the soap trade; in some districts it is very extensively manufactured, while in others it is made in comparatively small quantities. Soft soap is an amber-coloured to reddish-brown material of the consistency of butter. It is much more soluble in water than the ordinary hard soap, and usually rather more alkaline in its nature. Its detergent and scouring properties are, therefore, greater.

The alkali of soft soap is potash, although a little soda is also occasionally used in conjunction therewith; a soft soap cannot be made with soda only, in the same way as hard soaps cannot be made with potash. Soft soaps owe their consistency to the fact of the greater solubility and hygroscopicity of potash soaps.

Soft soaps are much more simply made than hard soaps.

The fats and oils are boiled with the alkali till the saponification is complete, and then the soap is made, and only wants to be run into firkins or tin canisters to be ready for sale. Simple, however, as it is in principle, soft soap is by no means easy to make. It is liable sometimes to go wrong in the boiling, and then there is much difficulty in setting it right. The aim of the soft-soap maker should be to produce a clear, transparent soap, pale in colour, fairly free from odour, not too alkaline in character, and in some cases "figging" well. Figging in soft soap is a peculiar appearance—streaks of white usually found to strike inwards from the sides of the vessel holding the soap. Figging is usually considered to indicate a good quality of soft soap, but such is not really the case. A first-class soft soap can be made which will not fig, while on the other hand a poor soap can be produced which will fig. The figging is usually ascribed to the presence in the soap of stearate of soda, which crystallises out on the soap becoming cold, the crystals which are thereby formed giving rise to the figging. Figging is mostly met with in winter time. Unless the proportion of soda and stearic acid in the soap is very large it does not occur in summer time.

The oils chiefly employed in making soft soaps are linseed oil, whale oil and cottonseed oil. These form the basis of all soft soaps. Linseed oil is the one chiefly used, as it saponifies easily and gives a good pale-coloured, transparent soap, of a good consistency, fairly free from odour, and which keeps well. Whale or other fish oils are largely used, being cheap. They however commonly produce dark-coloured though clear soaps, but much depends on the quality of the oil which is used. Fish oil soaps have a fishy odour, which is not altogether objectionable. Cottonseed oil makes a fairly good soft soap, pale in colour and transparent, figging well, which is not the case with the other two oils that have been named. Cotton oil soaps are liable, however, to acquire a rancid odour on keeping. The quality of the cottonseed oil has a material influence on the quality of the soap. The best refined oils produce pale-coloured, transparent soap; the commoner grades are apt to give darker-coloured soaps, which owing to the large proportion of stearin they contain are apt to fig strongly. Tallow is occasionally added in making soft soaps, to cause them to fig. Olive oil soft soap is made for special purposes, such as silk washing, etc., but olive oil, owing to its cost, is not commonly added to soft soaps. Sometimes nut oil is added.

When white soft soaps are required, as is sometimes the case for special purposes in the cotton trade, such must be made from good white tallow, coconut oil, and perhaps a small quantity of lard or other fat, and particular attention must be paid to the quality of caustic soda used, which should be of a good white colour.

The caustic potash used in making soft soap was at one time prepared by the soap-maker for his use, by causticising pearlash (carbonate of potash) with quicklime. Now, however, it is the custom for the smaller makers to purchase it ready prepared from the alkali-maker in iron drums. The method of making caustic potash has already been described in the chapter on alkalies (page 36), and need not be repeated here. When bought ready made, it is advisable to make an examination of it to see that it is up to full strength, of good colour, fairly free from carbonate, and does not contain much, if any, oxide of iron. Many of the lower grades of caustic potash which are produced are defective in one or other of these points.

It is advisable that the soap-maker should prepare at least two potash lyes of different strengths—one of 14° Tw., the other of 25° Tw. Some makers provide lyes of three

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strengths, 14° Tw., 23° Tw. and 38° Tw. Much of course depends on the construction of the soap boiler in which the soft soap is being made. If the boiler be one which is heated by fire only, then a weak lye of 14° Tw. may be used with advantage, while if the boiler is fitted for steam heating, with open or closed coils, then stronger lyes may be used, say 23° Tw. and 30° Tw. Because in the first case as the boiling proceeds the lyes get stronger, while when working with the open steam the tendency is for them to get weaker. It is, however, by far the best plan to make the soap in pans fitted with open and close steam coils.

In making soft soap, only about one half of the full charge of oil is run into the pan. By means of the closed steam coil or fire it is heated up, then a quantity of lye at 14° Tw., equal in volume to the oil, is run in, and open steam sent in. Run the lye in slowly, while the mixing of the lye and oil is carefully watched. Presently the oil will begin to saponify, then it must be well stirred, for it will begin to swell and rise in the pan. As soon as this is seen more lye, equal to the first quantity in volume, may be run in and the boiling continued. Two things may take place in the early stage of soap-making: the oil and lye may boil over, or it may set into a stiff, pasty mass. In either case trouble may be looked for. The remedy in the first case is to turn off steam and beat down the bubbling soap with the paddle; that in the second case consists in adding more lye, in boiling up, stirring well and breaking up the mass as much as possible, but the process becomes tedious, because it is difficult to break up the masses of soap, and they are not easily dissolved in the boiling soap in which they float. These troubles will be avoided if a quantity of finished soap be left in the pan from a preceding operation.

When the oil and lye have amalgamated, then the rest of the charge of oil may be run in and the further quantity of alkali at 32° Tw. may be added. It may be mentioned here that as a rule 100 lb. of oil require 200 lb. of caustic potash lye at 32° Tw. to saponify, so that the soap-maker may base his calculations as to the quantity of alkali required on these data.

The soap is now boiled, either by fire heat or the closed steam coil. Generally it is not needful to stir it, the boiling keeps it in continual agitation; it is a good plan now and again to send a sharp current of open steam through it or to stir it up with an iron paddle, taking special note of any hard lumps of soap that may settle down at the bottom of the pan.

After a time the saponification of the oil will be complete and the soap formed. To ascertain this, take out a sample of the soap with a spatula, and place it on a piece of glass and allow it to cool, when one of three things will be observed :—

1. The soap may be clear and translucent: this indicates that the soap is properly formed and only needs boiling down to the proper strength.

2. The spot of cold soap has a fatty border. In this case more lye is required, and the soap-boiler should add some of either 23°, or even as strong as 38° Tw., and boil up a little longer, when another sample may be drawn to see how the soap is progressing.

3. The spot of soap is of a grey colour, lustreless and somewhat granular in appearance. In this case too much lye has been added, and to remedy this a quantity of oil which has been mixed with a little weak lye should be added, and the soap boiled up further. The experienced soap-maker can tell by the manner of the soap boiling how it is progressing and whether it wants more lye or oil. The boiling should go on quietly, free from any jumping or bumping. The boiling down is carried on until a sample taken

out and cooled on a glass plate shows the proper consistency and brightness of appearance.

Some makers add a little carbonate of potash, which promotes the production of the brightness, but too much must not be added, or the soap will become thin, and a whiteness will form on it. Too much lye induces the same defect. A little experience coupled with the habit of careful observation will soon enable the soap-maker to tell when he has got his boiling of soft soap quite right.

When finished the soft soap is run into the firkins or other packages to cool, when it is ready for sale.

Linseed oil yields a soap of a dark amber colour, with a pleasant odour.

Whale oil yields a dark reddish soap, varying somewhat in colour according to the quality of the soap used, but always having a fishy smell. Other fish oils may be used with a similar result.

Cottonseed oil yields a soap varying from a golden to an amber colour, according to the degree of refinement of the oil. Freshly made cotton-oil soaps are free from odour, but on being kept are rather apt to become rancid and develop an odour.

Olive oil yields a fine soap varying from amber to greenish in hue.

Hempseed oil gives a green-coloured soap.

Coconut oil gives a fine white soap.

Tallow gives a stiff soap, apt to fig somewhat.

The colour of the finished soap much depends on the care and attention given to the soap during the process of making, and also on the manner of heating the soap pan. There is no doubt but that a fire-heated pan produces a darker soap than a steam-heated pan, therefore the latter form of pan is to be preferred. Light-coloured soaps are preferred by consumers to dark-coloured soaps, and command a readier sale.

The following mixtures of oils may be used :—

A.	Whale oil	1 ton.
	Linseed oil	2 ,,
B.	Linseed oil	2 ,,
	Cottonseed oil	1 ,,
C.	Cottonseed oil	2 ,,
	Linseed oil	1 ,,
D.	Cotton oil	1 ,,
	Whale oil	1 ,,
	Linseed oil	1 ,,

These will yield soaps which will not fig much, the two last having this property much more fully developed than the first two. If soaps are required which will fig, then the following oils may be used :—

E.	Palm oil	2½ tons.
	Tallow	¾ ,,
	Linseed oil	1½ ,,
F.	Palm oil	3½ ,,
	Linseed oil	1½ ,,
G.	Cotton oil	2 ,,
	Tallow	½ ,,
	Linseed oil	1 ,,
H.	Tallow	21 cwt.
	Palm oil	2 ,,
	Linseed oil	1½ tons.
	Cotton oil	7 cwt.

Many other mixtures may be used.

I.	Coconut oil	1 ton.
	Tallow	½ ,,
	Lard	½ ,,

This will yield a soft white soap.

Sometimes figging is brought about by using a little soda along with the potash, as, for instance, in the following recipe: 1000 lb. of oil are boiled with 535 lb. caustic potash lye at 32° Tw., to start the saponification. Then there are added 150 lb. potash lye at 42° Tw., and 470 lb. caustic soda lye at 32° Tw.

The finished soft soap is usually from 2¼ to 2½ times the weight of the oil used.

Good soft soap should contain 42·5 per cent. of fat, with 10 per cent. of potash and 47·5 per cent. of water; some samples have as low as 40 per cent. of fat, while others have as much as 50 per cent.

By using any of the above recipes a pure soft soap is made, but for the sake of cheapness and competition, some samples are filled and made at a cheaper price by using such materials as rosins, silicates of potash and soda, starch, Irish moss, and caustic soda.

Rosin is a good cheapening agent for soft soaps owing to its making a soap having good detergent properties. When using rosin it is a good plan to saponify by itself and then add it to the soap made from the other oils. Some makers employ soda to convert the rosin into soap, in which case the rosin is melted over water in a steam-jacketed pan, while in another pan ordinary soda crystals are dissolved in a small quantity of water. The proportions are 56 lb. of soda crystals to 112 lb. of rosin. The soda liquor is added to the rosin in small quantities at a time, waiting until all effervescence ceases before adding each succeeding quantity of soda. After all is added the soap is boiled up for a short time to finish the saponification. When this is completed the soap is run into the pan of soft soap.

Should the colour of the finished soap be a matter of importance, and as rosin of the usual run of grades produces darkish-coloured soap, then an improvement may be effected by adopting either of the following plans—using a better grade of rosin, or purifying it by the following process. The rosin is saponified by soda, as described above, then the rosin soap is salted out by the addition of ordinary salt and time allowed for the soap to settle out. Then the lye is run off, and with it a large proportion of the colouring matter of the rosin.

The rosin soap thus purified may be added to the soft soap.

The proportion of rosin which may be added may be one-seventh to one-tenth that of the other oils and fats used.

The following recipes may be followed in the ordinary way:—

A.	Linseed oil	400	lb.
	Tallow	135	,,
	Rosin	50	,,
	Caustic potash lye, 32° Tw.	740	,,
	Caustic soda lye, 36° Tw.	40	,,
	Pearlash	25	,,
B.	Linseed	250	,,
	Cottonseed oil	250	,,
	Rosin	50	,,
	Caustic potash lye, 32° Tw.	500	,,
	Caustic soda lye, 36° Tw.	145	,,
	Pearlash	25	,,

The colour of a soft soap is a matter of importance as regards its sale—the paler this is the more readily it sells. When rosin is used there is a very considerable darkening of the colour, even if the plan of purifying described above be adopted. Even when pure oils are used it is difficult to keep the colour pale, especially when fire heat is employed. Steam heat is far preferable on this account. Too prolonged boiling also leads to the darkening of the colour, and should be avoided as much as possible.

Silicated Soft Soaps.—One of the best filling agents for soft soap is silicate of potash. It has the advantages of having body or consistency, is clear and transparent, has some washing power, and, what is more, is easily used. Silicate of potash is used by itself and also in conjunction with farina. Some soap-makers add at the same time some caustic potash, but this is not necessary.

The soap while still hot should be run into the crutcher and allowed to cool down to about 180° F.; then the silicate of potash, at the rate of 10 lb. to the firkin of soap, is run in and crutched into the soap. The quality of silicate used is the ordinary neutral liquid at about 70° Tw.

Another plan is to take 2 cwt. of caustic potash lye at 38° Tw., add to this sufficient carbonate of potash to bring the gravity up to 4° Tw., then add this liquor to 10 cwt. of silicate of potash, after which it is ready to mix with the soap.

If farina is used in conjunction with silicate for filling, then 1 cwt. of farina is taken and stirred into 12 gallons of carbonate of potash lye at 7° Tw., until a clear transparent mucilage is obtained. This is added to the silicate of potash (10 cwt.) and the mixture to the soft soap in the required proportions, which will be at about the rate of 20 lb. to the cwt. of soap.

Another method of filling soft soap, which is much on the above lines, is to first crutch in silicate of potash at the rate of 7 lb. to the firkin, then to prepare a mixture of starch and caustic soda lye, and crutch in 7 lb. per firkin of this mixture. The starch preparation is made by taking caustic soda lye at 40° Tw., heating to about 150 or 160° F., then adding farina in small quantities at a time, waiting until each portion is dissolved before adding the next. The farina is added until a mass of the consistency of soft soap is obtained, when it is ready to use.

A writer in *The Oil and Colour Trades Journal*, 1895, p. 911, recommends a mixture of ordinary hard soap, silicate of soda and Irish moss jelly. The soap may be the ordinary pale soap, or better, one made from bone or other cheap fats, without rosin. The silicate is the ordinary neutral silicate of soda at 100° Tw. The Irish moss jelly is made in the following manner: 27 lb. are steeped in cold water for half an hour, to soften the material and wash away dirt and sand; 65 gallons of water are placed in a wooden tub and heated to the boil. Then the cleaned moss is added and the whole boiled for half an hour, after which it is drained off, and to enable it to keep for some time a small quantity of caustic potash lye may be added. Irish moss jelly, unfortunately, does not keep any length of time, or otherwise it might find very many more uses than it does at present. One cwt. of the soap is sliced and mixed with the jelly, then 1½ cwt. of silicate of soda is added and the mixture kept near the boil until all are thoroughly incorporated, when the filling is ready for use, and it may be added to the soft soap at the rate of 8 to 10 lb. to the firkin.

From time to time other filling agents are offered, but generally prove unsatisfactory, and sooner or later make themselves manifest, often to the detriment of the soap-maker and injury to his trade. The author's experience shows that in this, as in many other things, there is nothing like supplying a genuine article to enable one to build up and maintain a good trade.

DRY SOAPS, SOAP POWDERS.

Dry soaps, as they are called, have during the last few years become an important branch of the soap industry. They do not vary much in their composition, the greater number of them being composed of ordinary soap and sodium carbonate; some are scented, others are not. Some makes, sold under special names, contain other constituents which are supposed to give some special value to the soap.

The process of manufacture is very simple, and its simplicity has induced many persons to take up the manufacture of dry soaps. Still, even though simple, some care must needs be exercised to turn out a dry soap of good quality. A first-rate dry soap should be in a fine powder, smooth, not gritty to the feel, nor exhibiting any tendency to aggregate together in lumps, nor staining the packing paper in any way. It is considered a *sine qua non* of a good dry soap that it should lather freely. We may proceed to make a few observations as to the character of the materials which are used in making dry soaps.

The Soap.—This, the special ingredient in this class of goods, should be present in fair proportion. One of the best known makes contains from 18 to 20 per cent. of actual soap, another has as much as 30 per cent., some get down as low as 5 per cent., but such are dry soaps only in name and more or less frauds on the public. A fair quantity to put in is from 15 to 20 per cent. The soap ought to be well made from good materials, as free as possible from free fat and containing but a small proportion of water—15 per cent. is a fair quantity, but more than 20 per cent. should be avoided. The soap ought to be made from fats, which, like tallow, palm oil or coconut oil, give hard soaps, while the addition of a small quantity of such oils as cotton oil, linseed oil, rosin or other oils, or stock soap, which give soft kinds of soap, is not objectionable; too much should not be used, as then the soap becomes so soft that it does not grind easily and it becomes almost impossible to obtain a fine powder. A good soap for this purpose is made from 40 lb. bleached palm oil, 40 lb. tallow, 10 lb. cotton oil, and 10 lb. coconut oil. Another mixture is 40 lb. palm oil, 40 lb. tallow, 10 lb. linseed oil, and 10 lb. coconut oil. This will give a yellower-coloured soap than the last, the finished dry soap will be darker, and this is sometimes objected to by customers. Another mixture is 40 lb. bleached palm oil, 30 lb. coconut oil, 20 lb. tallow, 10 lb. linseed oil. But the variety of mixtures of fat from which the soap is made is great, and it will serve no good purpose to enumerate them in detail.

Sodium Carbonate.—This is used in the form of soda crystals. Occasionally, should the dry soap show signs of becoming pasty during working, a small quantity in the form of 58 per cent. alkali is often added. This appears to combine with the excess of moisture in the soap, to which the pastiness is usually due, and make it work properly.

Glauber's Salt.—This product, which is crystallised sodium sulphate, is often added to dry soap in place of soda crystals with the object of cheapening the cost of production, and so be able to turn out an article at a lower price than the best grade of dry soaps. Borax is occasionally added to dry soaps, and is a very good material to add; the only objection to it is that it is expensive.

Phosphate of soda has been added to dry soaps, but the writer sees no very material advantage in its addition. It is a neutral salt, without any detergent properties, while it is rather expensive.

Paraffin, in the form of wax or oil, is often added to dry soaps. The quantity added is but small, rarely exceeding 2 per cent. and oftener not more than ½ per cent. of the dry soap. It is generally conceded that paraffin increases the washing properties of soap. Perfumes of various kinds are often added, but the best known makes are not scented at all, and such odour as they possess is due to the fats used in making the soap.

Other bodies are sometimes added for various reasons to dry soaps. Such will be mentioned later on; the above form as it were the basis of all dry soaps.

Every dry-soap maker has his own manner of working. The general principle which underlies the great majority of the processes is to grind the soap and salts together. This may be carried out either by means of the edge runner mill, when the soda crystals or Glauber's salt are first ground, then the soap is thrown in and gradually worked in. With this manner of working there is sometimes a tendency to a pastiness if the soap be too soft. In such an event it may be remedied by throwing in a small quantity of 58 per cent. alkali.

The difficulty is that the edge-runner does not grind fine enough. A better plan is to use an edge-runner to mix the ingredients, and grind in a devil disintegrator. This is admirable for grinding dry soap and works better than any other form of grinding mill, yielding a product of great fineness, which is a very important feature in dry soap, and should always be aimed at.

Another plan of working which is sometimes followed is to melt the soda crystals by heating them in a pan. The water they contain, as water of crystallisation, is sufficient for this purpose, then add the requisite quantity of soap cut up into fine shavings, stir well, and allow to cool, and grind up in the usual way. There is, however, no advantage in this process over the one described above.

Having described the materials used and the method of making, some recipes may be given for making various dry soaps.

Standard Dry Soap.—20 lb. good soap, 70 lb. soda crystals, 10 lb. refined alkali.

Extra Dry Soap.—30 lb. soap, 60 lb. soda crystals, 10 lb. refined alkali.

Cheap Dry Soap.—15 lb. soap, 50 lb. soda crystals, 5 lb. soda ash, 30 lb. Glauber's salt.

Borax Dry Soap.—25 lb. soap, 60 lb. soda crystals, 5 lb. borax, 10 lb. refined alkali. A better quality can be made from 25 lb. soap, 10 lb. refined alkali, 50 lb. soda crystals, 15 lb. borax.

Paraffin Dry Soap.—20 lb. soap, 70 lb. soda crystals, 8 lb. refined alkali, and 2 lb. soft paraffin scale.

Oatmeal Dry Soap.—15 lb. soap, 70 lb. soda crystals, 8 lb refined alkali, and 7 lb. oatmeal.

Perfume may be added to any extent and of any character the soap-maker desires.

Disinfectant Dry Soap.—Dry soap may be the means of applying disinfectants, which are simply added in the desired quantities to the materials, as given in the above recipes. If the disinfectant is one which is liquid in character, then it is desirable to reduce the proportion of soda crystals, and increase that of the refined alkali to keep the soap in the form of refined powder, or some absorbent, like kieselguhr or French chalk, may be added to the soap. Perhaps the latter method has some advantage over the former plan.

It might perhaps be added that what is called washing crystal is simply soda crystals ground up with a little soap, about 3 per cent. Sometimes a little ultramarine blue is added to the dry soap in order to take away any yellowish tinge it might possess, and so make it appear whiter in colour.

A blue dry soap has been made which is nothing more or less than ordinary dry soap, to which sufficient ultramarine has been added to give it a blue colour.

The following are a few analyses of dry soaps that are now on the market:—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Water	50·28	47·85	52·65	52·17	59·16
Soap	7·69	19·25	8·50	25·50	3·50
Soda as Na_2CO_3 . . .	42·03	32·90	38·85	22·33	37·34
	100·00	100·00	100·00	100·00	100·00

These are made with sodium carbonate.

The following are some made with Glauber's salt and sodium carbonate:—

	No. 6.	No. 7.	No. 8.
Water	50·34	47·85	53·65
Soap	8·69	15·36	10·78
Soda as Na_2CO_3 . . .	21·36	15·48	12·32
Sodium Sulphate . .	19·61	21·31	23·25
	100·00	100·00	100·00

CHAPTER VIII.

GLYCERINE IN SOAP LYES.

When an oil is saponified by boiling with caustic alkali, glycerine is formed as one of the products of the reaction. The proportion of glycerine yielded by the different oils varies considerably; thus the characteristic ingredient of butter fat, butyrin, will yield as much as 30 per cent. of glycerine, while brassin, the characteristic constituent of rape oil, will only yield 8·7 per cent. of glycerine. The average percentage of glycerine yielded by the oils and fats is about 10. Allen gives the following table as to the yield of glycerine from the various oils and fats:—

Oil.	Glycerine per cent.
Porpoise	11·09
Whale	11·96
Menhaden	11·10
Lard	10·83
Tallow	9·9-10·0
Butter fat	11·06
Olive	10·1-11·4
Rape	9·82
Sesame	9·94
Cottonseed	9·50
Linseed	9·39
Castor	9·13
Coconut	12·11
Palmnut	11·70
Palm	9·71

This glycerine passes into the soap, and on the latter being salted out in the soap-kettle, remains in the spent lyes. Formerly it was thrown away, but of late years the demand for glycerine has caused attention to be paid to processes for the recovery of the glycerine from the spent lyes, a sample of which, examined by the author, had a specific gravity of 1·1548 (30·90 Tw.) and contained :—

8·50	**per cent.**	**glycerine.**
78·65	„	**water.**
·36	„	**caustic soda.**
·58	„	**sodium cabonate.**
2·86	„	**sodium sulphate.**
14·64	„	**sodium chloride.**

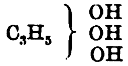
Glycerine is a water-white, very viscid liquor, having a specific gravity when pure of 1·2665 ; but it has such an affinity for water that it is difficult to obtain absolutely anhydrous glycerine, and the ordinary commercial glycerine generally has a specific gravity of 1·260 to 1·263, and contains a little water. It has a sweet taste, and was originally known in consequence as the sweet spirit of oils, and in the glycerine industry the crude material is known as the "sweet water". With water it mixes in all proportions. The following table showing the specific gravities and strengths of various mixtures of these two liquids will be found useful :—

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF AQUEOUS SOLUTIONS OF GLYCERINE.

Specific gravity. 15° C.	Per cent. of glycerine.	Specific gravity. 15° C.	Per cent. of glycerine.
1·2650	100	1·1990	75
1·2625	99	1·1855	70
1·2600	98	1·1715	65
1·2575	97	1·1570	60
1·2550	96	1·1430	55
1·2525	95	1·1290	50
1·2499	94	1·1155	45
1·2473	93	1·1020	40
1·2447	92	1·0885	35
1·2421	91	1·0750	30
1·2395	90	1·0620	25
1·2341	88	1·0490	20
1·2287	86	1·0365	15
1·2233	84	1·0240	10
1.2179	82	1·0120	5
1·2125	80		

Glycerine is also soluble in alcohol, but only slightly so in ether. A mixture of equal volumes of chloroform and alcohol dissolves it, but it is insoluble in chloroform, benzene, petroleum spirit and oils. It is a powerful solvent for salts, etc., being nearly equal to water in this respect.

It is composed of carbon, hydrogen and oxygen in the proportions indicated by the formula $C_3H_8O_3$; in its relationships it belongs to the alcohol group of organic compounds, it has basic properties, and with the monobasic acids, such as hydrochloric acid, oleic acid, stearic acid, it is capable of forming compounds containing one, two or three equivalents of the radicle hydroxyl, OH, and therefore having the formula



$$C_3H_5 \left\} \begin{matrix} OH \\ OH \\ OH \end{matrix} \right.$$

and is essentially the hydroxide of the radicle glyceryl.

It may be mentioned that although by a looseness of expression which is very common, glycerine is often spoken of as the base of the oils and fats, yet glycerine as such does not exist in the oils, but is formed during the various processes of saponification by the combination of the real base glyceryl, C_3H_5, with the radicle hydroxyl. The oils and fats are salts of this basic radicle glyceryl. Heated with strong sulphuric acid or with acid potassium sulphate it is dehydrated and acrolein (acrylic aldehyde), C_2H_3COH, is evolved, recognisable by its peculiar odour.

Nitric acid acts on it energetically, forming a variety of products, nitro-glycerine, oxalic acid, glyceric acid, etc., being formed according to the strength of the acid used, and the manner in which the operation is carried out. Heated with potassium permanganate in the presence of caustic potash, glycerine is converted into oxalic acid and carbonic acid, and as this reaction takes place in a definite manner, it is taken advantage of for the quantitative estimation of glycerine.

When glycerine is heated with organic acids combination takes place, and ethers are formed known as glycerine, and these have the special termination *in*, as acetin, olein, stearin and palmitin, with the prefix *mono*, *di* or *tri*, to show how many equivalents of the acid are combined with one equivalent of the base. Chemists, to show the analogy between glycerine and the alcohols, have given to it the systematic name glycerol, but it has been thought better to use the more familiar term glycerine in this chapter.

The first attempt to recover glycerine from the used soap lyes was made in 1858 by Reynolds, whose process consisted essentially in evaporation accompanied by distillation, and since that time a great many processes have been devised. Any process, to be successful, must depend to a large extent upon the character of the soap lyes. It is largely influenced by such factors as the quality of the alkali used to make the caustic lyes, whether it be from high grade caustic soda, low grade caustic soda, or by causticising soda ash or black ash lyes. The character of the fats and rosins will also have some effect on the method of extraction to be adopted. Messrs. Thomas, Fuller and King's process, devised in 1879, consists in first evaporating the lye so as to throw as much of the salt out as possible; it is then boiled with a little acid and the fatty matter which remains skimmed off, after which the liquor is again evaporated. The salt which comes out is collected, while the crude glycerine left behind is subjected to distillation.

Young neutralises the used lyes with acid and boils down by means of steam, filtering off any fatty matter that separates out. Whiting is next added and the mixture evaporated to a paste, which is then placed in a hydro-extractor; the liquor containing the glycerine is collected and subjected to distillation.

Pain adds acid to neutralise the lyes and separate any fatty matter that may collect, then adds tannic acid to precipitate the albuminous and gelatinous matter; this is filtered off, the liquor evaporated down and then distilled. When the caustic lyes used to saponify the fats are prepared from black ash or crude soda ash they are very liable to produce compounds such as cyanide compounds and sulphur compounds, which have a material influence upon the method to be adopted in recovering the glycerine.

Hagemann first adds lime and then a little rosin, and boils to neutralise the caustic alkali which may be present in the lyes. To the mixture is next added hydrochloric acid, which separates out the rosin or fatty matters which may be present; then there is added ferric chloride, which precipitates any cyanogen compounds in the form of Prussian blue; these are filtered off. Air is now blown in for some time, after which a small quantity of bleaching powder is added, which precipitates most of the sulphur compounds in the form of free sulphur, which is filtered off; next the liquor is neutralised by the addition of soda and then evaporated down.

Messrs. Allen and Nicholl's process consists essentially in acidulating the spent lyes with hydrochloric acid and then adding copper sulphate, which causes the precipitation of the sulphides, sulphocyanides and ferrocyanides, together with the fatty matter which may be present. The precipitate is removed by filtration, soda is added to neutralise the free acid and the liquor boiled down and distilled.

These are but a few of the processes which have been patented for the purpose of separating glycerine from soap lyes. The objects to be aimed at in any process which is to be commercially successful, are the removal of all albuminous and fatty matters which may be present in the lyes; the removal of the salt which is deposited in the process, and, thirdly, the exercise of economy in concentration and treatment.

The following method of extracting crude glycerine is in use. The lye is evaporated in an iron tank to a specific gravity of 40° to 50° Tw.; this evaporation may be conducted in shallow pans heated by a steam coil from another evaporator, or by placing the pan over a flue leading from the second boiling pan which will be referred to presently. After the concentration the lye is run into a tank and then allowed to cool, and any fatty or soapy matter which may separate out is collected and sent back to the soap pan. To the liquor is next added a quantity of caustic soda at 70° Tw. This causes the precipitation of the albuminous matter, which is separated in any convenient way. To the liquor is next added sufficient hydrochloric acid to make it neutral, when it is sent into the boiling pan and boiled down.

Occasionally another plan is adopted for separating the soapy and fatty matter that the lye contains. A series of four to eight tanks, either of iron, brickwork or stone, are arranged one above the other, and from the highest to the next there is an arrangement of syphon pipe so that the lye can be run from the bottom of the top one to the one below it, and a similar arrangement is adopted throughout the whole series. The running off from the bottom of the tanks permits of the collection on the surface of a fairly large proportion of tha soapy and fatty matter which the lye contains; this is neutralised and sent back to the soap pan, the lye being dealt with as described above.

One of the chief difficulties which are met with in preparing crude glycerine is the fact that on boiling down, the salt the lye contains crystallises out on the surface of the boiling tanks and on the steam coils which may be used for the purpose of heating these pans; this leads to considerable loss of heat owing to the non-conducting powers of the salt. It becomes necessary to take steps to prevent this crystallisation of the salt on to the kettle and steam coils and various means to this end are adopted.

Figure 59 is a sketch of a lye-boiling pan; in this the pan, as will be seen, is heated by fire, the arrangement of the flues being such that the heating is principally done at the sides of the pan. This pan is made conical and it is fitted with a conical vessel having perforated sides. This is attached by chains to the ground. The salt as it crystallises out falls into this perforated vessel, which from time to time is lifted out and the salt emptied into a draining vessel, the liquor which drains off from it being put back into the boiling pan. The liquor is concentrated down until it reaches a boiling point of 300° F., when it constitutes crude glycerine.

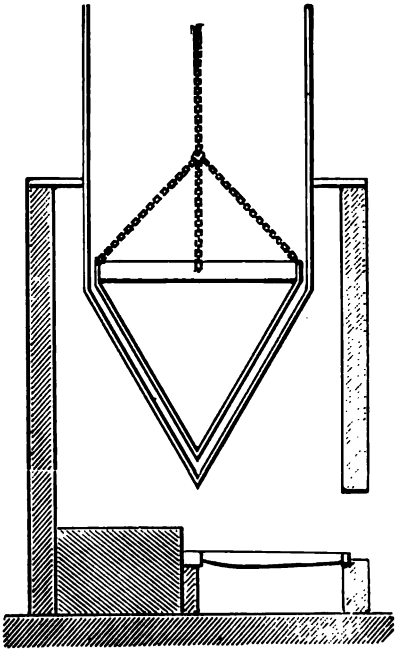
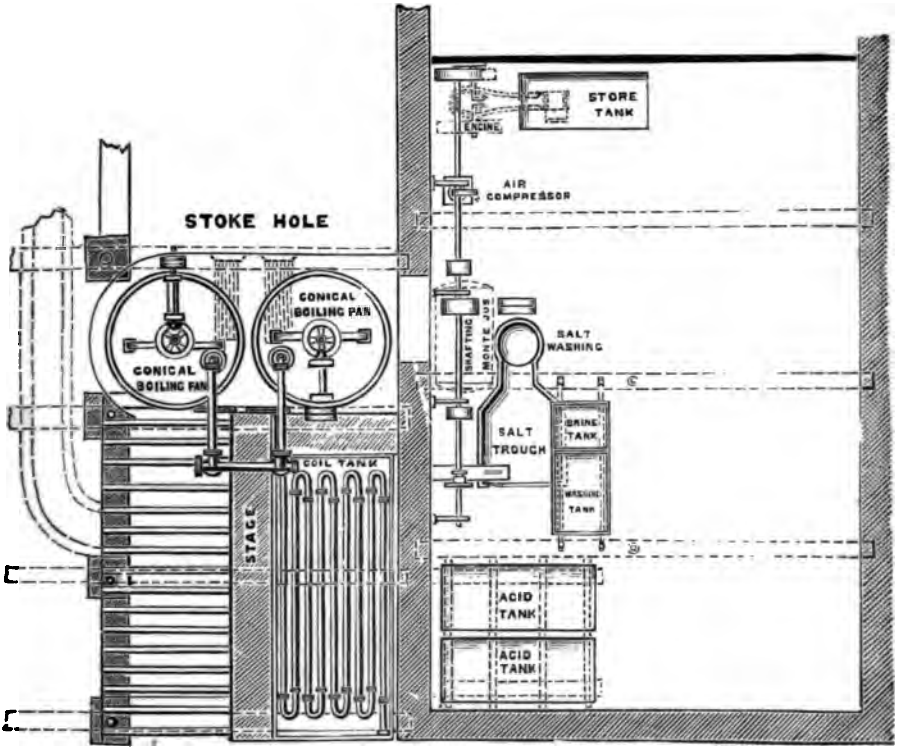


FIG. 59.—Boiling Pan for Soap Lyes.

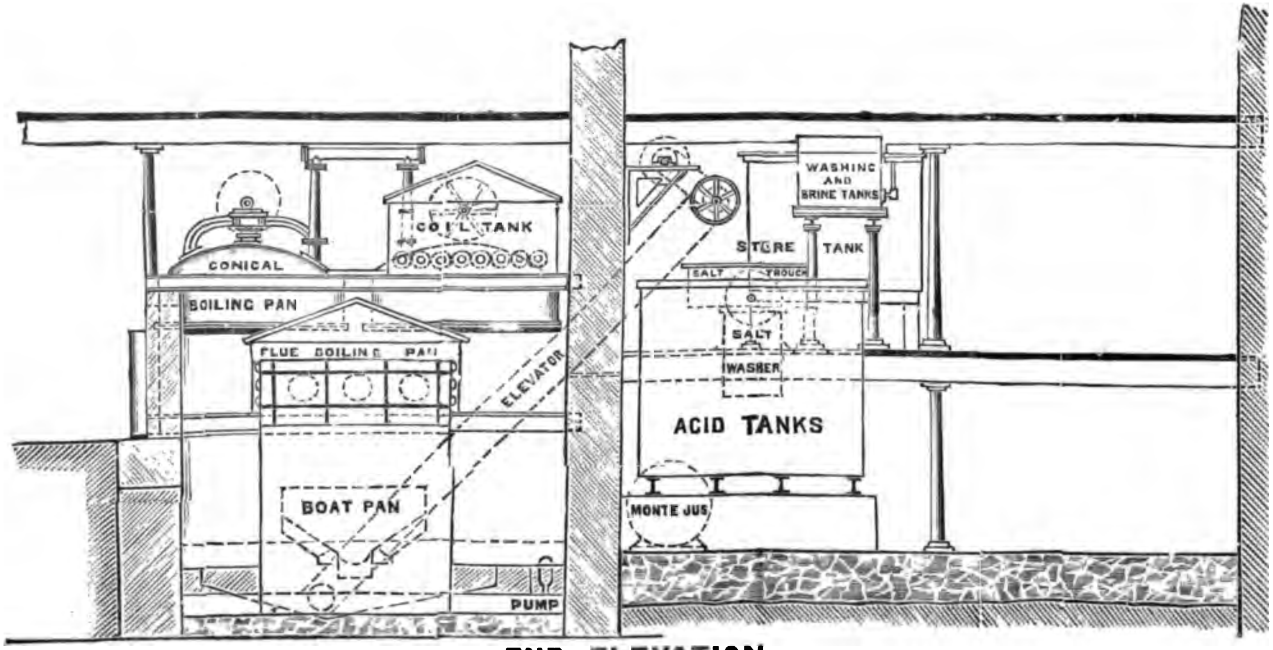
One of the most successful processes which have been devised for the separation of crude glycerine is that of Messrs. Thomas and Domeier, which is represented in figures 60 and

61. The lye is first concentrated in either a coil, tank or a flue boiling pan, from whence it is run into a tank. The concentration of the liquid during the boiling has the effect of causing the precipitation of many impurities, fatty and otherwise, which separate out on cooling in the tank. To the lye is then added 1 or 2 per cent. of hydrochloric acid, which causes the decomposition of any soap that may be present, precipitates any albuminous and fatty matter together with other impurities, and these, on the lye being allowed to stand for twenty-four hours, come up to the surface and are collected. The liquor is next placed in a boiling pan and boiled down,



— PLAN —

FIG. 60.—Glycerine Plant.



END ELEVATION

Fig. 61.—Glycerine Plant.

which may be done over a flue boiling pan, or by a conical boiling pan heated directly by a series of steam coils: the salt that crystallises out is separated from time to time. In this process, as will be seen, the steam which is generated from the boiling vessel is used for the purpose of concentrating the lye in a coil boiling pan. This process may be varied to suit the character of the lyes made at different works.

The salt contains a large proportion of the lye, and it is sent into a trough and washed with brine, which removes a good deal of the lye together with colouring matter, this brine being sent into the tanks to be passed through the process; the salt is thrown into the cage of a hydro-extractor, and then a brine lye extracted from it. The salt is then sufficiently pure to be used in salting out fresh batches of soap.

The crude glycerine obtained in the above processes is refined by a process of filtering through charcoal and distilling in a vacuum still, but for the details of this the reader is referred to chemical dictionaries.

CHAPTER IX.

LAYING OUT A SOAP FACTORY.

In the production of any article of manufacture there always comes in the consideration of producing it at the lowest possible cost. One has not only to consider the cost of the materials employed in the production of the goods, but—and there is much in this—other expenses connected therewith, works, management and labour, office expenses, rent, lighting, fuel, etc. While the cost of materials may not vary from place to place, yet there might be such a difference in the other expenses, that while one works may be making a good profit, another may only be just paying expenses. In the first case, probably, considerable attention has been paid to the arrangement of the works and the fixing of the machinery and plant; the cost of labour and fuel is low; while there is also a large output in relation to other expenses. In the other case the works is probably an old one, and extended from time to time; in such cases the cost of labour and fuel is apt to be high, while rent is high too. In one works the labour is almost entirely confined to that which is required to attend the machinery, and but little, and that the minimum, required in the handling of the raw and finished products. This is brought about by a judicious planning of the works and arrangement of the various machines, that the materials travel from one to the other steadily and regularly, without much labour attaching to the process. In another case, probably, the machines are scattered irregularly, and there is much labour involved in transferring the materials from one machine to the other; this labour costs money, and is a most important item in the cost of production.

There is another item to be considered, and that is the position of the works. In these days it is important to get the materials to the works at the lowest possible cost, and to send the finished products away with the least expense. Therefore the situation of the works in regard to the point of facilities for the delivery of its raw materials, fuel, etc., is an important question, and requires careful consideration. The best site for a works is one which will have facilities for freight afforded by rail, canal or river and road. It should be by the side of one of these means of transport; if close to the rail it is an excellent position for sending away its finished products, while possibly a canal or river presents the best means for the delivery of the raw materials. If the works is situated at some distance from either of these means, then the expense of carting to and fro becomes very great, and, unless there are other compensating advantages, will tend to reduce the profits very materially.

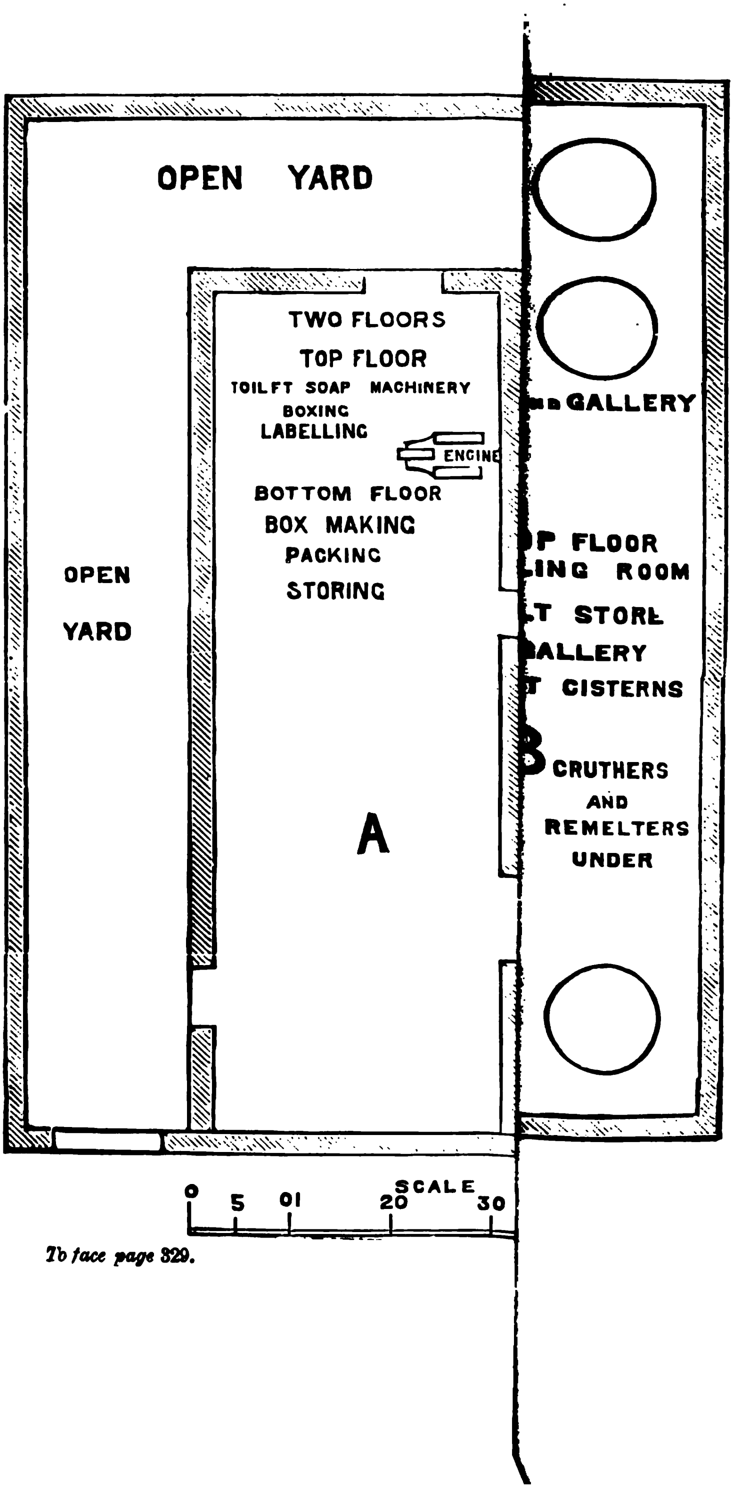
There is also another point to consider, and that is the question of water supply. The soap-maker uses a large quantity of water, hence he must have a plentiful supply of this article at, needless to say, the lowest possible cost. The water should also be of good quality, the softer and freer from lime and magnesia the better. At every soap-works there ought to be a well from which the water may be pumped; this supply may, if the works be in a large town, be supplemented from the town supply. On the question of water reference may be made to Chapter V. (pp. 170 *et seq.*).

In selecting a site for a soap-works there must also be considered proximity to the sources of supply of fuel and raw materials, which means cheap and low rates of freight to the works, and also proximity to the markets of sale of the finished article. These are questions of pro and con which can hardly be considered in a book like this, as circumstances will vary with every place. A London soap-works will have to pay more for its fuel than a Manchester soap-works, on account of its greater distance from the source of supply. On the other hand, it is able to get its raw materials rather cheaper, and it has a much larger market at hand for its products.

In planning a soap-works many points have to be considered, and a variety of factors taken into account, which influence, in a marked manner, the arrangement of the various buildings and machinery ; so much so that an arrangement which would be quite suitable and an economical one for one place, would be quite unsuitable and costly to work at another. It may be profitable to discuss some of these factors before going farther. In the first place it is advisable to consider the manner in which the fuel and raw materials, etc., reach the works, whether by canal, rail, river or road, either by one or all these ; the plans being drawn so that the least possible labour is required in putting these into position for use. Then there is the question of sending away the finished products, with a view of keeping down the labour item of putting these on boats or on rail for despatching to the various destinations.

Then comes the all-important question of the size and shape of the ground on which the works is to be erected, whether flat or sloping, rectangular or irregular in shape. A flat site is better than a sloping site, and in some respects a rectangular piece of ground is easier to plan out than an irregular piece.

Next comes the very important subject of the output or quantity of finished goods to be sent out at a given time. Combined with this is also the question of the character of the goods made, whether one kind of soap only or many kinds, and the character and extent of the processes used. Thus it



To face page 329.

has to be decided whether the soap-maker shall make his lyes from bought solid caustic, by causticising soda ash or alkali, or by making the alkali outright from salt. Upon all these depend the character and extent of the machinery to be fitted up, and therefore the size of the buildings.

There is also another point. Soap has to be wrapped in packets and packed into boxes and labelled. The question arises. will the soap-maker undertake the production of all printed matter and of the needful packing boxes? This is done in many large works with considerable advantage as to cost for these necessary items.

One principle in the arrangement of a works ought to be carried out as far as possible, that is to perform work in a progressive manner, the goods travelling from machine to machine in an orderly manner without too much handling and without travelling backwards and forwards over the same ground, or, in other words, the raw materials enter into the works at one end and pass out at the other end in the form of finished products.

Assuming that a works is to be built to turn out some 100 tons a week of various kinds of soaps, it may be fitted up on the lines shown in figure 62, which is an outline plan of the works. There are four blocks of buildings of two storeys in height. The front block (D E) in the plan is shown in sectional elevation in figure 63. This contains an entrance gateway in the centre, through which goods are received and are passed out. On the right side of the gateway is situated the time- or lodge-keeper's office (E), with weighing machine and small sundry and fittings store-room behind, over these being the chemical laboratory and chemist's office, these being most important adjuncts to a soap factory. On the left-hand side is placed the manager's office (D) with general offices over. The right-hand block (B) on figure 62 and 63 is the soap-boiling house; this block consists practically of two doors, as shown in B in figure 64; and in figure

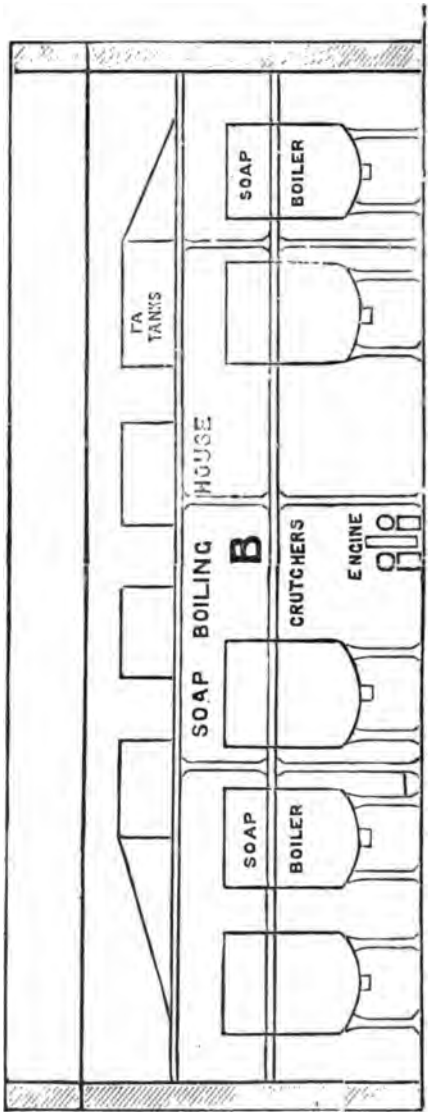
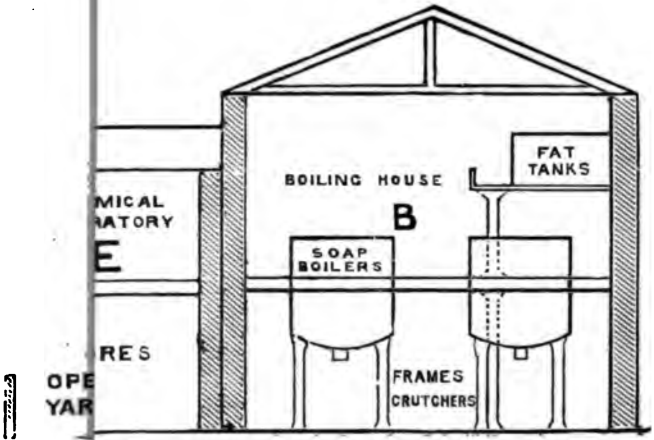


Fig. 64.—Elevation of Soap Works.

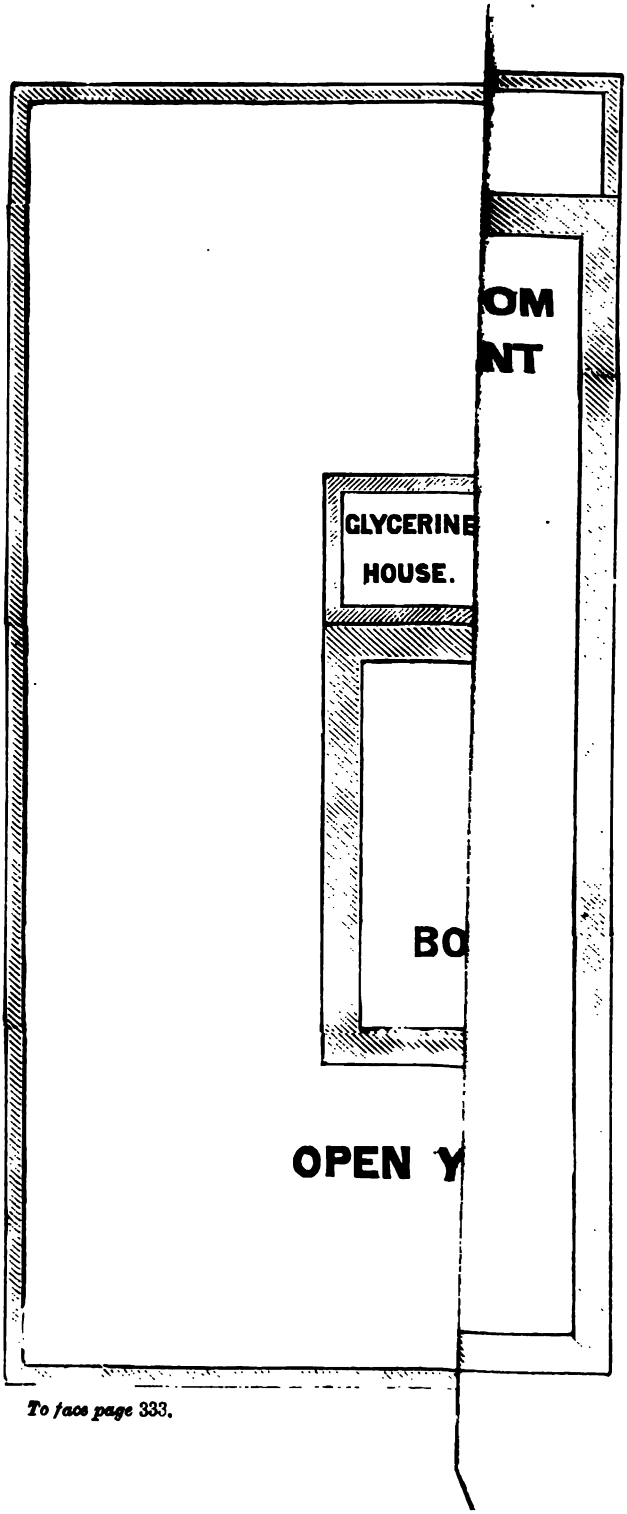
63, which is a sectional elevation of this block, eight boilers


MICAL
RATORY
E
RES
OPE
YAR
BOILING HOUSE
B
FAT TANKS
SOAP BOILERS
FRAMES
CRUTCHERS

To face

are shown which may be of any desired form, that shown in figure 29 being a good one. These are supported on pillars as shown, and may be surrounded by non-conducting composition to economise the heat as much as possible. These pans are so placed that the floor of the second storey forms a convenient working platform for them. As shown in the plan (figure 62) the pans are arranged along one side and at the ends. The other side of the building is in the lower portion, arranged as a frame room and to hold the engines and the crutchers. The frames are shown in figure 35, and the crutchers in figure 55, made by Messrs. W. Neill & Son. On the second floor the space not filled with the pans forms a very convenient store for the salt, which is kept on the floor, wooden sides about a foot high keeping it within bounds. Along one side of it runs a gallery on which are placed the tanks (figure 26) for melting and storing the fats; the barrels containing the latter being run up inclined gangways at either end of the gallery as shown in figure 64. The gallery enables the fat tanks to be so placed that the melted fats can be run into the soap pans direct. Should, however, it be considered undesirable that the fats be melted in tanks so placed, but more on a level with the soap pans, then it will be needful to either melt them in a blower such as figure 27, or to pump the melted fat from the tanks to the pans. If convenience is desired for making small lots of soap, then room may be found for a pan like that shown in figure 30, which is a small steam jacketed pan made by Messrs. Dopp & Sons, while if convenience is also needed for making soap by the cold process, then room may also be found for a few pans like that shown in figure 31. Above the soap pans should be arranged shafting to drive any agitators which may be fitted to the pans, or beaters such as shown in figure 32. Close to this is a water tower, this tower also acting as a house for the hoist and for the pump. On the top of the tower is placed a water tank, from which pipes are laid to the steam boilers, soap pans, lye tanks and wherever the water is wanted. This tank is kept filled from a well or spring by means of a pump. As there will be a great deal of condensed water formed in the steam pipes attached to the various soap pans, means ought to be taken to collect this water and send it through the pump to the tower, while it would be worth while to arrange that all the steam which passes through the closed steam coils and jackets of the pans be sent through condensers, and the condensed water so formed also sent either to the tower or, preferably, to the lye tanks, for, being pure, it is much to be preferred to well or spring water for dissolving the alkalies.

A on the plan and in figure 63 is a block of two storeys on the left-hand side of the works. In this building is carried on the making of toilet soap, boxing, labelling and printing on the top floor, while in the bottom floor is the box-making machinery, and the packing and storing are also done here. It is assumed that a works of this size will make its own boxes and do its own printing as far as possible. Surrounding this block is an open yard for the storing of timber, etc. At the back of the works between the two buildings is placed the block C. The lower floor of this is used as a frame room, and in it are also placed the slabbing machines, figures 38 and 39, the soap-cutting machines such as shown in figures 41, 42 and 43. The first is a barring machine made by Messrs. W. J. Fraser & Co., the second is a barring machine made by Messrs. Neill & Son, while the third is a combined barring and tablet-cutting machine made by a Continental firm. Stamping is also done here by such machines as are shown in figure 44. On the top floor are placed the alkali stores and the alkali tanks, figure 25. These may be placed on a gallery at the end nearest the boiling house, in which case the lye is run direct into the soap pans, or the tanks.



To face page 333.

may be placed on the floor, in which case pumps must not be used to send the lye into the soap pans. The yard contains two boiler rooms, one for the soap-boiling house, the other to work the engine for driving the box-making machinery, chimney, water-tank tower, hoists and glycerine recovery house, while there is also room for the storage of tanks if necessary.

It will be observed that the raw products are sent into the boiling house B; from thence the soap which is made passes into C to be cut up and stamped; then to A, where it is packed and warehoused ready to be sent away. The labour of handling the goods is reduced to a minimum, while it is possible to employ continuous mechanical conveyers to carry the soap from place to place.

In figure 65 is given a plan of a smaller works, consisting of two main blocks of buildings, one for the soap-boiling and the other for the finishing operations. The general description given of the larger works more or less applies to this. It has been planned, however, so that an enlargement could be carried out if required at some future time; thus, a new boiling house could be built by the side of the one shown, having the boiler house between.

The plans are not intended to be put forward as finished designs, but to indicate some of the general lines which may be worked upon in the laying out of a soap factory. Obviously they must be altered at various times to suit local circumstances, as was indicated above, while of course the character of the soaps made, and therefore of the machinery to be employed, must have some material influence upon the carrying out of the details of arrangement of the plant.

CHAPTER X.

SOAP ANALYSIS.

SOAP manufacturers often require to know the actual contents of soap that any given sample of their own or of other makers' preparation may contain. Occasionally they may desire to know more particularly the constituents of a particular sample of soap. Such information as is here alluded to, necessitates for its supply a chemical analysis—more or less fully—of the sample being made.

Soap, when pure, consists essentially of three substances, fat, alkali and water, in a state of more or less intimate union. Now as in any process of soap-making it is impossible, or nearly so, to saponify completely all the fat which is used, soap usually contains the fat in two conditions, *i.e.*, free and combined, while the alkali may be present, partly free and partly combined with the fat. In the great majority of cases it suffices to determine the above constituents to ascertain the value of a soap.

In some cases a more elaborate analysis is required, and other constituents, silicate of soda, salt and sulphate of soda and other bodies which may have been added for various reasons. Then again a soap-maker may desire to know the nature of the fats used in making the sample.

A complete analysis of soap will take cognisance of the following constituents:—

Free fat,
Combined fat,
Free alkali,
Combined alkali,
Water,
Sodium carbonate,
Sodium chloride,
Sodium sulphate,
Sodium silicate,
Borax,
Mineral fillings,
Glycerine,
Sugar,
Medicinal constituents.

Notwithstanding the great advance in the practice of analytical chemistry as applied to oils, fats and products prepared from them, still much remains to be done before the analysis of soap in every phase is brought to a state of perfection, and the analyst can boast that he has given a perfectly true report as to the exact composition of any particular sample of soap that may come under his notice.

Before commencing an analysis of any particular piece of soap it is of great importance to obtain a good sample of it, and herein we may briefly touch upon a point of difficulty that the soap analyst must guard against if he desires to obtain good results. If a bar of soap, especially one that has been made for some time, be cut across, it will be observed that there is on the outside a skin which is harder than the central portion of the bar. Now, if portions are taken from the outer and inner parts of the bar, and analysed, it will be found that different results are obtained, the outer skin containing much less water than the inner portion. Now as it is usually the custom in soap analysis to take several portions for the different constituents, it is obvious that concordant results will not be obtained unless the analyst is exceedingly careful in selecting his sample and in cutting it up. In order to avoid this difficulty many analysts have devised schemes for the analysis of a sample of soap from only one weighed portion. Some of these schemes have not been published, others have, and one or two of these will be noticed. One disadvantage of such schemes is that they take a considerable time to work through, and often time is an element. Then, again, the soap is subjected to some operations which may have some effect on the character of the other constituents; thus, for instance, supposing that as a preliminary the soap is dried, then the heat necessary for this purpose may bring about the saponification of some free fat with the free alkali present, and the soap would be returned as neutral when it may really be alkaline. Again, if the soap be treated for certain reasons with alcohol, the latter might also bring about the complete saponification of the last traces of free fat and free alkali.

On the whole, if care be taken in sampling the soap and making all weighings of the testing samples at the same time, it will be found better, and quite as good results will be obtained, to use different samples of the soap for the various estimations.

Water in Soap.—Clean thoroughly and heat for a short time over an air bath a porcelain evaporating basin, then allow to cool, and weigh it. Then scrape the sample of soap into fine shreds and weigh 10 grammes into the basin. Next place the basin of soap into a hot-air oven heated to about 110° to 120° C. for about three to four hours; take the basin out, allow to cool in a desiccator; then weigh it. Next replace it in the oven for about an hour, again allow to cool, and weigh it; repeat these operations until there is no further loss of weight. The loss of weight may be taken as water, although if in transparent soaps a little of the spirit be left in, it will also be volatilised and reckoned with the water. To take an example:—

	Grammes.
Weight of basin + soap	35·368
Weight of basin	25·368
Weight of soap taken	10·000
Weight of soap and basin (B)	35·368
Weight of soap and basin (A)	33·276
Loss of weight	2·092

2·092 × 10 = 20·92.

In this soap there is then 20·92 per cent. of water.

This, although the best method of determining the water in soap, is a slow one, taking some hours to do. It has one advantage, and that is the soap is in a suitable condition to use for further tests.

A quicker method is that described by Watson Smith.

An evaporating basin with a short length of glass rod is weighed, and into it is weighed 5 grammes of the soap to be tested. The basin and its contents are placed on a sand bath over a bunsen burner and heated, with constant stirring, until the soap begins to emit a charring or burning odour, which is readily perceptible. The heating is then stopped, and the basin and its contents allowed to cool, when they are weighed, the loss being the water in the soap.

	Grammes.
Weight of basin + glass + soap	36·979
Weight of basin + glass	31·879
Weight of soap taken	5·000
Weight of soap, etc., before heating	36·879
Weight of soap, etc., after heating	35·853
Loss of weight	1·026

1·026 × 20 = 20·52.

In this sample of soap there is 20·52 per cent of water.

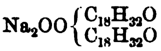
This method of working, carefully followed, gives good results.

Alkali in Soap.—The alkali in soap may be present in two forms, free and combined. A good sample of well-made soap should not contain any free alkali; but it is very difficult to make a soap which shall not contain any, and so the best of soaps have frequently small traces present. It is only when special means have been taken to prevent its being present that soap is free from this constituent. The combined alkali is that which is combined with the fat to form the soap.

The free alkali may be present in the soap as hydroxide or as carbonate: the former is the excess of the caustic alkali used in making the soap not removed in the finishing operations: the latter, when present, has usually been added as a filling material. It will be convenient if we first describe the estimation of the total alkali in the soap, then the free alkali both as hydroxide and carbonate.

Total Alkali in Soap.—Ten grammes of the soap are weighed out and dissolved in 100 to 150 c.c. of water by boiling. To the solution as much methyl orange is added as will just impart a yellow tint to the liquid; then from a burette a normal standard solution of sulphuric acid is run in (titrated) until a permanent pink coloration is obtained. The solution may be kept warm during the operation with advantage.. Note is taken of the number of c.c.'s of standard acid used.

It is customary to consider soap as a combination of soda, Na_2O, the oxide of the metal sodium with the anhydrides of the fatty acids; in this view sodium oleate would have the formula



$$Na_2OO\left\{\begin{array}{l}C_{18}H_{32}O\\C_{18}H_{32}O\end{array}\right.$$

Having this view of the composition of soap in mind, it is customary on the part of chemists to calculate the free and combined alkali in soap as soda (sodium oxide, Na_2O), and accordingly the number of c.c.'s of standard used is multiplied by 0·031, which gives the amount of soda in the 10 grammes of soap, and this multiplied by 10 gives the percentage of total alkali (Na_2O) in the soap. As an example in testing a sample of soap, the readings on the burette were as follows:—

Second reading	32·5
First reading	6·0
	26·5

26·5 × 0·031 = 0·8215.
0·8215 × 10 = 8·215.

The soap contains 8·215 per cent. of alkali (Na_2O).

In the author's opinion the customary view of the composition of soap as given above is wrong. He considers it preferable to view soap as being composed of basic radicle (which would be either the metal sodium or potassium according to the nature of the soap) with fatty acid radicle. Sodium oleate would then have the formula

$$NaC_{18}H_{33}O_2.$$

This view of the composition of soap would bring the matter in a line with the currently accepted view of the composition or constitution of salts, with which class of compounds soap may be grouped. In consonance with this view the alkali in soap should be calculated to sodium Na by using the factor 0·023 to multiply the number of c.c.'s of standard acid with a fatty acid radicle. Thus in the example given above we should have

$$26{\cdot}5 + 0.023 = 0{\cdot}6095.$$
$$0{\cdot}6095 + 10 = 6{\cdot}095.$$

There is 6·095 per cent. of total alkali (Na) in this sample of soap.

In the case of testing soft soaps, the method adopted is the same. The factors to be used in calculating are 0·047 for potash (K_2O) or 0·039 for potassium.

In this chapter, in all analyses of soap the alkali will be given as sodium (Na) in the case of hard soaps, or as potassium (K) in the case of soft soaps.

Free Alkali in Soap.—To ascertain the amount of free alkali in soap is rather a troublesome matter. The simplest plan is to weigh out 10 grammes of the soap, dissolve in 150 c.c. of water by boiling, add a few drops of an alcoholic solution of phenol-phthalein, which will produce a red coloration if free alkali be present, then titrate with normal standard sulphuric acid until the red coloration disappears. The alkali is calculated to NaOH by the factor 0·04 in the case of hard soaps; to caustic potash (KOH) by the factor 0·056 in the case of soft soaps. A good make of hard soap will not take more than 0·75 to 1 c.c. of the standard acid to neutralise any free alkali it may contain.

There are some objections, perhaps, to this method of working; in the first place it fails if the soap contains a considerable amount of carbonate of soda or potash, as these bodies are slightly alkaline to phenol-phthalein; if they are present then another process must be adopted. Then, again, it is stated by many chemists that on dissolving soap in water a certain amount of decomposition occurs by hydrolysis and an acid soap is formed together with a little free sodium hydroxide. If this action does really occur, then for the purpose of detecting free alkali in the soap, a solution in water is not available. The author, as the result of numerous analyses of soap, does not view this decomposition theory of soap solution with favour, and is very much inclined to the opinion that it does not occur. Soaps have passed through his hands which did not, with the processes above described, take more than 0·25 to 0·5 c.c. of acid to neutralise any free alkali they contained, and the decomposition theory of soap, if it is worth anything, calls for the production of more free alkali than is represented by the quantities of acid which have been named.

Another method of determining the free alkali in soap is to weigh out 10 grammes of the soap and dissolve with the aid of a water bath in about 200 c.c. of neutral alcohol. It is best to use absolute alcohol, but as this is expensive the ordinary methylated spirit may be used if it is subjected to a purifying process, the simplest method of conducting which consists in placing in the spirit some caustic soda, allowing to stand over a night, then redistilling about 90 to 95 per cent., the residue which remains in the still or retort being thrown away. Before use the alcohol or spirit should be neutralised by adding a little phenol-phthalein and sufficient caustic soda to produce a faint pink tint.

When the soap has been dissolved in the alcohol or the latter has dissolved as much as it will, the solution should be filtered through a dry filter, taking care to expose the solution to the air as little as possible. The solution should be made in a flask, and the filtering should be done through a funnel into a flask, the funnel being kept covered by a glass plate. When the liquid has gone through the filter, the residue may be washed with a small quantity of neutral alcohol, the washing being added to the main body of the filtrate.

To the alcoholic solution is now added phenol-phthalein as an indicator, when, if there be any free alkali, a red colour will be obtained. The solution is now titrated with the standard acid as before, until the red colour is destroyed. The amount of free alkali is calculated as before.

The alcohol only dissolves the soap and any alkali which may be present as hydroxide (caustic alkali); any in the form of carbonate, borate or silicate is undissolved and remains as an insoluble residue on the filter. To this reference will again be made.

The alcohol method, like the water method, of dissolving the soap is open to objections. One feature is the great liability that the mere act of dissolving the soap in such a menstruum will bring about saponification between any free fat and free alkali which may be present in the soap, thus leading to too low a quantity of the latter constituent being found. It is, however, in the case of carbonated soaps the only method which can be employed. In either the water or alcohol solution the combined alkali may be determined if after titrating with the standard acid and phenolphthalein of the free alkali methyl orange be added, and the titration be continued until the characteristic pink coloration be obtained. Thus, in an analysis of a sample of "pale soap" made by the author, employing a water solution and taking 10 grammes of soap, the following results were obtained:—

Free alkali, using phenol-phthalein as indicator.

Standard acid burette readings :—

Second reading	**1·5**
First reading	**0·0**
	1·5

1·5 × 0·04 = 0·06.
0·06 × 10 = 0·6 per cent. of NaOH.

Then added methyl orange and further titrated.

Second reading	**26·7**
First reading	**1·5**
	25·2

25·2 × 0·031 = 0·7812.
0·7812 × 10 = 7·81 per cent. of combined soda (Na_2O).

Or,

25·2 × 0·023 = 0·5796.
0·5796 × 10 = 5·79 per cent. of combined sodium (Na).

Alkali as Carbonate, Silicate, etc.—It is very difficult to give any general scheme which shall meet every case that may occur in the examination of soap for alkali present in the forms of carbonate, silicate, borate, sulphate, chloride, etc.; the soap analyst must be prepared, in dealing with soaps which contain any of the constituents mentioned, to devise a special scheme of his own, based on the results of a qualitative test which he may have applied to the soap. What is stated in the following remarks should be looked upon more in the nature of hints than as a cut-and-dried scheme applicable to any and every kind of soap. 10, or, if the proportions of the substances in question are small, 20, grammes of the soap are dissolved in methylated spirit, and the solution filtered from anything insoluble, the filter which is used having been previously dried and weighed. The insoluble portion which remains on the filter is washed with fresh spirit, when it is dried and weighed, the weight thus obtained giving the amount of matters insoluble in alcohol in the soap.

Boiling water is now poured over the filter, the contents of which are treated until they are thoroughly exhausted of all soluble matters. The filter is next dried and weighed, when the amount of any insoluble matter will be obtained. This portion may consist of added sand, silica, French chalk and similar substances, with, may be, some added organic matter not dissolved by water. After weighing it, the filter paper and its contents may be placed in a weighed porcelain crucible, burnt over a bunsen burner, then allowed to cool, and weighed. This last weighing will give the amount of insoluble mineral matter in the soap, and is then ready for further examination if need be.

The aqueous solution which has passed through the filter is now made up to a known volume and divided into two portions, A and B. To A is added a little methyl orange, and it is titrated with normal hydrochloric acid until the characteristic pink colour is obtained. This titration will give the amount of alkali present as carbonate, borate and silicate. The presence of carbonate will be indicated by effervescence occurring; the other two substances do not effervesce with acids. The solution which has been used in the titration is now heated to the boil, a little hydrochloric acid added, and then a little barium chloride; if any sulphate be present a white precipitate of barium sulphate will be obtained. This is filtered off, well washed with hot water, dried, burnt in a porcelain crucible over a bunsen burner and weighed. The weight of barium sulphate thus obtained multiplied by 0·609 gives the weight of sodium sulphate, Na_2SO_4, present. Thus the following figures were obtained in an analysis of soap for sulphate, 10 grammes of soap being used:—

Weight of crucible + ash + $BaSO_4$	6·6645
Weight of crucible	6·5680
	·0965
Weight of ash + $BaSO_4$	·0047
Weight of ash	·0918

0·0918 × 0·609 = 0·056.

0·056 × 10 = 0·56 per cent. of sodium sulphate in the soap.

The second portion, B, of the filtrate is divided into two equal portions. One portion is acidified with hydrochloric acid evaporated to dryness, the residue treated with a little weak hydrochloric acid, filtered from the silica which is rendered insoluble by this treatment. The silica is washed, dried, burnt in a crucible and weighed.

The presence of borax may be detected by placing a piece of turmeric paper in the solution as it is boiled down for the silicate; if borax be present the paper will turn a red-brown colour. To determine the amount of borax present is a most difficult matter, and no really satisfactory process can be described.

If any silicate or borate be present as well as carbonate, the latter is estimated by taking the other portion of the aqueous solution, and determining the amount of carbonic acid in this in special apparatus, such as is made for the purpose. Forty-four parts of carbonic acid, CO_2, correspond to 106 parts of sodium carbonate, Na_2CO_3; or to 62 parts of sodium oxide, Na_2O; or to 94 parts of potassium oxide, K_2O. These proportions may be employed in making the necessary calculations.

Generally speaking, soda is the only form of alkali which will be met with in hard soaps, and potash the only form found in soft soaps; rarely are both alkalies present in a soap at one time. Should it be needful to ascertain if both be present, the following course of procedure must be adopted: A sample of soap is neutralised by hydrochloric acid, the fatty matter separated and the solution boiled down to a small bulk; a piece of platinum wire is dipped into the solution and held in the lower portion of a bunsen flame, which then becomes coloured with a yellow light if sodium be present, with a pale lilac-tinted light if potassium be present. The observer is advised to try this experiment with pure sodium and potassium salts, to gain more experience of the results likely to be obtained.

The presence of sodium is readily demonstrated by the flame test, and if present it will obscure the characteristic flame test for potassium. The presence of the latter may be detected by adding to the aqueous solution obtained as just described a little platinum chloride and methylated spirit, when, if it be present, a yellow precipitate of the double potassium-platinum chloride will be obtained. Sodium does not give such a precipitate. If it be desired to ascertain the amount of both alkalies, then the total alkali present is determined in the usual manner with the seminormal hydrochloric acid, after which the potassium is precipitated out as the double chloride of platinum and potassium, the amount of which is ascertained by weighing on a weighed dry filter paper, and from the data thus obtained the amount of both potash and soda may be calculated. For details of this and other quantitative methods which are described in this chapter, the reader is referred to standard books on quantitative chemical analysis, such, for instance, as those of Mills and North, Sexton, Thorpe and others.

Fatty Matter.—The fatty matter of soap is present in two forms, free and combined; the former should, in the best grades of soap, be present only in trifling amount. In some so-called superfatted soaps, an excess of free fat, usually present in the form of wool fat or lanolin, is purposely added.

Free Fat.—To ascertain the amount of free fat in the soap, the dried 10 grammes of soap left after the determination of the moisture (*vide supra*) are wrapped in a piece of filter paper and placed in a Soxhlett fat-extraction apparatus and extracted with petroleum ether. The operation may be allowed to take one and a half hours; the ethereal liquid is run into a weighed glass, the ether evaporated off in an air bath and the residual free fat weighed. The fat so obtained will consist of the portion of fat which has resisted the saponifying process, any small proportion of unsaponifiable matter which may have been present in the fat or oils used to make the soap, any fatty material added to "superfat" the soap, and any fatty matters, such as mineral soap stock, which may have been added as a filling to the soap.

The total fat which is present in the soap is determined in the 10 grammes which have been used for the titration of free and combined alkali (*vide supra*). After the titration for the alkali a slight excess of acid is added, and the mass is heated over a bunsen burner until the fat separates out on the top of the aqueous liquor in a clear transparent layer of oil. Two plans may be followed for collecting and weighing this fat. The method commonly recommended is, with all those soaps which will give a solid fat, to allow the fat to cool and set into a solid cake; the aqueous liquid is now run off and clean water added. The mass is now heated until the fat is once more melted, when it is again allowed to cool; the cake of fat is separated from the wash water, dried between sheets of filter paper and weighed.

When the soap is of such a character as to yield fat that will not separate out as a solid cake, but remains more or less liquid or paste, 10 grammes of white wax or of paraffin wax are added to the fat, melted up along with it, and finally weighed with it. From the final weight that of the wax is deducted, leaving the weight of fat present in the soap.

There are some objections to this method of working, which requires care in execution if good and reliable results are to be obtained. It is difficult to remove entirely the whole of the fat from the sides of the glass beaker which is used in carrying out the operation; this tends to reduce the amount of fat found. Then it is difficult to free the cake of fat from all traces of moisture, and hence there is a liability from this cause to increase the apparent weight of fat. The two sources of error thus indicated, acting in opposite directions, may tend to neutralise one another. Another objection to the method is the time it takes.

The author recommends the following process, which, in his hands, gives good results: After titrating with standard acid for the alkali, and melting the fat as described above, a small quantity of petroleum ether is added and the mixture poured into a separating funnel; more warm, but not hot, water is added, with, if needful, more petroleum ether. The contents of the funnel are now well shaken and then allowed to stand to settle, when two layers will form, the upper one of ether with the fat, the lower of acidulated water. The latter is now nearly, but not quite, run off, and fresh warm water added to wash the fat, this being repeated if required. The ether layer is now run into a weighed glass beaker, the ether evaporated off, and the residual fatty matter weighed.

By any of the processes above described there is obtained the total weight of fat in the soap. This fat will contain the free fat, as well as that present in combination with the alkali as soap; the amount of the latter can be ascertained by deducting the amount of free fat which has previously been ascertained. The combined fat consists essentially of fatty and rosin acids. We do not obtain them in the form in which they are present in the soap, where they are combined with sodium Na as acid radicles, which may be represented by R in the compounds of which NaR is the typical formula, but as fatty acids of the type HR. It therefore follows that the weight of fatty acids found is slightly —1 in 282—in excess of the truth, and that a well-made analysis of soap, taking the water and fatty matter as found, the free alkali as NaOH, the combined alkali as Na, will come out slightly in excess of 100; this excess will range from 0·1 to 0·3, according to the quantity and character of the fatty matter present.

If the soap contains much coconut oil, the results obtained in determining the amount of fatty matter by either of the methods given will be too low, owing to the oil containing fatty acids which are soluble in water, and these pass into the wash waters, and so are not collected and weighed.

Mr. J. A. Wilson recommends the following process: 10 grammes of the soap are dissolved in water and decomposed by a slight excess of dilute sulphuric acid; the glass or flask containing the soap mass is then heated until the fatty matter collects in a clear layer on the surface of the aqueous liquid. The vessel and its contents are now cooled and the cake of fatty acids separated out, while the aqueous layer is filtered through a wet filter paper. The cake of fatty acid is washed three times with 250 cubic centimetres of boiling water, cooling and filtering each time. The various filtrates are collected; methyl orange is added as an indicator, and the liquor titrated with decinormal caustic soda until the pink colour changes to yellow. By this means the excess of mineral acid used in decomposing the soap is got rid of. To the liquid is added phenol-phthalein, and the titration continued until the characteristic pink colour is got; the amount of standard soda solution used corresponds to the amount of soluble fat acids present, and these are calculated to caprylic acid, $HC_8H_{15}O_2$, by multiplying by the factor 0·0144. The cake of fatty acids may be dried and weighed, thus giving the amount of insoluble fatty acids.

It may be mentioned here, that by collecting the fatty acids, dissolving them in neutral methylated spirit, using phenol-phthalein as an indicator, and titrating with standard caustic soda, there is obtained the amount of alkali required to combine with the fatty acids to form soap; if in previous tests more has been found then such excess must be present in other forms.

In case the soap analyst adheres to the method of calculating the alkali as sodium oxide, Na_2O, then he must reckon the fatty acids as anhydrides; the quality of these he may calculate from the amount of fatty acids found by multiplying the factor 0·97, which while not accurate for every case is sufficiently so for all the common grades of soap.

Sodium Chloride in Soap.—The amount of sodium chloride present in a sample of soap may be determined in the aqueous liquor which is obtained in the titration for alkali with standard sulphuric acid. This may be done either volumetrically or gravimetrically. In the volumetric process the liquid is neutralised with caustic soda, which is free from chloride, then a few drops of a solution of pure potassium chromate are added, and the liquid titrated with a normal solution of silver nitrate until a permanent orange or reddish colour is obtained. The number of c.c.'s of silver solution used, multiplied by 0·0585, gives the amount of sodium chloride present in the soap.

If it be desired to determine the chloride gravimetrically, then the aqueous solution is heated to the boil, and sufficient of a solution of silver nitrate added to precipitate all the chloride as silver chloride: the precipitate is collected on a filter, well washed, dried, burnt in a porcelain crucible, and weighed. The weight of silver chloride so found, multiplied by 0·407, gives the weight of sodium chloride in the soap.

Glycerine.—This constituent may be looked for in some makes of toilet soaps, in all soaps made by the cold and pressure processes, and in soft soap. Generally its amount is taken by difference, that is all the other constituents of the soap are determined, and any difference required to make up the full amount is taken as glycerine. No satisfactory method for its determination in soap has been devised; the method based on its conversion in oxalic acid by means of an alkaline solution of potassium permanganate is perhaps the best. This test will be referred to again later on.

To detect the presence of glycerine in soap the following tests may be applied: Decompose the soap with acid and separate out the fatty matter, evaporate the aqueous liquor down to a small bulk, mix it with some borax, dip a piece of platinum wire in the mixture, then hold it in the flame of a bunsen burner; if glycerine be present the flame will become tinged with a deep green colour. By heating concentrated solution of glycerine with bisulphate of potash, acrolein, distinguished by its powerful and characteristic odour, is obtained. Another test is to boil the aqueous solution down, render it faintly alkaline with caustic soda, and add it to a dilute solution of borax which has been coloured a faint rose-red by adding phenol-phthalein. The glycerine solution is added until the red colour disappears. On boiling the liquid the colour comes back, but it again disappears on allowing the liquid to cool down. It should be stated that this test is not specially characteristic of glycerine, as some other alcoholic bodies and some kinds of sugar give the same reactions; but as such bodies are not usually present in soap they may be disregarded.

Sugar is present only in transparent soaps, but in these often to a large amount. Its presence may be detected by the Fehling test as follows: The aqueous solution of the soap, after the fat has been separated, is boiled for half an hour with a few drops of sulphuric acid; the solution is then neutralised with caustic soda, some Fehling test solution is added, and the mixture boiled, when the presence of sugar is indicated by the formation of a red precipitate of cupreous oxide. If it be desired to determine the amount of sugar present, the aqueous solution is boiled with the acid, as described above, a slight excess of caustic soda added, and the solution heated to the boil; Fehling test solution is added as long as a precipitate falls down, or until the liquor acquires a blue colour, the liquid being maintained at the boil; the precipitate is next filtered off, well washed with water, dried, burnt in a weighed porcelain crucible, and weighed. The weight of copper oxide thus found, multiplied by 0·40875, gives the weight of cane sugar in the soap.

Starch in soap may be detected by means of the iodine test, which produces a deep blue to blue-black colour. The soap solution must be neutralised before applying the test. If the amount is to be determined the process is identical with that for estimating the sugar, the copper oxide obtained being multiplied by 0·40816 to obtain the equivalent weight of starch. It is obvious that if both starch and sugar be present, both will be found by the Fehling test, and they must be differentiated by other tests; but it is extremely unlikely that both will be present at the same time in a sample of soap.

When both sugar and glycerine are present in a soap, the best method of working consists in evaporating the aqueous solution down, then treating the residue with a mixture of one volume of chloroform with two volumes of alcohol, which dissolves out the glycerine; the solution is evaporated in the water bath and the residual glycerine weighed. The sugar may be estimated in the residue left by the alcohol and chloroform; it is dissolved in water and the sugar determined by the Fehling test in the manner described above.

Dr. Albert R. Leeds' scheme for the analysis of a sample of soap with only one weighing, first published in *The Chemical News*, is given below, modified slightly by the present writer.

DR. ALBERT R. LEEDS' SCHEME OF SOAP ANALYSIS.

Weigh out 5 grammes of the soap and dry at 100° C.

The loss of weight corresponds to the water.

Treat the dried soap in a Soxhlett apparatus with petroleum ether.

Ethereal extract contains the free fat; evaporate off the ether and weigh the residual fat.

Residue contains the soap and mineral matter; treat it with alcohol.

Alcoholic solution contains the soap and free caustic alkali. Add a few drops of phenol-phthalein and titrate with normal sulphuric acid. The amount used corresponds to the free alkali, which is calculated to NaOH (factor 0·04). Add water and boil off the alcohol, add a little methyl orange and titrate with normal sulphuric acid. Acid used corresponds to combined alkali, calculated as either Na_2O or Na (factors 0·031 or 0·023). Add slight excess of acid, boil and separate out the fat.

Solution contains glycerine. Evaporate to dryness after neutralising with sodium carbonate; extract with alcohol, filter, place the filtrate in a weighed basin and, after evaporating off the alcohol, weigh the residual glycerine.

Residue is the fatty matter. Dry and weigh it. Take half of it and dissolve in alcohol, add phenol-phthalein and titrate with normal alcoholic soda. From the amount used the molecular weight of the fatty acids may be calculated. Add ether and dry powdered silver nitrate (Gladding test, see farther on); shake well and allow to settle.

Precipitate consists of the oleate, stearate and palmitate of silver with excess of nitrate of silver. It may be neglected.

Solution contains resinate of silver. Filter from the precipitate, wash the latter with a little ether, transfer the filtrate to a separating funnel, add water, sufficient dilute sulphuric acid to decompose the resinate and some petroleum ether if necessary. Separate the ether layer and run it into a weighed glass, evaporate off the ether and weigh the residual rosin.

Residue from the alcohol contains Na_2CO_3, NaCl, Na_2 $SO_4Na_2SiO_3$ (or corresponding potassium salts), starch and any mineral matters. Treat it with a little water and filter through a weighed filter.

Solution.—Divide into four equal portions, *a*, *b*, *c* and *d*, and test each as follows:—

a. For Na_2CO_3, or K_2CO_3, titrate with normal H_2SO_4 with methyl orange, calculating the result to Na_2CO_3, or K_2CO_3.

b. For NaCl or KCl titrate with standard $AgNO_3$ or weigh as AgCl, calculating to NaCl or KCl.

c. For Na_2SO_4, weigh as $BaSO_4$, calculating to Na_2 SO_4 or K_2SO_4.

d. Na_2SiO_3 or K_2SiO_3. Decompose with HCl and weigh the residual silica (see above, p. 344).

Residue contains starch and added mineral matter. Dry the filter and weigh. This gives the amount of starch and mineral matter. Determine the amount of starch by Fehling test. The mineral matter may be determined by difference.

Some difficulty is often experienced in the process of digesting the soap with alcohol if an ordinary beaker be employed. To overcome this Spaeth proposes extraction in a Soxhlett extractor with alcohol, the soap being contained in a narrow glass vessel similar to a weighing bottle, but with perforations at the bottom and in the lid. The holes at the bottom are covered with ignated asbestos fibre, over which a layer of filter paper and finally a glass disc with fine perforations are placed. The bottle thus prepared is dried at 105° C. for an hour and weighed. The loss in weight gives the amount of water in the soap.

The bottle without the lid is then placed in the Soxhlett extractor and its contents extracted with neutral alcohol for about six hours. After complete extraction the bottle and its contents are dried at 150° C. and weighed, the result giving the amount of "filling material" in the soap. The determination of mineral substances, dextrin, gelatin, etc., in this is carried out in accordance with the usual methods.

Since the extraction is made with neutral alcohol, the amount of free fatty acids or alkalies in the alcohol extract can be directly titrated with standard alkali or acid.

REICHERT TEST FOR COCONUT OIL.

Coconut and palmnut oils are now such important ingredients in soaps that it is desirable to be able to ascertain when they are present. These oils very closely resemble one another and it is difficult, if, indeed, not practically impossible, to distinguish between them by chemical tests, especially in the presence of other oils and fats. These oils when present in a soap tend to make it whiter in appearance and increase the proportion of alkali present; the fatty acids have a distinctly lower combining weight, while their odour is peculiar and characteristic. There is one feature which serves to distinguish these two oils from all other kinds of soap stock, and that is, they contain acids such as capric and caproic acids which are soluble in water and which, when distilled with water or steam, are volatile. This property may be taken advantage of for the purpose of ascertaining if any are present and approximately how much, the test being known as the Reichert test, from the name of the chemist who first described it. Since then others have described modifications of it. The property of solubility of the lower acids of these oils in water causes the fatty matter of soaps containing them to be lower than it actually is when examined by the ordinary methods of analysis. The Reichert test as applied to soap is carried out in the following manner: Five grammes of the soap are boiled with a little alcoholic potash or soda solution in an evaporating basin to ensure the complete saponification of the fatty matter contained in the soap, the alcohol being completely driven off. The residual soap is dissolved in water and transferred to a retort, sufficient dilute sulphuric acid is added to decompose the soap, with some small pieces of pumice stone or tobacco pipe to prevent bumping. The contents are now heated and two-thirds of the amount distilled over; the distillate is collected, filtered through a dry filter paper, and the clear liquid is titrated with decinormal soda, phenol phthalein being added as an indicator. Note is taken of the number of cubic centimetres of alkali used to neutralise the acids which have volatised over. Five grammes of coconut oil require usually from 7 to 8 c.c., palmnut oil from 4·8 to 6 c.c. The test, it may be pointed out, is a purely arbitrary one, and requires always to be carried out in the same manner to enable comparative results to be obtained. The analyst is advised to make his own standards by first working on the pure oils and then with the soap to be tested. It is owing to its arbitrary character that this test has been subjected to various modifications at the hand of different observers, but it is at least questionable whether the alterations are an improvement on the original method. The process does not yield the whole of the volatile or soluble acids present in the soap or oil. There is another method of obtaining the quantity of soluble fatty acids present. Take 5 grammes of the soap, dissolve in water, neutralise exactly with seminormal acid, pour the liberated acids on a filter, collect the filtrate, wash the acids with water, the washings being added to the filtrate and titrate with decinormal alkali with phenol phthalein as an indicator. The number of cubic centimetres used may be taken as an indication of the Reichert value. So far, no process which is quite satisfactory has been devised for the determination of the volatile acids of coconut and palmnut oils.

Testing for Ground Nut Oil.—The oil expressed from the kernels of the monkey nut, which is placed on the market under the names of ground nut oil, or arachis oil, is often used in soap-making. This oil is characterised by containing arachidic acid, one of the stearic series of fatty acids having the formula $HC_{20}H_{39}O_2$. The isolation of this acid is a certain indication of the presence of ground nut oil. This may be effected by Renard's process, as follows: 10 grammes of the soap are dissolved in water, hydrochloric acid added to decompose the soap; the fatty acids which are separated out, are collected, washed well and dissolved in alcohol. A solution of lead acetate is added, when insoluble lead soaps are precipitated out; these are filtered off, then digested with ether, which dissolves out the lead oleate, etc., but leaves the lead palmitate and arachidate insoluble. Repeat the treatment with the ether, to ensure complete extraction of the soluble salts. Collect the lead palmitate and arachidate, decompose them by means of dilute hydrochloric acid by boiling, then allow the separated fatty acids to cool, and dissolve in 50 c.c. of warm 90 per cent. alcohol. This solution is allowed to cool, when, if any arachis oil is present, a crop of crystals of arachidic acid will be obtained; these are collected on a dry, weighed filter, washed with alcohol, dried and weighed. As ground nut oil contains, on the average, 5 per cent. of arachidic acid, by multiplying by twenty the weight of the crystals obtained, the amount of ground nut oil can be approximately ascertained. It may be added that arachidic acid has a melting point of 71° to 72° C., and the purity of the crystals got may be tested by determining their melting points. With care, very good results can be obtained.

Castor Oil.—The presence of castor oil in the fatty matter of a soap may be detected by the high specific gravity (0·9509 at 60° F.) of the fatty acids, and more particularly by their being insoluble in petroleum ether, although, if only a small quantity of castor oil is present, the other fatty matter may tend to bring about solubility.

The acetyl test can also be used. It is, however, difficult to determine accurately the proportion of castor oil which may be present.

Mineral Matters in Soaps.—The mineral additions to soap take two forms, soluble salts, like borax, soda crystals, sodium sulphate, silicate of soda; and insoluble bodies, like sand, fuller's earth, china clay, etc. The detection and determination of these constituents is not easy, and no general scheme can be laid down.

Soda Crystals.—Soda crystals are sometimes added to soap for the purpose of hardening it, or in the process of manufacture of dry soap and soap powders. In the ordinary method of testing soap it would be estimated along with the combined alkali of the soap—10 grammes, in the case of ordinary soaps, 2 to 3 grammes, in the case of dry soaps—and the soap extracted by means of alcohol and filtering from the undissolved sodium carbonate. The residue is washed with alcohol, then dissolved in water and titrated with normal standard acid, 1 c.c. of which corresponds to 0·053 grammes of anhydrous sodium carbonate, $Na_2 CO_3$. Sodium carbonate, when present, is distinguished by its effervescing with acids, and giving the characteristic yellow sodium flame. Sodium sulphate or Glauber's salt is sometimes added to soap and dry soap, for the purpose of hardening or cheapening the cost of production. Like soda crystals, it is left insoluble on digesting the soap with alcohol, but is distinguished from them by not effervescing with acids, and giving with barium chloride a white precipitate of barium sulphate. When present in soap, the amount may be ascertained by taking a known weight of the soap, digesting with alcohol, dissolving the residue in water, acidifying with hydrochloric acid, adding barium chloride, collecting the precipitate of barium sulphate $BaSO_4$, on a filter, washing well with water, drying, burning the filter, etc.; from the weight of barium sulphate obtained Na_2SO_4 can be calculated by multiplying by 0·609, or that of Glauber's salt, $Na_2SO_4 \, 10H_2O$, by multiplying by 1·382. In the case of both sodium carbonate and sulphate the analyst will have to exercise his own judgment as to whether he reports the anhydrous or the crystal form of these two compounds as being present.

Borax.—The presence of borax in soap is by no means easy to detect, while the determination of the quantity present is rather difficult. It is left insoluble on treating soap with alcohol, and, as it affects methyl orange in the same way as carbonate, it is estimated along with the latter salt with the standard acid. To detect its presence and determine its amount, the following procedure should be adopted: Digest the soap with alcohol, collect the undissolved salts on a filter, washing them with a little alcohol; then dissolve them in water and divide the solution into three parts. Titrate one with standard hydrochloric acid, using methyl orange as an indicator; take a second portion of the solution, acidify with hydrochloric acid and evaporate nearly to dryness, then dip a piece of turmeric paper in the hot solution; if borax be present it will turn a reddish brown. As a further proof evaporate to complete dryness, add a little methylated spirit and set fire to the spirit; if borax be present the edges of the flame will be tinged green. If borax be found present, to estimate its amount take the third portion of the solution and determine the carbonic acid it contains by the apparatus which is supplied by chemical apparatus dealers for that purpose. The amount of carbonic acid, CO_2, found should be calculated to sodium carbonate, Na_2CO_3. The amount of standard acid necessary to neutralise that calculated and this deducted from that used in the actual titration with the first portion of the aqueous solution represents the amount of borax present. One c.c. of standard acid equals 0·221 grammes of borax $Na_4B_2O_7 10H_2O$. Of course, great care is needed in carrying out the various operations to ensure accuracy of results.

Silicate of Soda.—The presence of silicate of soda increases the alkalinity of a soap and affects the titration with the standard acid, the latter showing more combined alkali than is actually present as soap. The presence of silicate of soda or potash is shown by testing for silica in the following manner. The insoluble residue left on treating the soap with alcohol is dissolved in water and acidified with hydrochloric acid; the liquid is next evaporated to dryness and heated strongly for some time; by this means the silica is rendered insoluble. The residue is digested with water and a little hydrochloric acid, when, if silica and, therefore, silicate of soda or potash be present, it will be left behind as an insoluble gritty mass. By taking a known quantity of the soap and weighing it, the silicate of soda in the soap can be approximately ascertained. It may be pointed out here that soda crystals (sodium carbonate), sodium sulphate, borax and silicate of soda are all insoluble in alcohol; hence they are left as insoluble on digesting the soap with that solvent, and may possibly be all present; in which event the following mode of working may be adopted. Dissolve the residue left by the alcohol in water and divide this solution into three portions, A, B and C. Take A, add methyl orange and titrate with normal hydrochloric acid to ascertain the total alkali, which will be the sum of carbonate, borax and silicate present; afterwards use the same portion for determining the sulphate with barium chloride as described above. In B determine the carbonic acid. Take C, neutralise with hydrochloric acid, boil down to dryness, and while doing so test for borax by means of turmeric paper, digest the dry residue with water and a little hydrochloric acid, filter off, wash, dry and weigh the silica.

Sand and Mineral Matters.—Some soaps contain such bodies as sand, ground pumice, kieselguhr, French chalk, ultramarine, oxide of iron and other mineral colouring matters. It is not possible to give here a scheme for the complete analysis of such bodies; their isolation from the soap is best effected by first digesting the soap with alcohol, separating out all insoluble matter and treating this with cold water. Anything left insoluble on such treatment must be bodies such as those above named, with starchy matters. Their examination must be conducted according to the ordinary rules of chemical analysis, plus a microscopical examination to detect kieselguhr. As all the substances named above are such as are not altered by heat, their amount may be ascertained by burning a known weight of the soap in a crucible, digesting the residue with hot water, filtering off any insoluble matter, drying, burning this in a weighed crucible and weighing.

Carbolic Acid in Soap.—Sometimes it is desired to ascertain the amount of carbolic acid present in soap. To effect this, 5 grammes of the soap are dissolved in water, and a slight excess of caustic soda is added to make the solution alkaline, the mixture is now shaken up with ether in a separating funnel. After being allowed to stand, the aqueous liquor is run off, and salt is added to throw out the soap; this is filtered off, washed with salt brine, the washings being added to the filtrate. It will be found best to make up the volume of the filtrate to one litre. Five hundred c.c. are taken and rendered slightly acid with dilute sulphuric acid, and bromine water added in measured quantities until the appearance of a yellow colour in the liquid shows that the bromine is in excess. The quantity added is noted. Then the bromine water must be standardised which is done as follows: 5 grammes of good soap are dissolved with 0·5 grammes of carbolic acid. If pure carbolic acid has been used in the preparation of the original sample, then Calvert's No. 2 acid may be used for standardising; if crude carbolic acid, then Calvert's No. 5 should be used. This prepared soap is treated as was the original sample shaken with ether, rendered alkaline with caustic soda, thrown out with salt, and made acid with sulphuric acid, finally testing with bromine water: The quantity of the latter used in this case represents 0·5 grammes of pure or crude carbolic acid, as the case may be, and from it the quantity present in the original sample may be calculated.

Medicinal and Colouring Matters.—Directions cannot well be given here for the detection and determination of these bodies, they are so numerous and require such special tests, that no general instructions, such as could be given here, would be of much service.

Rosin in Soap.—Rosin is used so much in the manufacture of soap that it becomes of importance to be able to ascertain its presence in any particular sample of soap, and to determine the amount. This is by no means easy, and unless considerable care be exercised erroneous results are easily obtained.

The only satisfactory direct test for rosin in soap is that of Liebermann-Storch. The fatty and resinous acids are separated from the soap by means of sulphuric acid. The acids are then dissolved in acetic anhydride with the aid of a gentle heat, the solution being cooled down. A little sulphuric acid of 1·53 specific gravity is then added, when, if any rosin be present, a reddish violet coloration appears. This is not permanent, but quickly disappears. If the solution be warm the violet colour is not obtained, but a yellow coloration appears. A small quantity of rosin can be detected by it. Cholesterol or wool fat is the only substance which vitiates this test; it may be removed from the soap by means of ether.

For the quantitative determination of the amount of rosin, two methods which give good results are available, *viz.*, Gladding's and Twitchell's.

Gladding's Rosin Test.—This test depends upon the fact that resinate of silver is soluble in ether, while the oleate, stearate, palmitate, etc., of silver are insoluble or nearly so in that medium. This test may be carried out in the following manner: Five grammes of the soap to be tested are weighed and dissolved with the aid of heat in as little alcohol as possible, a small quantity of an alcoholic solution of caustic soda is added, and the mixture gently heated on a water bath. The object here is to ensure the complete saponification of any free fat the soap contains, as if this be not done such free fat will be ultimately extracted and weighed as rosin. To the alcoholic solution of soap an equal volume of ether and then about two grammes of powdered silver nitrate are added and the mixture well shaken. By this means the silver salts of the various fatty and resinous acids are formed; the former are insoluble and are thrown out as precipitates, while the resinate of silver passes into solution in the ether. After standing about an hour, the mixture is filtered direct into a separating funnel, the residue in the funnel being washed with a little ether. To the filtrate in the funnel is added water, a little sulphuric acid and petroleum ether. By the action of the acid the rosin acid is liberated and passes into solution in the ether. The aqueous layer is run off, the ethereal layer is run into a weighed glass, the ether evaporated off and the residual rosin weighed. As silver oleate is slightly soluble in ether, the results, when oleates are present in the soap, tend to be too high. A deduction of 0·0023 may be made from the total weight of rosin obtained for each 10 c.c. of ether used in the test.

Various modifications of Gladding's test have been published from time to time, but the writer considers the above to be the simplest method and as reliable as any. It is not the method originally published by Gladding, but has been modified therefrom.

Twitchell's Test.—This test depends upon the fact that when rosin is dissolved in alcohol, hydrochloric acid has no action on it, while fatty acids under the same conditions are converted into ethylic ethers which are soluble in water. About three grammes of the mixed fatty and rosin acids are accurately weighed and dissolved in 50 c.c. of absolute alcohol. The use of absolute alcohol is essential, for if ordinary rectified spirit of wine or methylated spirit be used the fatty acids are but little acted on, and erroneous results are obtained. The vessel (better, a flask) containing the solution is immersed in a mixture of ice and water to keep it cool, and a current of dry hydrochloric acid gas is passed through. In about forty-five to fifty minutes the operation is complete, the mixture is allowed to stand for one hour longer so as to ensure that the etherification of the oil acids be completed: 250 c.c. of water are added, and the mixture boiled for a short time until it is clear. The mixture is run into a separating funnel, and some petroleum ether added. The mixture is shaken up, and then the contents of the funnel are allowed to separate, the acid-aqueous layer is run off, the ether layer is washed with hot water. Next there is added a solution of half a gramme caustic potash in 5 c.c. alcohol and 50 c.c. water. This dissolves out the rosin, but leaves any ethylic fatty ethers dissolved in the petroleum ether. The aqueous solution is separated from the ether, it is then decomposed by adding a little sulphuric acid, and the separated rosin collected by means of ether, and after evaporating off the latter is weighed. A volumetric modification of Twitchell's process has been described, but it is best to use the gravimetric method just explained.

It may be pointed out here that to ascertain the character of the fats used in making a sample of soap is rather difficult. Attention should be paid to any particular odour the separated fat acids may have. Then the melting point, molecular weight and iodine value should be ascertained, and from the results an opinion can be formed as to the fats present.

The following are some analyses of various kinds of soap, most of them being the work of the writer. In these analyses the combined alkali is given as sodium (Na) in hard soaps; potassium (K) in hard soaps. The free alkali as caustic soda ($NaOH$), or caustic potash (KOH), as the case may be:—

Good Curd Soap (Tallow).

	Per Cent.
Water	23·84
Free alkali.	0·65
Combined alkali	5·57
Salt	1·25
Fatty acid.	68·60

Primrose Soap.

	Per Cent.
Water	30·25
Free alkali	0·32
Combined alkali	0·28
Free fat	0·46
Combined fat	47·32
Rosin	16·16
Salts	0·21

Castile Soap.

Water	26·53
Free alkali	1·50
Combined alkali	6·27
Salts	2·31
Fatty matter	62·87
Free fatty matter	0·52

Cold Water Soap.

Water	24·62
Free alkali	0·44
Combined alkali	6·88
Salts	0·58
Rosin	22·36
Fatty matter	45·12

Toilet Soap.

Water	6·35
Combined alkali	7·78
Salts	0·31
Glycerine, etc.	1·32
Fatty matter	84·24

Marseilles Soap (Manufacturers').

Water	27·45
Free alkali	1·04
Combined alkali	5·38
Salts	1·38
Free fatty matter	1·01
Combined fatty matter	63·74

Mottled Soap (Manufacturers').

Water	38·62
Free alkali	1·92
Combined alkali	4·66
Salts	4·98
Free fat	1·54
Combined fat	48·28

Pale Soap.

	Per Cent.
Water	31·23
Free alkali	0·13
Combined alkali	5·30
Fatty matter	62·61
Salts	0·73

Silicated Soap.

Water	22·08
Silicate of soda	3·45
Alkali.	5·40
Fatty matter	68·50
Salts	0·62

Mottled Soap.

Water	44·26
Silicate of soda	2·14
Salts	1·21
Colouring matter	0·82
Alkali, free	0·62
Combined Alkali	4·16
Fatty matter	46·79

Mottled Soap (Manufacturers').

Water	28·5
Free alkali	0·6
Combined alkali	5·4
Fatty matter	65·5

Soft Soap (London Make).

Water glycerine	46·5
Combined alkali	7·0
Free alkali	0·5
Fatty matter	46·0

Soft Soap (Scotch Make).

Water glycerine	47·3
Free alkali	0·6
Combined alkali	6·8
Fatty matter	45·3

APPENDIX A.

DENSITIES CORRESPONDING TO BAUMÉ'S HYDROMETER FOR LIQUIDS LIGHTER THAN WATER.

B.°	Density.	B.°	Density.	B.°	Density.	B.°	Density.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·745
21	0·930	34	0·859	47	0·798	60	0·749
22	0·924	35	0·854	48	0·794		

APPENDIX B.

COMPARISON OF HYDROMETER SCALES, BAUMÉ AND TWADDELL, FOR LIQUIDS HEAVIER THAN WATER.

B.°	Tw.°	Specific Gravity.	B.°	Tw.°	Specific Gravity.	B.°	Tw.°	Specific Gravity.
0	0	1·000	23	38	1·190	46	93·6	1·468
1	1·4	1·007	24	39·8	1·199	47	96·6	1·483
2	2·8	1·014	25	42	1·210	48	99·6	1·498
3	4·4	1·022	26	44·2	1·221	49	102·4	1·514
4	5·8	1·029	27	46·2	1·231	50	106	1·530
5	7·2	1·036	28	48·4	1·242	51	109·2	1·546
6	8·9	1·044	29	50·6	1·253	52	112·6	1·563
7	10·4	1·052	30	52·8	1·264	53	116	1·580
8	12	1·060	31	55	1·275	54	119·4	1·597
9	13·4	1·067	32	57·2	1·286	55	123	1·615
10	15	1·075	33	59·4	1·297	56	126·8	1·634
11	16·6	1·083	34	61·8	1·309	57	130·4	1·652
12	18·2	1·091	35	64	1·320	58	134·2	1·671
13	20	1·100	36	66·4	1·332	59	138·2	1·691
14	21·6	1·108	37	69	1·345	60	142·2	1·711
15	23·2	1·116	38	71·4	1·357	61	146·4	1·732
16	25	1·123	39	74	1·370	62	150·6	1·753
17	26·8	1·134	40	76·6	1·383	63	154·8	1·774
18	28·6	1·143	41	79·4	1·397	64	159·2	1·796
19	30·4	1·152	42	82	1·410	65	163·8	1·819
20	32·2	1·161	43	84·8	1·424	66	169·2	1·846
21	34·2	1·171	44	87·6	1·438			
22	36	1·180	45	90·6	1·453			

APPENDIX C.

COMPARISON OF DIFFERENT THERMOMETRIC SCALES.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
-40	-40	2	35·6	44	111·2	86	186·8
39	38·2	3	37·4	45	113	87	188·6
38	36·4	4	39·2	46	114·8	88	190·4
37	34·6	5	41	47	116·6	89	192·2
36	32·8	6	42·8	48	118·4	90	194
35	31	7	44·6	49	120·2	91	195·8
34	29·2	8	46·4	50	122	92	197·6
33	27·4	9	48·2	51	123·8	93	199·4
32	25·6	10	50	52	125·6	94	201·2
31	23·8	11	51·8	53	127·4	95	203
30	22	12	53·6	54	129·2	96	204·8
29	20·2	13	55·4	55	131	97	206·6
28	18·4	14	57·2	56	132·8	98	208·4
27	16·6	15	59	57	134·6	99	210·2
26	14·8	16	60·8	58	136·4	100	212
25	13	17	62·6	59	138·2	101	213·8
24	11·2	18	64·4	60	140	102	215·6
23	9·4	19	96·2	61	141·8	+103	+217·4
22	7·6	20	68	62	143·6	104	219·2
21	5·8	21	69·8	63	145·4	105	221
20	4	22	71·6	64	147·2	106	222·8
19	2·2	23	73·4	65	149	107	224·6
18	0·4	24	75·2	66	150·8	108	226·4
17	+1·4	25	77	67	152·6	109	228·2
16	3·2	26	78·8	+68	+154·4	+110	+230
15	5	27	80·6	69	156·2	111	231·8
14	6·8	28	82·4	70	158	112	233·6
13	8·6	29	84·2	71	159·8	113	235·4
12	10·4	30	86	72	161·6	114	237·2
11	12·2	31	87·8	73	163·4	115	239
10	14	+32	+89·6	74	165·2	+116	+240·8
9	15·8	33	91·4	75	167	117	242·6
8	17·6	34	93·2	76	168·8	118	244·4
7	19·4	35	95	77	170·6	119	246·2
6	21·2	36	96·8	78	172·4	120	248
5	23	37	98·6	79	174·2	121	249·8
-4	+24·8	38	100·4	80	176	+122	+251·6
3	26·6	39	102·2	81	177·8	123	253·4
2	28·4	40	104	82	179·6	124	255·2
1	30·2	41	105·8	83	181·4	125	257
0	32	42	107·6	84	183·2	126	258·8
+1	33·8	43	109·4	85	185	127	260·6

APPENDIX D.

TABLE OF SPECIFIC GRAVITIES OF FATTY OILS AT 15°C (60°F.).

Oil.		Weight of 1 gall.	Trade weight per gall.
Almond oil	0·919	9 lb. 3 oz.	9 lb.
Arachis (ground-nut) oil .	0·920	9 „ 3 „	9¼ „
Castor oil	0·964	9 „ 9½ „	9½ „
Coconut oil	0·925	9 „ 4 „	
Cottonseed oil	0·923	9 „ 4 „	9¼ „
Linseed oil	0·932	9 „ 5½ „	9¼ „
Olive oil	0·915	9 „ 2½ „	9 „
Palm oil	0·9405	9 „ 6 „	
Rape oil	0·914	9 „ 2 „	
Sesame oil	0·923	9 „ 4 „	9¼ „
Lard oil	0·912	9 „ 2 „	9 „
Tallow oil	0·912	9 „ 2 „	9 „
Neatsfoot oil	0·914	9 „ 2½ „	9 „
Tallow	0·940	9 „ 6 „	
Sperm oil	0·883	8 „ 14 „	8¾ „
Whale oil	0·925	9 „ 4 „	9¼ „
Mineral oil	0·875	8 „ 12 „	8¾ „
„ „	0·903-7	9 „ 1 „	9 „
„ „	0·925	9 „ 4 „	9 „

In the summaries of the constants given under each oil, gravities at other temperatures are given.

APPENDIX E.

TABLE OF THE SPECIFIC GRAVITIES OF SOLUTIONS OF CAUSTIC SODA.

Degrees Twaddell.	Specific gravity.	Per cent. by weight of		Lb. of actual NaOH contained in 1 gallon of lye made from commercial caustic of		
		Na_2O.	NaOH.	77 per cent.	74 per cent.	70 per cent.
1	1·005	0·368	0·474	0·048	0·046	0·043
2	1·010	0·742	0·957	0·097	0·092	0·087
3	1·015	1·114	1·436	0·146	0·131	0·129
4	1·020	1·480	1·909	0·194	0·185	0·180
5	1·025	1·834	2·365	0·243	0·231	0·219
6	1·030	2·194	2·830	0·291	0·278	0·262
7	1·035	2·521	3·252	0·335	0·320	0·303
8	1·040	2·964	3·746	0·389	0·371	0·350
9	1·045	3·244	4·184	0·438	0·417	0·393
10	1·050	3·590	4·631	0·486	0·461	0·438
11	1·055	3·943	5·086	0·536	0·510	0·483
12	1·060	4·292	5·536	0·586	0·558	0·528
13	1·065	4·638	5·982	0·636	0·607	0·573
14	1·070	4·972	6·413	0·680	0·653	0·617
15	1·075	5·311	6·911	0·742	0·707	0·668
16	1·080	5·648	7·285	0·786	0·749	0·709
17	1·085	5·981	7·715	0·836	0·798	0·755
18	1·090	6·311	8·140	0·886	0·845	0·800
19	1·095	6·639	8·564	0·937	0·894	0·846
20	1·100	6·954	8·970	0·986	0·941	0·890
21	1·105	7·276	9·386	1·037	0·989	0·938
22	1·110	7·594	9·796	1·087	1·037	0·981
23	1·115	7·910	10·203	1·137	1·123	1·026
24	1·120	8·223	10·607	1·187	1·175	1·071
25	1·125	8·533	11·107	1·238	1·181	1·117
26	1·130	8·893	11·471	1·296	1·237	1·170
27	1·135	9·251	11·933	1·354	1·292	1·222
28	1·140	9·614	12·401	1·413	1·350	1·277
29	1·145	9·965	12·844	1·470	1·413	1·337
30	1·150	10·313	13·303	1·529	1·460	1·381
31	1·155	10·666	13·859	1·600	1·528	1·445
32	1·160	11·008	14·190	1·646	1·541	1·456
33	1·165	11·347	14·637	1·705	1·627	1·539
34	1·170	11·691	15·081	1·764	1·684	1·593
35	1·175	12·025	15·512	1·822	1·739	1·645
36	1·180	12·356	16·139	1·904	1·817	1·719
37	1·185	12·692	16·372	1·942	1·853	1·753
38	1·190	13·016	16·794	1·998	1·887	1·804
39	1·195	13·339	17·203	2·055	1·962	1·856
40	1·200	13·660	17·629	2·122	2·026	1·916
41	1·205	14·058	18·133	2·185	2·085	1·973
42	1·210	14·438	18·618	2·252	2·147	2·033
43	1·215	14·823	19·121	2·323	2·221	2·097
44	1·220	15·124	19·613	2·392	2·280	2·161
45	1·225	15·502	19·997	2·444	2·338	2·206
46	1·230	15·959	20·586	2·562	2·417	2·285
47	1·235	16·299	20·996	2·593	2·475	2·341
48	1·240	16·692	21·532	2·669	2·548	2·410

Degrees Twaddell.	Specific gravity.	Per cent. by weight of		Lb. of actual NaOH contained in 1 gallon of lye made from commercial caustic of		
		Na_2O.	NaOH.	77 per cent.	74 per cent.	70 per cent.
49	1·245	17·060	22·008	2·739	2·615	2·474
50	1·250	17·424	22·476	2·809	2·681	2·536
51	1·255	17·800	22·962	2·881	2·750	2·602
52	1·260	18·166	23·433	2·952	2·818	2·666
53	1·265	18·529	23·901	3·020	2·886	2·730
54	1·270	18·897	24·376	3·095	2·955	2·795
55	1·275	19·255	24·858	3·171	3·027	2·863
56	1·280	19·609	25·295	3·237	3·090	2·932
57	1·285	19·961	25·750	3·308	3·158	2·988
58	1·290	20·318	26·210	3·381	3·227	3·053
59	1·295	20·655	26·658	3·452	3·364	3·117
60	1·300	21·156	27·110	3·524	3·394	3·182
61	1·305	21·405	27·611	3·603	3·439	3·253
62	1·310	21·785	28·105	3·682	3·514	3·224
63	1·315	22·168	28·595	3·760	3·593	3·395
64	1·320	22·556	29·161	3·849	3·674	3·475
65	1·325	22·926	29·574	3·919	3·742	3·539
66	1·330	23·310	30·058	3·997	3·816	3·610
67	1·335	23·670	30·535	4·072	3·891	3·681
68	1·340	24·046	31·018	4·156	3·967	3·754
69	1·345	24·410	31·490	4·232	4·042	3·824
70	1·350	24·765	31·948	4·312	4·116	3·894
71	1·355	25·152	32·446	4·396	4·196	3·970
72	1·360	25·526	32·930	4·478	4·274	4·043
73	1·365	25·901	33·415	4·561	4·354	4·109
74	1·370	26·285	33·905	4·645	4·434	4·194
75	1·375	26·650	34·382	4·728	4·513	4·269
76	1·380	27·021	34·855	4·810	4·592	4·344
77	1·385	27·385	35·328	4·893	4·670	4·418
78	1·390	27·745	35·795	4·975	4·794	4·493
79	1·395	28·110	36·258	5·058	4·828	4·567
80	1·400	28·465	36·720	5·141	4·907	4·642
81	1·405	28·836	37·203	5·227	4·989	4·720
82	1·410	29·203	37·674	5·312	5·071	4·797
83	1·415	29·570	38·146	5·397	5·135	4·873
84	1·420	29·930	38·610	5·482	5·233	4·950
85	1·425	30·285	39·071	5·567	5·314	5·027
86	1·430	30·645	39·530	5·653	5·396	5·104
87	1·435	30·995	39·986	5·738	5·467	5·181
88	1·440	31·349	40·435	5·823	5·558	5·258
89	1·445	31·700	40·882	5·908	5·640	5·335
90	1·450	32·043	41·335	5·923	5·721	5·412
91	1·455	32·460	41·875	6·093	5·816	5·502
92	1·460	32·870	42·400	6·191	5·909	5·608
93	1·465	33·283	42·935	6·290	6·004	5·679
94	1·470	33·695	43·467	6·389	6·009	5·769
95	1·475	34·092	43·980	6·487	6·193	5·856
96	1·480	34·500	44·505	6·586	6·287	5·948
97	1·485	34·899	45·013	6·685	6·381	6·035
98	1·490	35·245	45·530	6·784	6·476	6·126
99	1·495	35·691	46·041	6·884	6·571	6·216
100	1·500	36·081	46·545	6·982	6·665	6·303

APPENDIX F.

TABLE OF STRENGTH OF CAUSTIC POTASH SOLUTIONS AT 60°F.

Specific gravity.	Degrees Twaddell.	Per cent. KOH.	Lb. of KOH per gal.
1·060	12	5·59	0·59
1·110	22	11·31	1·25
1·150	30	15·48	1·77
1·190	38	19·29	2·21
1·230	46	23·22	2·84
1·280	56	27·87	3·56
1·330	66	31·32	4·16
1·360	72	35·01	4·76
1·390	78	38·59	5·36
1·420	84	40·97	5·81
1·440	88	43·83	6·31
1·470	94	47·16	6·93
1·520	104	51·09	7·76
1·600	112	55·62	8·89
1·680	136	60·98	10·24
1·780	156	67·65	12·04
1·880	176	75·74	14·23
2·000	200	86·22	17·24

APPENDIX G.

TABLE OF AMOUNTS OF ALKALI REQUIRED TO SAPONIFY OILS.

Oil.	Per cent. of NaOH.	Per cent. of KOH.
Olive oil	13·56 to 13·91	19·1 to 19·6
Almond oil	13·82 „ 13·92	19·47 „ 19·61
Ground-nut oil . .	13·56 „ 13·93	19·13 „ 19·66
Sesame oil	13·49 „ 13·66	19 „ 19·24
Cotton oil	13·56 „ 13·92	19·1 „ 19·66
Linseed oil	13·30 „ 13·85	18·74 „ 19·52
Whale oil	13·38 „ 15·92	18·85 „ 22·44
Coconut oil	17·48 „ 19·05	24·62 „ 26·84
Palmnut oil	15·62 „ 17·51	22 „ 24·76
Tallow	13·70 „ 14·05	19·32 „ 19·8
Palm oil	13·92 „ 14·44	19·63 „ 20·35
Castor oil	12·49 „ 12·88	17·6 „ 18·15
Rosin	12·07 „ 13·66	17 „ 19·3

APPENDIX H.

TABLE OF THE SPECIFIC GRAVITY AND PERCENTAGE CONTENTS OF COMMON SALT SOLUTIONS AT 15°C.

Specific gravity.	Degrees Twaddell.	Per cent. of salt.
1·00725	1·4	1
1·01450	2·9	2
1·02174	4·3	3
1·02899	5·8	4
1·03624	7·2	5
1·04336	8·7	6
1·05108	10·2	7
1·05851	11·7	8
1·06593	13·2	9
1·07335	14·7	10
1·08097	16·2	11
1·08859	17·7	12
1·09622	19·2	13
1·10384	20·7	14
1·11146	22·3	15
1·11938	23·8	16
1·.2730	25·5	17
1·13523	27·4	18
1·14315	28·6	19
1·15107	30·2	20
1·15931	31·8	21
1·16755	33·5	22
1·17580	35·1	23
1·18404	36·8	24
1·19228	38·4	25
1·20098	40·2	26

APPENDIX I.

TABLE SHOWING AMOUNT OF LIME IN MILK OF LIME.

(Calculated from Blattner.)

Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.	Degrees Twaddell.	Grms. CaO per litre.	Lb. CaO per cubic foot.
2	11·7	0·7	28	177	11·1
4	24·4	1·5	30	190	11·9
6	37·1	2·3	32	203	12·7
8	49·8	3·1	34	216	13·5
10	62·5	3·9	36	229	14·3
12	75·2	4·7	38	242	15·1
14	87·9	5·5	40	255	15·9
16	100	6·3	42	268	16·7
18	113	7·1	44	281	17·6
20	126	7·9	46	294	18·4
22	138	8·7	48	307	19·2
24	152	9·5	50	321	20·0
26	164	10·3			

APPENDIX K.

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF AQUEOUS SOLUTIONS OF GLYCERINE.

Specific gravity 15°C.	Per cent. of glycerine.	Specific gravity 15°C.	Per cent. of glycerine.
1·2650	100	1·1990	75
1·2625	99	1·1855	70
1·2600	98	1·1715	65
1·2575	97	1·1570	60
1·2550	96	1·1430	55
1·2525	95	1·1200	50
1·2499	94	1·1155	45
1·2473	93	1·1020	40
1·2447	92	1·0885	35
1·2421	91	1·0750	30
1·2395	90	1·0620	25
1·2341	88	1·0490	20
1·2287	86	1·0365	15
1·2233	84	1·0240	10
1·2179	82	1·0120	5
1·2125	80		

APPENDIX L.

HADFIELD'S PATENT SOAP FRAME AND SLABBER.

THE soap frame and slabber recently devised and patented by Mr. Hy. Hadfield, of Whaley Bridge, is represented in figure 66. It consists essentially of two parts, the frame or cooler and the slabber. The latter is movable, and may be transferred from one frame to another. The frame or cooler is made with fixed iron sides, and in that respect differs from all frames hitherto in use, which have movable sides.

FIG. 66.—Hadfield's Soap Frame.

The bottom is made movable inside the frame, and is fitted with a screw arrangement worked by a chain gearing from one end of the frame, by means of which it can be moved up and down the frame. In use the frame is filled with the soap paste, and when this has become cold and set, by working the chain and screw gearing the block of soap can be pushed up out of the frame. At this point comes in the use of the slabbing arrangement. This consists of a framework that can be securely fitted to the sides of the frame. This framework carries first a gauge which regulates the extent to which the block of soap is lifted up, and second two cutting wires that travelling along cut two slabs off the block of soap that has been forced above the edge of the frame. The block is then forced up to a certain height as measured by the gauge referred to, then it is cut by drawing the wires along; the slabs thus cut are removed; the block further pushed up, and now drawing the wires back two more blocks are cut off. These operations are repeated until the whole of the block of soap has been cut into slabs. By the use of this new frame, the framing and slabbing of soap is much simplified and carried on more economically and efficiently than by the older methods.

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