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SOAP MANUFACTURE

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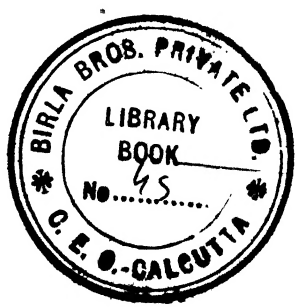
THE CHEMICAL PROCESSES

A HANDBOOK FOR STUDENTS AND THOSE ENGAGED IN THE MANUFACTURE OF HARD SOAP

BY

J. H. WIGNER, PH.D.

Formerly Chief Chemist to Messrs Wm. Gossage & Sons, Ltd., Widnes



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CHAPTER I

INTRODUCTION

Introduction—the conventional method of soap boiling—properties required in commercial soaps—soaps for various technical purposes.

SOAP in a crude form was known to the Romans; its original use was apparently as a salve, but in the Middle Ages it came into general use as a washing agent, and by the end of the eighteenth century it was apparently used among civilised people almost as universally as it is to-day. The production in Great Britain alone at that time is said to have amounted to 20,000 tons per annum, and it was thus a well-established chemical manufacture long before the modern era of chemical industry.

The raw materials from which soap is made are the animal and vegetable oils and fats, and to some extent rosin. These when mixed with a suitable amount of solution of caustic soda and heated gradually undergo chemical change, forming soap and glycerin. This reaction can be accelerated by boiling. When it is complete, and the mixture allowed to cool, the mixture sets to a solid mass of crude soap. In this state it contains all the impurities of the fats and alkali, and in all probability an excess of one or the other. Nowadays commercial caustic soda is very pure and the impurities in it are of little consequence, but in the early days the only forms of alkali available were exceedingly impure, and the soap made in this way must have been a very crude product.

From time to time various improvements were made in the process. It was realised that to obtain a good product it was necessary to saponify the fat completely, and that excess of caustic soda was objectionable owing to its

irritant effect on the skin. The old soap makers used crude tests, such as the feel of the soap when solid, to judge of the presence of unaltered fat, and its taste to determine whether excess alkali was present, but these have long been superseded by better and quite simple chemical tests.

A marked advance in the manufacture was the method of purifying the soap by adding salt to the boiling mixture. When this is done the salt dissolves in a portion of the water present, and when sufficient has been added a solution is formed in which soap is practically insoluble. When boiling ceases the latter rises to the surface, and the salt solution which separates contains most of the impurities and any excess of alkali, and some of the glycerin. This solution is called "spent lye," and the process of adding salt to produce this separation is known as "graining out." Formerly the spent lye was run to waste, but nowadays it is worked up for the glycerin it contains, and most of the salt used is incidentally recovered. The upper layer of soap is known as the curd; when cold it forms a hard mass, and has the usual properties of soap, but little is sold in this form nowadays, as a later stage in the process, now in almost universal use, greatly improves the texture and general appearance of the product.

Simple chemical control in the factory now makes it easy to ensure that practically all of the fat is converted into soap in the first operation, but when there was no better means of ascertaining this than the crude method of feeling and tasting the soap it was bound at times to happen that a portion of the fat escaped saponification.[1] To get over this difficulty it became customary to boil the soap for several hours with a fresh supply of strong caustic soda.

[1] Apart from the fat left unsaponified through lack of care in the operation, it was at one time thought that complete saponification on the first change was impossible. No experimental evidence has been given to support this assumption, and as the conversion of fat into soap by caustic alkali is not a reversible reaction there is no reason to suppose that there is any truth in it. A strong solution of soap at boiling-point is very slightly hydrolysed, and if only the theoretical amount of alkali is employed a small amount of fatty acid or acid soap will be formed, but if care is taken to maintain an excess of alkali corresponding to that formed by hydrolysis, which is very small, the saponification will attain practically 100 per cent.

This operation was known as the "strong" or "strengthening" change. (In soap-boiling language a "change" is the term used for a complete operation; "strong" lye is an expression used for caustic soda solution, and the term "strength" implies the existence of an appreciable amount of caustic in either lye or soap.) When this operation was finished the soap was grained out as usual, but the lye in this case contained so much caustic soda that for economy it had to be used up in making a later boil of soap. This process is a safeguard when purely rule-of-thumb methods are employed, but nowadays, since equally perfect saponification can be obtained on the first change, it is seldom if ever really necessary, and as there are several objections to its use it has been to a large extent given up.

When it became necessary, in the nineties, to recover the glycerin from the spent lye it was not at first understood that in ordinary circumstances the greater part of it remained in the soap. By redissolving the soap curd in water and graining out again a further quantity could be obtained in the lye, and by repeating this operation a number of times it was found that a large percentage, though by no means the whole, of the glycerin could be ultimately recovered. This operation of redissolving the soap and graining out again in order to produce a further amount of lye is called "washing." Naturally the percentage of the glycerin recovered depends on the extent of the washing, but it was a long time before there was any attempt to carry this out on any rational basis; in this case rough-and-ready methods do not help at all, as there is nothing in the appearance of the soap to indicate whether it contains much or little glycerin.

The last refinement in the process is the operation known as "fitting." The curd which separates at any stage of the process consists mainly of soap and water, which are combined to form a hydrate. This hydrate, however, never separates completely from the lye, a somewhat variable amount of the latter remaining entangled in it. The soap hydrate will dissolve completely in water, and also in water containing a limited amount of salt.

When a soap curd is boiled up with a relatively large amount of water it will dissolve completely, but if the amount of water is only small it dilutes the lye in the soap curd sufficiently to enable it to dissolve a certain amount of soap, but not nearly all of that present. In these circumstances the bulk of the soap hydrate remains undissolved, a small portion only dissolving in the diluted lye, and when the boiling is stopped and the mixture allowed to come to rest it separates into two layers. The lower of these is a solution of soap hydrate in a salt solution, and the upper, as far as we know, is a form of soap hydrate, probably differing slightly from that in the curd.

The fitting process serves several very useful purposes. In the first place it frees the soap of certain impurities which cannot be removed by washing. Various kinds of very finely divided solid matter, mostly dark in colour, adhere obstinately to the soap curd on graining out, and thus discolour the soap to a greater or less extent. On fitting, however, the physical conditions are different, and these impurities no longer adhere to the soap in the upper layer, and thus fall into the lower layer of soap solution, in which to a large extent they remain suspended. This lower layer was called by the French soap makers the "nigre," and this term is also used in this country. The soap it contains is ultimately worked up in a subsequent boil, but as the impurities are difficult to remove from it such soap is generally used to make a boil of some inferior class of soap.

The upper layer of good soap is of uniform composition, unlike a soap curd, which is a mechanical mixture of soap hydrate and lye. When solid it is brighter in appearance, and as it is also tougher it is better able to withstand the mechanical treatment of stamping and making into tablets. Another advantage is that it is relatively constant in composition. The conditions which affect the proportion of soap to lye in a soap curd cannot be controlled with great accuracy, and consequently soap curds are somewhat variable in composition. Fitted soap, on the other hand,

being chemically homogeneous, varies but little in composition if made under standard conditions, in respect, at any rate, of the percentage of real soap or fatty acids it contains. As made in the usual way it may contain rather below 63 per cent of fatty acids, though variations of 1 per cent or so either way are common. These variations are due to lack of uniformity in the conditions in which the operation is carried out, and it is now known how to control them. Thus a fitted soap may be made to a standard test of, say, 63 per cent, or if preferred at some lower percentage down to about 60 per cent, the unintentional variations from the mean being of the order of ·25 per cent.

The fitting operation is in one sense extremely simple. So long as sufficient water is worked into the mixture, soap and nigre will be formed and will separate into two layers, and further additions of water do not alter the general character of the system unless so much is added that the whole of the soap redissolves. But every addition of water makes a difference in the proportion of the soap which finds its way into the nigre, as well as to the composition of the soap, and hence to obtain definite results very careful control is required. A full description of the operation is given at a later stage.

The upper layer of soap is called "neat" soap, but this expression is used only in referring to the soap while still hot and fluid. When it is removed from the pan, and either allowed to solidify without further additions, or mixed merely with a little perfume and colouring matter, it is generally called "genuine" or "pure" soap. Most makes contain, in the finished state as bars or tablets, between 62 and 64 per cent of fatty acids, from ·35 to ·55 per cent of salt, and small amounts of alkali carbonate and hydrate, the latter not exceeding about ·1 per cent. Glycerin is present in variable amount, according to the extent to which the soap has been washed, but is usually between ·6 and 2 per cent; glycerin and water together amount to 30 to 32 per cent.

Most of the hard soap of commerce is made by the

boiling process, but only a portion of it is put on to the market in the form of genuine soap. Cheaper products are made, though probably to a much less extent than formerly, by mixing the pure soap with solutions of sodium silicate or other alkaline salts, and the making of these products successfully is almost more of a problem than the soap-boiling operation proper. The so-called soap powders are made by mixing the neat soap hot from the pan with soda ash and other materials, the mixture being converted, sometimes by simple means but often with the aid of very elaborate plant, into powder form. On the other hand, instead of adding cheap materials to the soap some of the water originally present may be removed; in this case the soap is usually converted into flakes and dried in one operation. The flakes may either be sold as such, or converted into toilet soap, or even occasionally ground to a fine powder. In addition, numberless proprietary articles are made which contain soap in greater or less proportion.

The base soap when finished with in the soap pan is thus not, as in former days, the finished product of the factory, but is usually the starting-point for a number of other operations. Most of these involve considerable technical difficulties of one kind or another, and between them take up much of the time of the scientific staff. It is probably mainly for this reason that very little attention seems to have been paid by soap makers in general to the technique of the basic process.

This process has been developed in such a way that the making of soap of good quality is a matter of craftsmanship rather than of scientific method, and the general tendency has been to leave matters pretty much in the hands of the soap boilers. More than the mere making of good quality soap is however necessary if the process is to be a success. It is necessary to ensure that the maximum possible quantity is made from the materials employed, that its composition is under control, so that it may be made to conform with any desired standard, and finally that the yield of glycerin obtained in the lyes is adaptable to the

varying requirements and prices of the glycerin market, and is obtained in the minimum amount of lye, so that the cost of its conversion into crude glycerin may be as low as possible.

The manner in which soap boiling is generally carried out makes such ideal efficiency almost impossible. The soap boiler may or may not know the weight of the fats he has to deal with, and he may be able to judge accurately enough, by means of simple tests, the amount of caustic soda to be used, but the amounts of water and salt or brine to be used at any stage are left very much to his judgment, which is guided merely by the appearance of the soap in the pan. Naturally in a process in which the quantities used are not normally measured there can be no exact knowledge of the effects of variation of these quantities on the products of the reaction. It is doubtless thought that as neither water nor salt is a very costly material it is not worth while going to the trouble of measuring them, particularly as the quality of the soap made does not seem to suffer even when so much is left to chance; but actually the use of incorrect amounts of salt and water has a very material effect on the yields both of glycerin and of good soap, and also to some extent on the composition of the latter.

Little or nothing seems to have been known on these matters until a few years ago, and no information on the subject is to be gathered from the current text-books. In recent times, however, more attention has been given to the matter, and much that was previously obscure has been cleared up by repeated careful experiments on the manufacturing scale. Thus the distribution of the glycerin between the soap and the lye is known to obey a simple rule; in the chapter dealing with glycerin in the spent lyes it is shown how this knowledge may be applied in determining what yield of glycerin can be economically obtained, and how to adjust the composition of the contents of the pan so as to obtain this yield and at the same time to maintain the concentration of glycerin in the lye at the maximum figure consistent with the yield obtained. In

the fitting operation experiments have shown how the proportion of the total soap in the neat soap and nigre respectively depends upon conditions which are under control, and also how variations in these conditions affect the composition of both the nigre and the neat soap.

The only types of soap, other than genuine soap, with which this book is concerned are those made by mixing neat soap with alkaline solutions, generally sodium silicate, or with salt solutions. These soaps, being sold in bar or tablet form, must conform to the usual standards of texture and appearance, and the mixtures of soap and solution have to be very carefully adjusted if good results are to be obtained. The problem in all cases is to make a mixture of a definite fatty acid percentage from neat soap and silicate or other solution, and this also involves adjusting the strength of the latter with some degree of precision; small variations from the correct strength affect the quality of the product seriously. This applies more particularly to the type of silicated soap usually known as "liquored soap." The required strength of silicate solution to use in these mixtures varies according to the amount of actual soap in the mixture, and also with its nature, so that a fresh problem arises with each different fatty acid standard and with each separate soap base. An investigation was made into the nature of the mixtures which give good soaps of this type, in the hope that it might reveal certain rules by which the mixtures might be regulated. These experiments have already simplified the problem considerably, but more work might very well be done on this subject. It seems quite likely that calculations based on certain solubility determinations of the base soap might give the strength of silicate solution required to form a mixture of any prescribed fatty acid percentage and thus do away with the need for separate trial mixings on every batch of soap made. The most interesting feature of these experiments was the fact that mixtures of soap with relatively small amounts of silicate solution were found to be practically identical with fitted soaps, and also that by

applying recently obtained knowledge of the conditions which govern the fatty acid percentage in neat soap it was possible to make soaps of this class by mixture of neat soap with carefully regulated proportions of salt and water. These methods, which are of some practical importance, are dealt with in a later chapter.

In carrying out the investigations which led to these results very numerous experiments were made. These were on all scales, from laboratory boils with a few hundred grammes of fat, to large-scale boils with thirty tons or more. The small-scale boils were invaluable for general guidance, but no reliance was placed on the results until they were confirmed by measurements and analyses on large-scale experiments. Comparatively few of the experimental results are quoted in the text, since to do so would have greatly increased the bulk of the volume, but sufficient information is given to enable those who practise soap boiling to verify for themselves any statements made. Confirmation in this way is far more convincing than the quoted results of experiments made by others.

When once the more exact methods are in operation their advantages are soon manifest, but practical men who can make good soap without the aid of figures may at first dislike having to make any kind of calculation. In meeting this difficulty the use of graphic methods has been found of great value, and nomograms have been constructed which meet all requirements. A strip of celluloid on which is scored a fine blackened line is preferable to a straight-edge for reading them, or a length of sewing-cotton, held taut so as to pass through the two datum points, serves equally well.

The Properties of Soap. — Before proceeding to discuss manufacturing problems it will be well to consider what are the chief properties required in commercial soaps.

The most important property of soap is its washing power; there are certain technical uses for soap which depend on other properties, but these are of minor importance. The various soaps in commerce are made from a

great variety of fats and rosin, and one would naturally expect their washing powers to differ, and as a matter of fact this is the case. The differences, however, are less than might be expected, and as they are by no means easy to measure it is difficult for the ordinary user to decide which of two somewhat similar types is the better for washing purposes. Thus in the trade for household soaps washing power counts for much less than general attractiveness in get-up and appearance. The properties upon which distributors lay most stress are intrinsically of little importance, but they are vital from the commercial standpoint. The chief of these are colour, hardness, texture, and odour.

With regard to colour it may be said that this has little bearing upon the washing properties, though it may affect the appearance of the materials washed in an indirect way. All water-supplies contain some quantity of lime or magnesium salts, and water is classified as hard or soft according to the quantities of these present. These substances form with soap insoluble lime or magnesium compounds, part of which deposit on the fabric during washing. Such deposits carry with them some of any colouring matter which may be present, and thus the goods washed, particularly if the water is hard, may deteriorate in appearance if a dark-coloured soap is employed. This is an argument in favour of white or pale-coloured soap, but apart from this the colour is no indication of its washing power. In this connection it has been stated that sodium silicate, if present in a soap, reacts with the lime and magnesia and prevents the formation of the objectionable lime and magnesia soaps. This, if true at all, is only so to a very limited extent, and is no argument for employing a silicated rather than a pure soap. Silicated soaps, however, are found to cause a deposit of silicic acid on the fibres, and as this is pure white in colour such soaps may have a whitening effect on the goods washed, which masks to some extent any dullness in colour due to other deposits on the fabric. After repeated washings this layer of silicic acid tends to

become removed in patches, particularly if a silicate-free soap is subsequently used, and the final result may be very unsatisfactory.

To produce soap of a good colour one must employ either practically colourless raw materials, or fairly good materials well bleached. Coconut oil, first-class tallows, and the best bone grease are among the best-coloured natural materials, and hardened whale oil and certain distilled fatty acids may also be suitable. For pale soaps there may be added palm-kernel oil, certain seed oils, tallow and grease a little below the best, and so on. Various bleaching processes are employed to produce white or nearly white fat. Palm oil, for example, which has a high natural colour, yields a pale-coloured product by passing air through it at a temperature rather above 100° C., and if the oil is given a certain preliminary treatment to remove other impurities the colour may become nearly pure white. Treatment with activated fuller's-earth is often very successful with oils which are only slightly off-coloured, and may also be used with palm oil. Bleaching the soap in the pan is also of use with certain types of pale soap. For this purpose oxidising bleaches may be used, the cheapest and most efficient being probably sodium hypochlorite, or reducing substances such as sodium hydrosulphite.

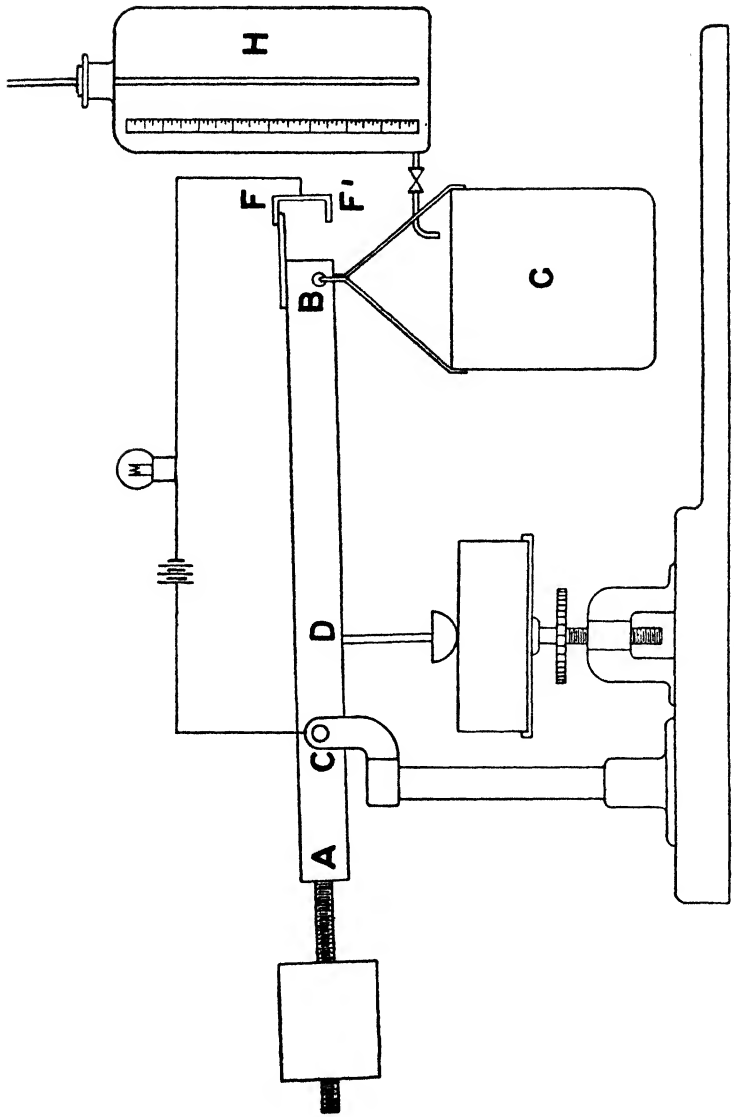
Much of the colouring matter in the fats is removed in the usual course of washing for the recovery of glycerin, and the conditions which favour a good yield of glycerin tend also to remove the maximum of colour from the soap. Some of the colouring matters, however, cannot be removed at all in this way, and unless they can be destroyed by bleaching must remain in the finished soap.

Hardness is a property to which most soap makers attach great importance, in fact they are probably more critical in this respect than the average user. The saturated fatty acids all produce sufficiently hard soaps, any tendency to softness being due to the unsaturated acids. For this reason the use of such oils as cotton-seed and soya-bean must be kept within reasonable limits, and oils of very high iodine value, such as linseed and whale oils,

are of very little use in their natural state, although they have considerable value when hydrogenated. Rosin has also a definite softening effect, although quantities up to 25 per cent can be used without detriment if the fats alone would form a very hard soap. The addition of cresylic acids, as in the so-called carbolic soaps, also has a softening effect, and if the proportion exceeds three or four per cent it may be necessary to modify the fat charge to counteract this. Liquored soaps if properly made should not be greatly softer than the base soap; careful measurements on those reduced with salt solution to about 60 per cent showed no falling off in hardness.

It is useful to have some device for measuring the hardness of soap, particularly as this enables records to be kept of this characteristic. A type of penetrometer which the author has found convenient in use is here illustrated diagrammatically. In this instrument the pressure on the soap is exerted through a metal ball, thus imitating to some extent the soap maker's usual test by pressure with the finger.

AB is a stout metal bar moving freely about its support at C. From the end B a light metal bucket is suspended by a hook. At D, which may conveniently be one fifth of the distance from C to B, a rod is rigidly fixed which carries a hemisphere of phosphor bronze the diameter of which is 2 cm. A lead weight at A serves as a counterpoise to balance the whole. By the movement of the bar the ball impinges on a block of the soap to be tested, which rests on a platform capable of being moved up and down by means of a screw. Stops above and below the bar restrict its movement in a vertical plane within convenient limits. A small electric current, sufficient to light a flash-lamp bulb flows through the bar and an attached strip of spring steel, the free end of which can make contact with the upper or lower arm of a rigid brass frame F. This is connected through the battery and lamp back to the bar. The amount of travel allowed in the experiment is the distance between the two arms F and F′. A glass bottle H can deliver water into the bucket G through a tube, the



Apparatus for measuring hardness.

flow being controlled by a pinchcock. This bottle is provided with a measuring-scale, and an open tube passes through a cork in the neck to near the bottom of the bottle, thus ensuring a constant head of water and uniform rate of flow.

To carry out a test, the piece of soap to be tested is placed on the table, and is raised until the light pressure on the ball causes the bar to rise until it finally makes the circuit with the upper arm F and lights the lamp. The pinchcock is now opened wide, and water allowed to flow into the bucket. The ball presses deeper and deeper into the soap, and when the specified amount of travel is complete the circuit is closed again, through the lower arm F', and the flow of water stopped. The amount of water required to do this is a measure of the force required to make a definite indentation in the soap. The number of grams of water delivered into the bucket divided by 5, and by the area of the circle impressed on the soap (which is a constant for the instrument), is called the hardness of the soap. The readings cannot be considered as absolute, but if the diameter of the ball, the distance of travel, and the head of water and size of the orifice are all standardised, different instruments will give the same results. Repeat tests are found to agree very satisfactorily.[1]

This instrument has been found of use in examining experimental soaps in which variations are made from a standard charge, and even more in testing liquored soaps, as the hardness of these is often a useful criterion of the correctness of the mixture.

The desirable odour of a soap is largely a matter of taste. Soaps for laundry and textile purposes should be as nearly as possible inodorous. In household soaps a slight fragrance is generally imparted by the use of small quantities of the cheaper essential oils, such as citronella,

[1] If FF' is 1·97 cm. the circle impressed on the soap will have an area of 2 sq. cm. If 1 kg. of water is required to produce this impression the pressure on the soap is 2·5 kg. per sq. cm., which is called 2½ degrees of hardness. Ordinary soaps vary from about 1½ (rather soft) to 5 degrees (hard). It is convenient to make a scale of degrees of hardness on the water-bottle, 1 degree for each 400 c.c.

and in some cases, such as tallow rosin soaps, the odour of rosin is considered desirable, American rosin being much used for this purpose. A type of rosin also made in America by extraction from tree stumps has a different and less pleasant odour. The one thing to guard against by all means possible is any trace of rancidity. This may develop in a soap even when good materials are used, and is usually attributed to leaving fat unsaponified. The tendency for it to occur may be minimised by the presence of a small amount of free caustic soda in the finished soap. Rosin appears to counteract the tendency to rancidity to some extent, and for this reason one or two per cent is usually added to the charge of toilet soaps. Certain chemical substances are said to be useful inhibiting agents, but the trouble should not occur if perfectly sweet fats are used, along with care in the manufacture and attention to the above-mentioned points.

The texture or structure of a soap is partly dependent on its purity. Genuine soaps, if allowed to cool in frames, possess a kind of fibrous appearance which becomes more evident when the surface has somewhat dried. A well-developed structure of this kind is known as "feather," and as it occurs only with genuine soaps, or those very slightly liquored, it used to be considered by soap makers as a merit. Probably the general public did not understand this, and may either not have noticed it at all, or regarded it as a slight defect in manufacture. Soaps cooled quickly, as in soap cooling machines, show very little feather, and even with framed soaps the extent of it seems to depend a good deal upon the nature of the fat charge. On the whole, much less importance seems to be attached to feather nowadays than formerly.

The more heavily liquored soaps, those below about 60 per cent of fatty acids, should appear to have a perfectly uniform structure. Any suggestion of granularity is probably an indication of excess of electrolyte in the runnings, and the soap is liable to be softer than one made with the correct mixture.

Of the properties of soap that really matter the most

important is its detergent power. The ability of soap to remove dirt depends not only on the fats of which it is made, but on the conditions under which it is used, that is to say the temperature, the amount of added alkali, and also the concentration of soap itself in the solution. As regards the latter a concentration equivalent to about ·19 per cent of fatty acids, or ·3 per cent of genuine soap seems to give the best results. The most suitable temperature depends on the nature of the fatty acids present, and vice versa. Broadly speaking, the most soluble soaps, those containing a large percentage of fatty acids of low molecular weight or of unsaturated acids, are the most suitable for low temperatures, those consisting largely of higher saturated acids for a temperature near boiling-point. Thus in composing a soap charge the manufacturer has to take into consideration the temperature at which the soap is most likely to be used. Bar soaps for domestic purposes are largely used at temperatures not above 45° C., and for this purpose a soap containing a good percentage of coconut oil, some of the seed oils, some tallow or palm oil and a moderate amount of rosin is suitable. Such a composition is typical of the so-called washer soaps. On the other hand, a soap required for use in a laundry at boiling-point should consist largely of the higher saturated acids, and for such purposes it is doubtful if anything is more efficient than one made entirely from tallow or tallow substitutes. But owing to their low solubility in water at low temperatures, such soaps are apt to give trouble in rinsing, and so some compromise may have to be made.

The addition of alkali to a washing solution has a marked effect on the removal of dirt. If a number of soap solutions are made, each containing the optimum percentage of soap, it is found that increasing additions of sodium carbonate to these improve their dirt-removing power up to a certain point, the tests being made under standard conditions, using similar pieces of artificially soiled material. The author carried out a long series of tests of this kind and found a marked increase in the detergent power with increase of alkali content up to about ·04 per cent Na_2CO_3.

Beyond this the detergent power fell off, slowly at first and then more rapidly. The optimum was found to be the same both at medium and high washing temperatures. Other workers have obtained similar results, though some place the optimum somewhat higher, especially at the higher temperatures; these variations in results are not, however, very important. What is of more interest is the fact, established by other experimenters, that it is immaterial what alkali is used for this purpose so long as a fairly definite *p*H value is attained. Thus suitable quantities of the different sodium phosphates and other alkaline substances give apparently identical results with sodium carbonate.

This being so, it is clear that to compare the detergent powers of different soaps it is necessary to make them into solutions of a standard strength to which is added a standard amount of soda ash. The tests should then be carried out at various definite temperatures, using pieces of fabric soiled in a suitable way with a standard material.

The choice of a method of soiling the trial pieces of material is not easy. The dirt which naturally accumulates on clothes and household articles is of various kinds. Broadly speaking, it may be said to consist of oily or fatty substances and of very fine solid matter of various kinds. In washing experiments it has been found that the removal of the fatty dirt from domestic articles is a much easier matter than that of the solids, and one may therefore confine attention to the latter. It is quite impossible to make any mixture of materials which fairly represents the different kinds of dirt that accumulate on clothes, and the only way out of this difficulty is to take some definite substance, dark in colour and in a fine state of division, which can be deposited in definite quantity on the fabric. Colloidal graphite seems as suitable a material as any, and the author has used a commercial preparation, "Oildag," diluting this in the proportion of 1 in 200 in ordinary petrol. The fabrics used for the tests are calico and flannel, and all experiments should be made with the same make of each material. Before soiling the material it is

thoroughly washed and ironed: it is then passed through a bath of the graphite suspension and hung up to dry.

In carrying out a test the soap solution to be tested is placed in a tall beaker, of some four inches diameter, over a source of heat, and its temperature is kept constant throughout the experiment. The soiled cloth is held between two circular clips, which are fitted with a handle a few inches long, by means of which the fabric can be moved up and down through the solution at a constant speed. Each test lasts a definite time, say ten minutes. When finished, the fabric in the clip is rinsed in tepid water, and it is then detached from the clip, any surplus water carefully mopped off and hung up to dry. When nearly dry it is ironed, to make the surface more easy of inspection.

Estimation of the amount of dirt removed is made by comparing the washed cloth with a series of similar pieces which have been soiled to various degrees by immersing in more diluted suspensions of the graphite. These suspensions may vary from 5 per cent to 95 per cent of the concentration in the original mixture. If the washed piece corresponds in tint with the one having 75 per cent of the standard soiling one may say that approximately 25 per cent of the dirt has been removed. This method, if not exact, avoids errors which exist in many other methods tried, and gives useful comparative results.

The lathering power of a soap is a matter of importance, partly because of the effect it has on the judgment of the user, and also because it has a certain effect on the washing power. When a piece of soap is rubbed between the hands or against a fabric in water, the rate at which a lather is formed depends on the proportion of highly soluble soap in it. Thus soaps containing a considerable proportion of coconut or palm-kernel oil rapidly give up enough soap to the water to form a solution strong enough to foam, and are thus considered quick-lathering soaps. In contrast with this are soaps made, for example, of tallow only, in which there are practically no low molecular acids to form highly soluble soaps, though when a solution is once

formed it lathers well on agitation with air, and the foam is generally more persistent than that produced by the more soluble soaps.

When clothes are washed in a laundry machine the soap is generally dissolved in advance, so that rapid solubility is of little consequence. Lathering, however, seems to have a real effect on the progress of the operation. The turbulent motion has the effect of disseminating bubbles of air through the mass of the liquor, making it easily compressible, and this facilitates the passage of the liquor through the meshes of the cloth and so helps the removal of dirt. It may happen during the course of the operation that the lather dies down and in this case launderers consider that some of the dirt tends to become deposited again on the fabric, from which it is more difficult to remove than formerly. Whether this is strictly true or not, the fact remains that with certain soaps the lather is more permanent than with others, and this is an important matter to which the soap manufacturer has to pay due attention.

Scientific investigations on the foaming of soap solutions have not so far enough been of any great help to soap makers. It is generally assumed that very complete saponification of the fat is essential, and that the high molecular constituents tend to produce greater stability in the foam, but soap makers will be well advised to experiment for themselves in examining the foaming properties of any soaps, such as those for the laundry trade, in which this matter is of importance. One way of testing is to take a fair quantity of washing solution made up to the standard composition at the specified temperature and shake a trap for a definite time. A convenient [illegible] to do this is a stout glass tube, like [illegible] soda soaps, [illegible] between one and two inches in diameter [illegible] are also eighteen inches long. A definite quantity of solution, enough to fill the tube about one third, is used for each experiment, and the time is noted which is required for the foam either to subside entirely, or to shrink to a certain definite extent.

It is interesting to note that soaps which lather best may

not necessarily have the best detergent power. Some instances have occurred in which two soaps differing slightly in composition have been tested for both properties and the one which gave the better lather was found to be slightly inferior in washing effect to the other. Those who wish to modify their soap charges so as to give the best results should therefore not rely on one of the tests only, though the washing test described gives a good rough idea of the lathering property also.

The Use of Soap for other Technical Purposes

Soap is used for various purposes in many different trades, and sometimes for other objects than the removal of dirt. The soap-maker's problem in finding suitable soaps for these purposes is often not easy, as the consumer may not know what type of soap is the most suitable for the purpose. If it is possible to ascertain the exact purpose for which the soap is required, and the conditions under which it is used, the choice of a suitable type should be easy.

In the textile trades soap is largely used for removing the natural impurities from the fibre, and detergent properties are the main consideration. White or nearly white soaps should generally be used, to avoid any possible discoloration in case slight deposits of lime soap occur. In some textile industries, however, it is customary to soften the water to zero hardness, in which case the colour is of less importance. As a rule, rosin in the charge should be avoided.

In some textile industries the rinsing of the soap is important and depends on the milling of woollen cloth, for example, where. Thus soaps, it is undesirable to employ a soap with any marked or pale, as this might affect the finished product. In other cases a certain amount of soap is intentionally left on the fibre after washing, and for this purpose a white soap is required. The same applies in cases in which an actual dressing containing soap is applied to the fibre. For many purposes a soap of the toilet type, containing

not over 20 per cent coconut oil, is useful, and a pure white soap made of nothing but mutton tallow is also occasionally used.

Soap is used in the manufacture of lubricating greases in admixture with mineral oil. For many of these lime soaps are used, and are generally made by the grease manufacturer himself. Ordinary soda soaps are, however, preferred for certain types of grease, and the grease manufacturer may work to a definite formula and know the type of soap required. Apparently a fairly good tallow rosin soap is often used for this purpose.

In some industries soap is made into a strong stock solution, possibly 10 per cent or so, and has to be pumped some distance along mains. For this purpose the soap base had best consist of olein and coconut oil so as to make a solution which does not easily set. The detergent properties of such a soap are naturally poor and it is as well to adjust the composition of the charge so as to give the degree of solubility required and no more. The amount of coconut oil required may approach 50 per cent, the unsaturated constituents being supplied by commercial olein, or possibly arachis oil. The small proportion of high acids in the latter may however cause trouble.

Silk manufacturers and certain other users require an olive-oil soap. Even the green "sulphur" olive oil is an expensive material, and the user who demands and is in the habit of getting a soap made from this material alone must be prepared to pay a good price for it. Otherwise it is very desirable to have the content of olive oil exactly specified, as soaps on the market described by distributors as olive oil soaps often contain little more than a trace of this constituent.

Apart from the ordinary potash and soda soaps, compounds of other metals with fatty acids are also used to some extent in various industries—*e.g.* nickel, chromium, iron, aluminium, and copper soaps. The last three kinds are mainly used in the waterproofing of canvas and the waterproofers usually prepare them from solutions of the metallic sulphates and commercial hard soaps. The soap

bases employed for this purpose must yield metallic soaps which are fairly soluble in petrol and the colour may be of some consequence. In the case of the iron soap, which is itself dark brown in colour, this is unimportant, but aluminium soaps are white, and for these a white soap base is indicated. A similar soap to that suggested for the textile trade serves for these, and also for some of the copper soaps. In the case of the latter, however, the problem is a little complicated by the fact that varying proportions of the constituent fats produce different tints in the copper soaps, the effect in particular of varying the percentage of nut oil being quite perceptible even when the soda soaps are indistinguishable in colour. For this reason it is necessary to maintain a constant composition of any soap for this purpose.

For making iron soaps, and possibly some copper soaps which may be used for waterproofing lower-grade fabrics, a cheaper soap base containing palm oil instead of tallow may be found adequate.

CHAPTER II

RAW MATERIALS

Raw materials, and the amounts of fatty acid and glycerin yielded by them—general properties of various fats and oils—the nature of soap curds and neat soap.

Raw Materials.—The materials ordinarily used in the manufacture of hard soaps are fats and oils, rosin, and caustic soda. Every kind of oil or fat consists of a complex mixture of glycerides, compounds which under suitable conditions may be made to take up water and form fatty acids and glycerin. The fatty acids are open chain compounds, and those which occur in natural oils and fats contain an even number of carbon atoms in the molecule, ranging from six to twenty or more. Some of these, such as lauric and stearic acids, are saturated, that is they contain the maximum possible number of hydrogen atoms in the molecule: the unsaturated acids contain respectively two, four, six, and so on, fewer hydrogen atoms than the corresponding saturated acids. The soaps made from individual acids differ in their physical properties. Those below C_{12}, which occur in some quantity in coconut and palm-kernel oils, are very soluble, and have of themselves practically no lathering or washing properties. From this point upwards solubility decreases with increasing number of carbon atoms in the case of the saturated compounds, and unsaturated acids form more soluble soaps than saturated. The hardness of the soap, when in its ordinary commercial form containing about 30 per cent of water, depends mainly upon the proportion of saturated acids, oils yielding a large amount of unsaturated acids forming, when used by themselves, soaps too soft for general purposes. This fact led about thirty years ago to the invention of the process of "hydrogenation," or "hardening," in which the unsaturated

constituents of a fat are partially saturated with the object of forming from such materials a product in some respects resembling tallow. The early products were not particularly good, but as the process had great possibilities every effort was made to improve it, and many products of to-day, even if not identical with tallow, are good-coloured, nearly odourless fats, which in suitable admixture with other materials may be converted into very good soaps.

Rosin, the remaining organic material used in soap manufacture, is totally different chemically from the fats. It yields no glycerin and is composed mainly of an acid entirely different from the fatty acids. By itself it does not form a usable soap, but it may be used to a certain extent to mix with the fat charges of certain types of soap. It imparts a characteristic odour to the soap which some consider pleasant, but tends to make it softer. A very small quantity of the best rosin is usually added to the charge of toilet soaps in order to check any tendency to rancidity.

Caustic soda used formerly to be prepared by the soap manufacturer, who in some cases first produced sodium carbonate by the Leblanc process. It is now possible to purchase the very pure soda ash made by the ammonia soda process and causticise it in the soapworks, but it is much simpler, and often no more expensive, to purchase ready-made caustic soda, either solid or in solution. The latter method is most convenient when the soapworks are not too far from a factory producing caustic soda, as the solution can be delivered direct from the chemical works to the soap-maker's storage tanks. Commercial solutions are usually either 70°, 80°, or 90° Tw. The stronger the solution that is bought the less is the relative cost of transport. On the other hand, the stronger solutions solidify more readily in cold weather and may cause more trouble in the blocking up of pipelines. Electrolytic caustic solutions contain a small amount of salt, but in this case the specific gravity of the solution as delivered is a little higher than the nominal figure and the liquor contains the full amount of sodium hydrate.

The Yields of Fatty Acids and Glycerin from Fats

It is important to the soap maker, both for purposes of control and for costing, to be able to ascertain the amounts of fatty acids and glycerin obtainable from the fats employed. These amounts are variable, depending on the nature of the fatty acids, and on the percentage of free acids in the fat. To make this clear take first the case of a simple triglyceride, tristearin. In reaction with caustic soda this yields sodium stearate and glycerin, but as soap makers ordinarily think in terms of fatty acid rather than of real soap it is convenient to consider the reaction as yielding stearic acid and glycerin, thus,

$$\begin{matrix} C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \end{matrix} \!\!\rangle C_3H_5 + 3H_2O = 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

1 molecule tristearin 890 parts	3 molecules water 54 parts	3 molecules stearic acid 852 parts	1 molecule glycerin 92 parts

100 parts of tristearin would thus yield 95·73 parts stearic acid and 10·34 parts glycerin.

Glycerides of lower fatty acids yield less fatty acid and more glycerin. Thus in the case of lauric acid, molecular weight 200, an important constituent of coconut oil, 638 parts of trilaurin yield 600 parts of lauric acid and 92 parts glycerin, or 100 parts yield 94·04 of lauric acid and 14·42 of glycerin.

Natural fats are never pure substances like the above, but are invariably mixtures of glycerides of a number of fatty acids, and in addition contain variable amounts of free acids arising from the decomposition of some of the fat by natural causes. Every commercial fat may therefore be regarded as consisting of two parts, one portion a mixture of pure fatty acids, and the other a mixture of glycerides of the same acids. The amount of fatty acids and glycerin obtainable from the glyceride portion varies according to the average molecular weight of the fatty acids, and can be ascertained by analysis. Several

methods of analysis have been suggested, but the most suitable for routine purposes are the determination of water and dirt, and of the so-called acid and saponification values. These methods are capable of considerable accuracy, and give results from which the total acids and glycerin yielded by the fat and the amount of caustic soda required to saponify it can be calculated.

Methods of Determination.—A weighed portion of the fat is dissolved with gentle heat in light petroleum, and the solution passed through a filter which has been previously dried in a steam oven and weighed. The residue on the filter is washed free of fat, and after drying weighed again. This is called the *dirt*, and consists of the various impurities, such as fibrous matter, fine sand, and so on, which are insoluble in the fat. Dirt and water are sometimes classed together as "impurities," but this term is misleading as another class of impurity also exists in the fat. This consists of organic substances, insoluble in water but soluble in fat and in light petroleum, which are of a different nature from the true fat and yield neither fatty acid nor glycerin. When these are determined they are described as "unsaponifiable matter." In most fats the amount is small and the determination need not be carried out as a matter of routine. The effect of disregarding them is to raise the apparent molecular weight of the fatty acids by an amount proportional to the amount in which they are present, and also to increase the apparent amount of the total fatty acids. The error is really of little consequence, as in the course of manufacture this material probably passes into the soap, and is weighed and returned in the result of the routine soap analysis as fatty acid. The most important of these substances are cholesterol and phytosterol, which occur in animal and vegetable fats respectively.

Water is simply determined by difference, by driving it off by gentle heat from a weighed quantity of the fat and weighing again.

The *free fatty acids* are always determined by titration with alkali, and the true value of the molecular weight of

the fatty acids must be used in the calculation. If instead of doing the test in the works laboratory the analysis supplied by the sellers is used, this may involve a correction, as some different value may possibly have been employed. In the conditions of sale of fats and oils the percentage of free fatty acids has to be calculated according to an arbitrary rule. In the majority of cases the value taken for the mean molecular weight is 282, that of oleic acid, and this is generally close enough for the oils and fats in question. For palm oil, however, the calculation must be based on the molecular weight of palmitic acid, 256, and for coconut and palm-kernel oils on that of lauric acid, 200. The adoption of these figures in the first instance was probably due to imperfect knowledge of the nature of the oils, but the figures are unfortunately chosen, and not sufficiently exact when it is desired to know the real percentage of free fatty acid present. Thus for example palm oil, containing in reality 32 per cent of free fatty acids, might be returned on the analysis as having only 30 per cent.

For reasonably accurate results the values for molecular weights given on p. 31 may be employed, but it is better to determine the acid and saponification values in the following manner.

The *acid value* of a fat is the number of milligrams of KOH required to neutralise the free acids in 1 gram of the fat. The *saponification value* is the number of milligrams required to saponify the fat completely. The difference between these is evidently the number of milligrams required to saponify the glycerides only, and is called the *ester value*. In the formulæ these will be shortly called AV, SV, and EV respectively. The determination is carried out by shaking up a weighed quantity of the fat with alcohol previously neutralised and freed from esters. The mixture is kept well agitated, as the fat only partially dissolves in the alcohol, and titrated with standard alcoholic potash solution (about half normal), using phenolphthalein as indicator. The number of parts of KOH per 1000 of fat is the acid value. To the same solution is now added a

measured amount of alcoholic potash solution somewhat in excess of what will be required for complete saponification, and the mixture is boiled under a reflux condenser. The glycerides slowly saponify and go into solution as soap. When all fat globules have disappeared the mixture is boiled a little longer for safety, and the excess of KOH is then titrated back with half normal hydrochloric acid. The total number of milligrams of KOH per gram of fat used in the operation is the saponification value, and the number used in saponifying the glycerides is the ester value.

It is generally best to deduct the amount of dirt and water present from the weight of fat taken, and thus the acid and saponification values are found on what is called the pure oil. In this way the error in calculation of the mean molecular weight, except that introduced by the presence of the small amount of unsaponifiable matter, is eliminated. This figure should be nearly constant for each type of fat and it is better always to work it out. Any marked variation from the mean figure indicates either an error in the analysis or that the fat is in some way abnormal.

From the acid and saponification values can be calculated the percentage of free fatty acids, the total fatty acids and glycerin yielded, and the theoretical amount of caustic soda required for saponification.

The caustic soda required for saponification is proportional to the saponification value. As KOH = 56·1, NaOH = 40, and $\frac{1}{2}Na_2O = 31$, the caustic soda required for 1000 of fat is $SV \times \frac{40}{56{\cdot}1}$ as NaOH or $SV \times \frac{31}{56{\cdot}1}$ as Na_2O, or reduced to percentages,

$$\text{NaOH per cent} = SV \times {\cdot}0713$$

or

$$Na_2O \text{ per cent} = SV \times {\cdot}05536 \quad . \quad . \quad (1)$$

The glycerin is proportional to the alkali consumed in saponifying the glycerides—*i.e.* to the ester value. Three molecules of KOH = 168·3 are equivalent to one of glycerin = 92; therefore the percentage of glycerin is

$$\text{EV} \times \frac{9{\cdot}2}{168{\cdot}3}, \quad \text{or} \quad \text{EV} \times {\cdot}05467 \quad . \quad . \quad (2)$$

The methods of calculating the percentages of free and total fatty acids and their mean molecular weight are a little less obvious, though easy enough to understand by bearing in mind the nature of the substances of which the fat is formed.

The molecule of a triglyceride may be regarded as built up of three molecules of fatty acid and one of glycerin, three molecules of water being eliminated. Thus the molecular weight of a triglyceride is that of three molecules of fatty acid (or acids) $+ 92 - 54$. Using M to denote the molecular weight of the fatty acid, or the mean molecular weight when more than one acid is present, we may say that the chemical equivalent of the triglyceride is $\text{M} + \frac{38}{3}$. Thus an amount of alkali which will neutralise M parts of fatty acid will saponify $\text{M} + 12{\cdot}67$ parts of glyceride.

If a material consists entirely of fatty acids, 1000 milligrams of it will require for neutralisation a certain number of milligrams of KOH, and this number is the acid value (it is also the saponification value). This number multiplied by the molecular weight of the acids and divided by that of KOH will obviously be the weight of the fat, therefore

$$1000 = \text{SV} \times \frac{\text{M}}{56{\cdot}1}, \quad \text{and} \quad \text{M} = \frac{56100}{\text{SV}}.$$

If the fat consist of triglycerides only, the equivalent of the fat is $\text{M} + 12{\cdot}67$—that is, the corresponding amount of fat to 56·1 of KOH is $\text{M} + 12{\cdot}67$ and

$$1000 = \frac{\text{SV}\ (\text{M} + 12{\cdot}67)}{56{\cdot}1} \quad \text{or} \quad \text{M} = \frac{56100 - 12{\cdot}67\ \text{SV}}{\text{SV}}.$$

In the case of a fat containing both free acids and glycerides it is found that the free acids are on the average identical with those combined with glycerin, and therefore

the proportion of the latter to the total acids is $\frac{SV}{EV}$. Since the addition of 12·67 to the molecular weight applies only to the acids which are combined with glycerin the above equation therefore becomes

$$M = \frac{56100 - 12{\cdot}67\ EV}{SV} \quad . \quad . \quad . \quad (3)$$

and this holds good for fats in general, and is the equation ordinarily used for calculating the mean molecular weight of the acids.

The total fatty acids in 1000 of fat are the amount of KOH required in saponification $\times \frac{M}{56{\cdot}1}$—that is,

$$\frac{SV}{56{\cdot}1} \times \frac{56100 - 12{\cdot}67\ EV}{SV},$$

which simplifies to $1000 - \frac{12{\cdot}67\ EV}{56{\cdot}1}$, or fatty acids per

100 fat = 100 − ·0226 EV . . . . . (4)

The free fatty acids are a fraction equal to $\frac{AV}{SV}$ of the total acids and therefore, making use of equation (4), amount to $\frac{AV}{SV}(100 - {\cdot}0226\ EV)$ per cent. . . . (5)

Alternatively, if M is known the expression $AV.\frac{M}{56{\cdot}1}$ may be used.

The mean molecular weight of the fatty acids is nearly constant for any given type of fat, the variation from the mean being seldom more than about two units. One can make use of this fact, in cases in which the saponification value is not determined, for determining with fair accuracy the yield of fatty acids and of glycerin, and the amount of caustic soda required, knowing only the percentage of free fatty acids in the sample. If arbitrary values have been used for calculating the latter, as in the case of nut

oils or palm oil, a correction must be made in conformity with the average value for the mean molecular weight. The following figures are approximate averages of a very large number of tests, and may be used in this way:—

Coconut oil	206
Palm-kernel oil	216
Palm oil	273
Tallow, whale oil, and most common seed oils	ca. 280

Though the calculations required to obtain the above figures are simple, it is useful to have a quick method of checking them. This may be done by the use of one or other of the accompanying alinement charts.

Diagram 1 shows the amount of caustic soda required as parts of Na_2O for any given quantity of fat, based on the saponification value.

Diagram 2 shows the amount of Na_2O per 100 of fat, based on the mean molecular weight of the fatty acids, and the percentage of free fatty acids. This is convenient to use when only the latter figure is determined, the appropriate value for the M.M.W. being taken from the table above.

Diagram 3 gives the percentage of glycerin liberated, and Diagram 4 gives the total percentage of fatty acids, both from the same data.

In every soapery losses of fatty acid and glycerin are bound to occur, and in addition more than the theoretical amount of caustic soda will be used. Such losses if not carefully checked will almost certainly be higher than they need be, and the correct ascertainment of the quantities of fatty acids, etc., in the materials bought is the first step in determining them. When suitable steps have been taken to determine the actual amounts of fatty acid and combined alkali which leave the factory as soap, and the amount of glycerin in the crude produced, the percentage losses in these materials are seen at a glance. By applying corrections corresponding to these losses to the figures obtained as above it becomes possible to tell with accuracy how much fat, etc., and how much caustic soda will be

required for a ton of any particular soap, and knowledge of the amount of glycerin that may be expected as by-product provides a reliable item on the credit side. These particulars are essential for any accurate costing.

Soap makers frequently have occasion to consider modifying some of their soap charges, or to introduce new charges to suit some specific purpose. In these cases it is necessary to determine the probable cost with reasonable accuracy, but generally one has to consider the average composition of materials of certain types rather than the analysis of any one lot. For such purposes the nomograms are quite sufficiently accurate, and save a great deal of calculation. They have the additional advantage of enabling one to examine rapidly and compare the figures of a number of alternative charges, more than would probably be worked out if the calculations had to be made in the ordinary way.

The Properties of Raw Materials.—A vast number of natural oils and fats are known, all of which are capable of being used in the manufacture of soap. Some are, however, of minor importance to the soap maker and many others are not available in large quantities, or are relatively too costly, so that the list of soap-making materials in common use is limited to a dozen or two. An enormous amount of experimental work has been carried out on the chemical and physical properties of these materials, and information with regard to the proportions of the various fatty acids in the composition of different fats, their mean molecular weights, iodine values, "titres," and so on, is available in the specialised literature on this subject, and need not be given here. It may be useful, however, to give a few general ideas on the outstanding properties of some of the most important materials.

Tallow is the best known of all soap-making fats. Most of it is either beef or mutton tallow, although a good deal is sold which is a mixture in unknown proportions of the two. Tallow when well made, is practically white, but much of the material on the market is of very poor

colour and decidedly strong odour. The best qualities of beef tallow are largely used for toilet soap; mutton tallow may be even better in colour but seems to have a greater tendency to rancidity. Tallow fatty acids are largely stearic and oleic, with an average molecular weight of about 280. The titre, or setting-point of the fatty acids is variable, usually in the case of beef tallow from about 41½° to 45°, mutton tallow tending to be somewhat higher. Tallow soap is not readily soluble and is not therefore used by itself for domestic soaps. It is hard, and when in solution makes a firm and fairly permanent lather. Its detergent properties are best developed at fairly high temperatures.

Greases are essentially tallows, but have a somewhat lower titre and higher iodine value. They are seldom of very good colour or odour, though there are exceptions. The soap is somewhat softer and more soluble but does not otherwise differ greatly from tallow soap.

Hydrogenated oils are extensively used as tallow substitutes. Those at present on the market are mainly from whale and fish oils. Now that the preliminary difficulties in their manufacture have been largely overcome they are useful products, having only a slight odour and forming soaps not differing greatly in their essential properties from tallow soaps. The process of hydrogenation, which consists in saturating the double bonds of the unsaturated constituents, is not carried to completion, but only far enough to produce a fat having as nearly as possible the essential properties of tallow. It is interesting to note that the titre of such a fat is several degrees lower than that of the tallow of corresponding properties. This test, in fact, while of some use in discriminating between tallows for different purposes, has less value as applied to other materials.

Other oils than the above may be hydrogenated if the market conditions are favourable. Thus hardened linseed and cotton-seed oils were at one time used extensively, but at present the seed oils are too dear for this purpose.

Palm-oil soap is not far removed in its properties from

tallow soap. The oil has a very high natural colour, and when reasonably pure a strong but rather agreeable smell. The west coast of Africa was formerly almost the sole source of supply, and much of the oil was extracted by the natives in small quantities by very primitive methods. In this oil the glycerides were to a large extent decomposed, in certain kinds almost completely so, and consequently the oil, consisting very largely of fatty acids, had a much higher melting-point than oils made under better conditions. From its tendency to remain solid at a high temperature it was classed as hard oil. In such oils the colour has changed, so that occasional lots may be brown or almost black, and the odour was often offensive. Oils with a lower fatty acid content became known as medium or soft oils. Nowadays large quantities of factory-made oils much superior in purity are available.

For practically all purposes palm oil must be bleached before use, and generally speaking the lower the fatty acid content the better will be the colour of the fat after bleaching. The orange colouring-matter, similar to that of carrots, is a natural constituent of the oil, and is present even in the best oils.

Coconut and palm-kernel oils can be classed together. Both contain large quantities of lauric acid, the lowest acid which has any value for soap making. They are invaluable for mixing with other oils to confer on the soap greater solubility and readiness of lathering. The average fatty acids of coconut oil have a lower molecular weight, and also include rather less of the unsaturated acids than those of palm-kernel oil, and thus the characteristic properties are somewhat better developed in the former than the latter. The soaps made from them are hard and tend to confer this property on a mixture. Good oils are nearly colourless, some coconut oil being almost snow-white. The only objection to these materials is the tendency of their soaps to irritate the skin. This is probably due to some specific action of the acid radicles of the lower acids, and not to the fact that the combined alkali is higher than with other soaps, the amount of alkali

liberated by dissociation being actually lower. In mixture with other fats up to an amount of about twenty per cent this effect is not generally noticeable, and such a proportion is largely used in toilet soaps, but amounts exceeding twenty-five per cent or so should generally be avoided.

Seed oils differ considerably, but have certain characteristics in common. Most of them have considerably higher quantities of unsaturated acids, including some with two or more double bonds, than tallow and palm oil, and the soaps even of the best of them are softer. In making hard soaps cotton-seed and soya-bean oils are probably the most used, though soft-soap manufacturers make use of certain others, such as maize and linseed oils.

Olive oil, even the most impure quality, is an expensive raw material, and is not used to any great extent in ordinary soap charges. In certain quarters it is assumed to have merits of a special kind, but there does not seem to be any justification for the special claims made for it. The different qualities and makes differ a good deal in composition, but so far as is known there is no outstanding difference between it and other oils of the same class to suggest its having exceptional properties. As olive oil is produced in large quantities in the Mediterranean countries the poorer qualities were naturally largely used there for soap making, and the tendency in the silk industry to prefer soaps made from this oil is probably due more to the fact that in the early days of that industry such soaps were the most readily available to the silk manufacturers of southern France and Italy than to any intrinsic merits.

Among commercial oils arachis oil is the one which comes nearest in composition to olive oil, but it is somewhat inferior to the latter owing to its containing some 5 per cent of saturated acids higher than stearic, which affect the solubility and lathering properties of the soap. The odour is not altogether unpleasant but slightly mawkish. At a suitable price it is a useful constituent of soaps for use at medium temperatures.

Rosin is a constituent which was probably used in the

first instance solely on account of its cheapness. It forms a soda compound which dissolves freely in water, and the solution foams readily. In chemical constitution it has no near relationship to the fats, and yields no glycerin. It is obtained by distillation of the natural exudation from various kinds of pine, the volatile portions constituting turpentine and the still residue the rosin as used by soap makers. In colour it may vary from extremely pale yellow through various stages to nearly black, and it is sold according to its colour grade. The odour is generally considered pleasant, especially in masking the odour of tallow, and modifying that of palm oil and some of the seed oils.

Rosin soap has in itself no detergent power, but if mixed with fats that yield hard and relatively insoluble soaps, such as tallow and palm oil, it may in one way improve their washing properties. Soaps made from these fats alone require a temperature near to boiling-point to give the best results, and the addition of rosin, in much the same way as the addition of nut oils, makes the soap more soluble, and along with this property goes that of being more suitable for use at a lower temperature. For ordinary purposes about 25 per cent of rosin in the charge is considered to be the maximum, chiefly on account of the softening effect of rosin on the soap. In the cheap glued-up soaps, in which pure soap is mixed with very strong silicate and carbonate solutions, larger amounts can be used, frequently 35 per cent or even more.

Rosin should not be used in the charges for soap powders, as it tends to make the soap tacky. It is considered a desirable component of the charge for toilet soaps, in quantities of 1 to 2 per cent, as it diminishes the risk of rancidity.

For imparting the characteristic odour to the soap American rosin is the most esteemed. A different type of material made in America by extraction of the wood of tree stumps has somewhat different and in general less desirable properties.

The Composition of Soap Curds and Neat Soap

The series of experiments which led to the development of a new method in soap boiling consisted in the first instance merely of attempts to copy the composition of the mixtures which occur in the different stages of large-scale boils. The first of these were made on the fitting operation.

It is known that if a sample of a few hundred grams is taken from a soap pan immediately after fitting, and maintained for some hours at a temperature near 100° C. it will separate into neat soap and nigre in the same way as the mass in the pan, and one would therefore expect that if a similar quantity could be made up to identically the same analysis it should behave exactly similarly. It is not practicable to make up such a mixture from pure soap, salt, glycerin, and water, and therefore in early experiments amounts of a few hundred grams of fat were saponified, grained, and washed, with the idea of making a curd identical in composition with that produced in the soapery. The first experiments failed, because the curds obtained, which had been produced by purely rule-of-thumb methods, were found to contain a lower percentage of fatty acids than those made in the pan-room, and thus the conditions for the rest of the experiment could not be exactly copied. The cause of this was not at first understood, and in order to clear up this problem a large number of samples of curds and the corresponding lyes were taken from manufacturing pans and analysed.[1] Fatty acids were determined in the curds, and salt in both curds and lyes. The analyses showed that the percentage of salt in the lyes from the large pans was in general lower than that in the small-scale

[1] In analysing samples of soap curd it must be remembered that a curd is not uniform throughout in its composition, owing to the fact that the separation of lye from it is always incomplete, so that two separate quantities taken for the two tests may not be quite identical in composition. The best way to get over this is to take a sample of several hundred grams from the pan and make this homogeneous by carefully mixing a weighed amount of it with a weighed amount of water. The analyses of this sample are then of course calculated back to the original amount of curd taken.

experiments, and also that lyes from any one kind of soap in the pan-room tended to vary in strength quite considerably; moreover those with the highest salinity were as a general rule accompanied by the curds poorest in soap, the richest curds being obtained when the salinity of the lye was below the average. This fact solved the immediate problem and it was found possible to obtain rich curds in the small experiments by producing lyes with the minimum salinity. The application of this fact on the large scale led to similar results.

The figures obtained in the course of these experiments led to a further result of great interest. It was found on scrutinising the figures that a certain numerical relationship existed between the percentages of salt in the lyes and the curds, and of the fatty acids in the curds. This may be expressed as follows:—

$$\frac{\text{Percentage NaCl in curd}}{\text{Percentage NaCl in lye}} = 1 - \frac{\text{Percentage F.A. in curd}}{100} \times K,$$

K in this case being constant, or very nearly so, for all soaps. Its mean value is 1·515, variations being almost all within the range 1·50 to 1·53.

This fact, coupled with what is otherwise known about curd soap, throws a useful light on its composition. A sample of ordinary curd, if allowed to settle for some time at a temperature near 100° C., will often separate a further amount of lye, and if it is spun while still hot in a centrifuge a relatively large amount of lye can be removed, taking with it possibly four fifths of the salt that was originally in the curd. If it were possible in this way to remove the whole of the salt from the curd in the form of lye there would remain a substance consisting of soap water and possibly glycerin only, and as the weight of this is K times the weight of fatty acid, it must contain $\frac{100}{K}$—*i.e.* $\frac{100}{1{\cdot}515} = 66$ per cent of fatty acids. In the author's own experiments the highest test obtained in the residual soap was about 64 per cent, with about ·3 per cent NaCl. We may thus say that a soap curd is either a mixture of lye with a soap

hydrate containing 66 per cent of fatty acids, or conceivably of rather less lye along with a soap hydrate containing a very small proportion of salt. In either case we may say, "A soap curd may be regarded as consisting of soap hydrate containing 66 per cent of fatty acids and lye identical in composition with that from which it has separated." This has been called the 66 per cent rule. For the purposes to which the rule is applied it is quite immaterial whether the whole of the lye is mechanically separable from the soap hydrate, or whether the greater part is separable while a small fraction forms a homogeneous mixture with the true soap hydrate.

This rule is found to hold good in any conditions that may occur during the course of a normal boil of soap. In ordinary circumstances there are other substances in the pan in addition to soap, water, and salt, the only ones of importance however being sodium hydrate, sodium carbonate, and glycerin. With regard to the last-named, special experiments were made to determine whether quantities even greatly in excess of those generally present could affect the rule, but it was found that they did not. It is known from other investigations that glycerin is distributed through all the water in the pan, not merely that in the lye, and on account of the close chemical relationship between glycerin and water it is easy to understand that a mixture of glycerin and water may quite well take the place of water alone in the hydrate without otherwise affecting its composition. The alkalies behave towards soap in a similar way to salt, though in a different degree, and thus any amount of either of them may be considered as equivalent to a certain amount of salt, and their distribution between the curd and the lye must necessarily follow the same rule.

Though one might expect variations in the physical conditions, such as atmospheric pressure and boiling-point of the liquid, to produce small variations in the composition of the hydrate, in practice these are generally too small to have any measurable effect. An interesting departure from the rule was however found on boiling a

soap made from arachis oil on a strong salt solution. This soap is normally very soft, and the attempt was made in the hope of obtaining a curd which would set hard. It was boiled on a salt solution which was gradually increased in strength. No marked effect was obtained until the strength of the salt solution approached 17 per cent, but continued boiling on this lye produced a soap of satisfactory hardness. When tested this was found to contain a percentage of salt which pointed to a hydrate containing about 70 per cent of fatty acids. The experiment indicates that variations from the rule may occur when the conditions are quite abnormal but not with such variations in the salt content of the lye as may occur in ordinary practice.

The accuracy with which the rule holds good in ordinary conditions is illustrated by the following figures. Eleven examples were taken at random from a long series of tests made on commercial boils of different types of household soap. The analyses were made by the usual routine methods. In these experiments it was possible to weigh both the curd and the lye, and also to determine the total amount of salt in the pan, so that there was a check on the figures. In only two cases was there any notable divergence from the 66 per cent rule, these being marked *, and in both these cases there was a slight divergency

F.A. in soap %	NaCl in lye %	NaCl in soap %		F.A. % in soap hydrate
		Found	Calculated	
53·7	9·5	1·76	1·76	66·0
52·3	9·1	1·87	1·89	65·9
54·6 *	9·0	1·44	1·56	65·0
57·8	8·8	1·10	1·10	66·0
56·0	8·7	1·33	1·32	66·1
53·5	9·1	1·69	1·71	65·7
57·1 *	8·2	1·17	1·10	66·6
57·8	9·4	1·17	1·17	66·0
58·0	9·1	1·12	1·10	66·2
56·7	9·2	1·34	1·30	66·3
54·7	9·6	1·68	1·65	66·3

between the total amounts calculated from the tests and that known to be in the pan. Experience shows that possible errors are not likely to exceed these in amount.

The 66 per cent rule is of great value in controlling the operations of graining and fitting, in fact the whole of the rational system of control depends upon it, as will be shown later. It is expressed graphically in Diagram 5, which will be found useful in all practical applications of the rule.

The term "free solution" on the diagram requires explanation. The water in a soap curd is partly in the entangled lye, and partly combined with soap to form the soap hydrate. It is natural to refer to the latter as combined water, and in this case one might refer to that in the lye as free water. Now the lye is the portion of the curd which is mainly affected by the water added in the process of fitting; possibly the whole of this water goes in the first instance to the dilution of the entangled lye. In the rational control of the fitting process it is necessary to take into account the composition of such diluted lye, and it is convenient to have an expression which denotes the lye in either its original or diluted state, quite apart from the soap hydrate which ultimately dissolves in it. This is the sense in which the expression free solution is used.

With regard to the diagram it may be stated that when, on fitting, the free solution is diluted to a known extent, so that the percentage of salt in it is known, the percentage of salt in the neat soap can be deduced from the salinity of this solution and the fatty acid percentage of the neat soap, in other words the composition of the neat soap agrees with the 66 per cent rule, the (diluted) free solution in this case taking the place of the lye in the system curd soap and lye. Thus, if the salinity of the free solution and the fatty acid percentage of the neat soap are known, the percentage of salt in the latter can be read off from the diagram. To take an example, a neat soap of 63 per cent fitted with the free solution at 8 per cent will contain ·36 per cent NaCl; conversely if a neat soap

contains 63 per cent of fatty acids and ·36 per cent NaCl the free solution must have contained 8 per cent NaCl.

A knowledge of the nature of the soap curd makes it easy to understand what happens in the operation of fitting. The curd is boiled up with water, and as soon as the percentage of salt in the free solution is reduced below a certain limit it will begin to dissolve soap. If the operation is stopped at this stage the contents of the pan will settle into two layers, the lower layer now consisting of a weak solution of soap in the free solution. After each further addition of water the free solution becomes further diluted, and it becomes capable of dissolving more and more soap. The successive stages are what are known as coarse, medium, and fine fits respectively, though these phrases have no exact significance, but merely denote roughly the appearance of the soap when submitted to the usual test on a trowel. During these stages the solution which will form the lower layer, otherwise the nigre, dissolves more and more of the soap from the upper layer, and thus diminishes the amount of neat soap, which is the main product. At the same time the composition of the latter also undergoes changes. The neat soap from the coarsest fit, apart from certain exceptional cases, has a high fatty acid percentage, often well over 63 per cent, but this slowly diminishes through the successive stages of increased dilution of the free solution. In ordinary soap pans these changes cannot be continued indefinitely, as the settling into two layers becomes slower and slower the more the free solution is diluted, and in practice it is found that a limit is reached when the neat soap contains about 60 per cent of fatty acids. The fatty acid content of the nigre corresponding to this varies somewhat according to the mixture of fats employed, but is usually rather above 40 per cent.

There is at present no explanation available as to the cause of this variation in the composition of the neat soap, but the change is progressive, and it is easy to obtain data from experiments which enable one to control the fitting so as to produce a soap of any required fatty acid

percentage within the limits between which this is practicable. In endeavouring to gain an insight into the nature of the neat soap it is well to consider what is known about soap curds. The mass constituting a soap curd is obviously heterogeneous. The action of gravity causes the bulk of the lye formed to separate from the curd, but leaves a variable amount entangled in it. It can be decided only by experiments more exact than any that have been published whether the curd as we know it consists of a soap hydrate entirely free from salt, and lye containing the whole of the salt present, or of a soap hydrate containing a small amount of salt plus some lesser amount of lye. In the case of neat soap the nature of the upper layer is obviously different. Beaker samples taken from a pan on fitting, and allowed to settle, separate extremely sharply from the nigre, a mirror-like surface usually separating the two layers. The neat soap has every appearance of being homogeneous, at least in the sense of its not containing separable phases. Although the analysis is that which would be given by a mixture of 66 per cent soap and nigre, or what amounts to the same thing, of 66 per cent soap and free solution, it is almost inconceivable that such a mixture, even if in the form of a very fine dispersion, would be perfectly stable and would have a composition which is evidently fairly sharply defined by the concentration of salt in the free solution, and there are other reasons which make this suggestion very improbable. Thus the weight of the evidence goes to show that the neat soap is a soap hydrate of a composition which varies according to the concentration of salt in the free solution, always containing more water than the hypothetical 66 per cent hydrate, and containing a small amount of salt which increases with the increase in the degree of hydration.

One would naturally assume that the nigre which is in equilibrium with any particular neat soap should be considered as a solution not of the 66 per cent hydrate but of the particular hydrate which constitutes the neat soap, in the free solution. Owing, however, to the fact

that such hydrates seem always to be of the same composition as a mixture of 66 per cent hydrate and the existing free solution, the composition of the latter cannot be affected by the fact that the hydrate may contain salt.

The results of some experiments which show the relationship between the test of the neat soap and the salinity of the free solution are given in Chapter V. In the meantime one cannot claim to understand all the principles which govern this phenomenon, but there is no difficulty in making soaps to any required standard within certain limits with the aid of a few experiments to give the necessary data.

One other matter may be briefly disposed of before leaving this subject. It is often stated that the composition of the neat soap is not fixed but varies through the mass, the upper layers having a higher fatty acid percentage than the lower. This matter has been disregarded in what has already been said because this effect, even though it may exist, should ordinarily be only trifling in amount. Soap is normally fitted at a temperature slightly over 100°, and samples allowed to settle completely at this temperature separate into two exceedingly well-defined layers, as anyone can see for himself by inspecting a well-settled beaker sample. In a soap pan, on the other hand, the temperature is gradually falling, and the effect of the electrolyte is enhanced by a lower temperature. Thus neat soap, if fitted at about 100°, might be expected, if it were cooled to 90° and maintained at that temperature, to undergo a secondary separation, thus liberating minute globules of a nigre somewhat weaker in soap than the original. Such globules, on account of their small size, would tend to sink through only a portion of the depth of the neat soap, and thus it is easy to understand a tendency for the lower layers of neat soap to be contaminated with them to some extent, thus reducing the percentage of fatty acids found in them. But the importance of this effect depends altogether on its amount. If the pans are well lagged and fairly free

from draughts the difference between upper and lower layers is negligible, though it might be noticeable in relatively tall, unlagged pans much exposed to cold air. The arguments for lagging pans well, even with an exceptionally good insulating material such as glass wool, far outweigh those against doing so, and in a well-planned soapery this matter is of minor importance.

CHAPTER III

EXPERIMENTAL BOILS

Experimental boils—boils on a miniature scale made by an exact method—the requirements for adapting this method to the manufacturing scale—method of weighing the contents of a soap pan.

Experimental Boils.—Most soap makers produce a large variety of soaps, to suit the requirements of different trades and localities. Some of these remain as far as possible of a constant composition year after year. Many, however, may be slightly modified without detriment, and this is frequently done as new classes of material become available, and others dearer or more difficult to obtain.

Now that the approximate composition of all the common fats is known, it is quite possible to work out the proportions of the various fatty acids present in any soap charge, and it would be most convenient if one were able to standardise a charge in this way, and to make up the required composition from various mixtures of fat. In practice this is out of the question, owing to the complexity of the mixtures which make up any kind of fat, and the soap maker in compounding a new charge has to fall back on his experience of the properties of soaps made from different kinds of fat. In these circumstances one cannot be certain that a new charge will have the precise qualities required, and it becomes necessary, before taking it as a standard mixture, to make one or more experimental boils.

Such boils are often made in ordinary manufacturing pans, with as small a charge as possible, but this course may lead to difficulty. When much variation is made in a charge it is quite possible that the first attempt at a change may give a poor or even a bad result, and the disposal of this quantity of poor quality soap causes trouble, and possibly some expense if the soap has to be

mixed with one of a lower grade. Oftener still the trial boil may be fairly good with the possibility that a further slight modification might improve it further, but when large boils are made only a limited number of experiments can be carried out.

For these reasons it is preferable to carry out the experiments, in the first instance at any rate, on a scale sufficiently large to enable the soap to be framed and made into bars and tablets for examination, but so small that the quantities of soap produced, whether good or bad, can be easily disposed of in the working pans. For this purpose a few hundredweight of soap per boil are ample. Such a boil can be carried out from start to finish in less than two days, and the finished bars or tablets may be ready for examination in two or three days more. Ordinary soap from a large pan can hardly be examined in much less than a fortnight from the time the boil was started, but it is possible in this time to make quite a number of small-scale trials with varying proportions of materials and from these the best may be selected for making a large trial boil.

A pan suitable for this purpose is quite a simple affair. It should preferably have a dished bottom like an ordinary soap pan, and be fitted with a good sluice valve or gland cock for running off the lye. No skimmer pipe is necessary as the neat soap can be baled into the frame. A single open steam coil is sufficient for boiling, and there should be a water main at hand by which water can be run into the pan by a flexible pipe. No mains are needed for the materials used, as these can be delivered over the side of the pan, the quantities being weighed out on a platform scale. It is of great advantage to be able to weigh the contents of the pan by means of a gauge as described on p. 56. This may be of the simplest form and can be made on the spot. The gauge itself may be a thick glass U-tube some three to four feet long, the liquid used being water. If this is provided with a carefully calibrated scale very accurate results can be obtained; the error should not exceed about 3 lb. with 5 cwt. of soap in the pan.

the steam supply, adding a small amount of water if necessary. If the mass shows signs of becoming extremely thick this may be due to a temporary deficiency of alkali; the remedy is to add more caustic, and if that does not thin the mixture some brine may be added from the measure, which generally has the desired effect. Occasionally the reaction becomes too violent, and the soap begins to boil up in the beaker of its own accord. In this case shut off the steam and check the action by adding cold water. In half an hour or so all the alkali in the measure will have been added and the soap should appear as a smooth, thickish, and somewhat translucent liquid. The amount of caustic present will almost certainly be below the requirements, but tests should now be begun. For this purpose test papers are used, made by soaking filter paper in either a 0·5 per cent solution of Titan yellow, or a 0·1 per cent solution of thymolphthalein. With these indicators the colour change, to pink in the case of the former, and to blue in that of the latter, indicates the presence of free caustic soda in the mixture; the common indicators, litmus and phenolphthalein, are affected by the sodium carbonate always present and are useless for this purpose. To test the soap take about 1 c.c. in a small heated basin and mix with it a few drops of brine. A piece of test paper dipped into the lye which separates will indicate the presence or otherwise of an excess of caustic. If more is required run in a few c.c., boil up for a minute or two, and test again. This should be continued until the reaction for free alkali persists after further boiling, and when this is the case saponification may be taken to be complete, and the mass is ready for graining out.

At this stage the contents of the beaker may be considered to consist of soap hydrate and water, the amount of the former being 1·515 times the weight of fatty acids present—that is, in this case, 606 grams. For the sake of argument we may assume the total weight to be 820 grams, leaving 214 grams of free water. There has now to be added such a quantity of brine as will make with the free water a solution of salt of the strength required

in the lye. This strength may be known from previous experiments; failing this, one must assume a probable percentage, which in this case is likely to be about 10 per cent. The required amount of brine for this is read off from diagram 6 as 134 grams, which at S.G. 1·2 equals 112 c.c. This amount is measured out, and preferably brought to the boil before being added to the boiling soap in the beaker. After a minute or two the steam is shut off and the contents allowed to settle. If the salt solution is too weak there will separate not a true lye, but a very weak soap solution, in other words a nigre. To test for this simply withdraw a small quantity of lye and cool it. It should remain quite fluid, but if it sets to a jelly some more salt must be added, and any such additional amount should be measured.

About thirty minutes is usually allowed for settling, and the lye is then pipetted off and weighed. The contents of the beaker are also weighed, and from the weight of the curd is ascertained its fatty acid percentage. Thus if the curd in this case weighs 730 grams, the percentage of fatty acids in it is $\frac{400}{7{\cdot}3} = 54{\cdot}8$ per cent. Considering the short time allowed for settling this would be considered a good result. The weight of the beaker contents less that of the soap hydrate, in this case 606 grams, gives the weight of free solution, and as the amount of salt is known one now knows the percentage of salt in the lye required to grain out satisfactorily.

The next operation is a wash. The curd is re-dissolved in water and once more thrown out of solution with brine. In this method the amount of lye produced need not be left to chance, and it is desirable in large-scale working to produce a definite amount, as successful glycerin recovery depends upon the ability to do so. In this case assume that 4 parts of lye are to be produced for each 10 of fatty acid, an amount which should remove about one third of the glycerin remaining in the curd. This will be 160 grams of lye, and if the strength of the lye is 10 per cent NaCl 16 grams of salt will be required, an

amount contained in 62 grams of brine. (Note that the salt in the curd can be disregarded, as it is already in the form of a salt solution of this strength.) Thus 98 grams of water and 62 grams of brine are required for the wash. First add the water, which should be boiling, to the boiling soap in the beaker, and when the contents appear to be smooth and homogeneous add the 62 grams of boiling brine. Lye should once more settle out and if the curd has the same weight as the first the amount of lye will be 160 grams, as required. Actually successive curds are not likely to be quite identical, and on that account the amount of lye will probably be slightly different from that calculated. Thus if this curd weighs 715 grams, corresponding to a fatty acid content of 56 per cent, the amount of lye withdrawn will be 175 grams instead of 160 grams, from a more watery curd one withdraws correspondingly less lye. With careful graining these variations are unimportant. Further washes, if required, are made in exactly the same way.[1]

The soap may now be fitted. From the weight of the curd the amount of free solution is calculated. Say in this case the curd weighs 715 grams, the weight of free solution is $716 - 606 = 110$ grams. The operation consists merely in working water into the soap in such quantity as to dilute the free solution to some predetermined extent. Dilution to about 8·5 per cent NaCl would produce a coarse fit, the nigre from which would contain less than the average amount of soap. A high dilution, on the other hand, enables much more soap to dissolve and produces a very smooth fit. To dilute the 110 grams of free solution to 8·5 per cent requires only 19 grams of water, while to reduce it to 5 per cent requires 110 grams. There is thus a very wide range over which the soap may be said to be fitted, and the operation as usually carried out on the manufacturing scale is not at all exact. In this case a medium fit may be chosen, aiming at a dilution

[1] No regard is paid to the appearance of the soap, but it may be interesting to the experimenter to note its appearance both in the beaker when steam is shut off, and on a steel spatula used in the same way as the soap boiler's trowel.

of the free solution to 7·5 per cent. This will require the addition of 37 grams of water, and the final weight of the mass should be 753 grams. On boiling up the curd once more with steam any water condensed should in this case be allowed for, as the total of water to add is only small. The soap should therefore be well boiled until it rises nearly to the top of the beaker, and the contents weighed again. It will probably now require only some smaller quantity, say 25 grams, to make it up to full weight. Now add rather less than this, say 20 grams, of boiling water, boil up the soap again for a minute or two, and the operation is finished.

The beaker should be covered with a clock-glass and kept near to boiling-point for several hours. The separation into neat soap and nigre is usually extremely good. After cooling and removal in one block from the beaker, the nigre and the surface crusts are cut away from the good soap for examination. The neat soap should weigh 400 grams or more.

When this method is used to form an opinion on the soap-making qualities of any particular sample of fat it is best carried out just as above, so as not to confuse the result by the admixture of other fats or of dirty materials. On the other hand, if the experiment is made with the object of judging the quality of a new charge, the necessary complications which occur in the manufacturing scale can quite well be imitated, in the beaker experiment; thus nigre, scrap soap, and rosin can be dealt with at the appropriate stages, and the soap may even be bleached in the beaker with hypochlorite. In the latter case the whole of the chlorine in the bleaching liquor after the bleach is finished must be assumed to be present as sodium chloride, and must be allowed for on graining.

On examination of this method of making soap it is evident that no modification is made in the essentials of the process; the only alterations are in the methods of ascertaining what are the correct quantities of caustic soda, salt, and water to be employed. The alternatives to the ordinary tests used by the soap boiler when working

on the large scale are perfectly simple, and no practice is required to carry them out successfully. It is clear that this method has advantages over the ordinary procedure in making it possible to produce definite amounts of lye on each change, a matter which is essential to the economical recovery of glycerin, and also in the ability to modify the nature of the fit to suit varying circumstances.

In the conventional method of soap-boiling the finish of each operation is judged by tests which are too vague to be altogether satisfactory, and it usually takes months of training before a soap boiler becomes reasonably expert. By making use of simple methods of measurement such as those just indicated this kind of expert knowledge becomes superfluous, and in a short time any good process worker can learn to carry out all the operations with a degree of precision not usually possible.

The Requirements for adapting the Quantitative Method to the Manufacturing Scale

In employing this method no alteration is made in the ordinary course of the operations; the modifications consist solely in the adoption of other means of deciding what are the correct amounts of caustic soda, salt, and water required to give the best results in the three main operations. To do this it is necessary to know with tolerable accuracy the amounts of the chief components of the pan. These are soap, salt, and water, and in practice the two constituents of soap, fatty acids and alkali, must be taken into consideration.

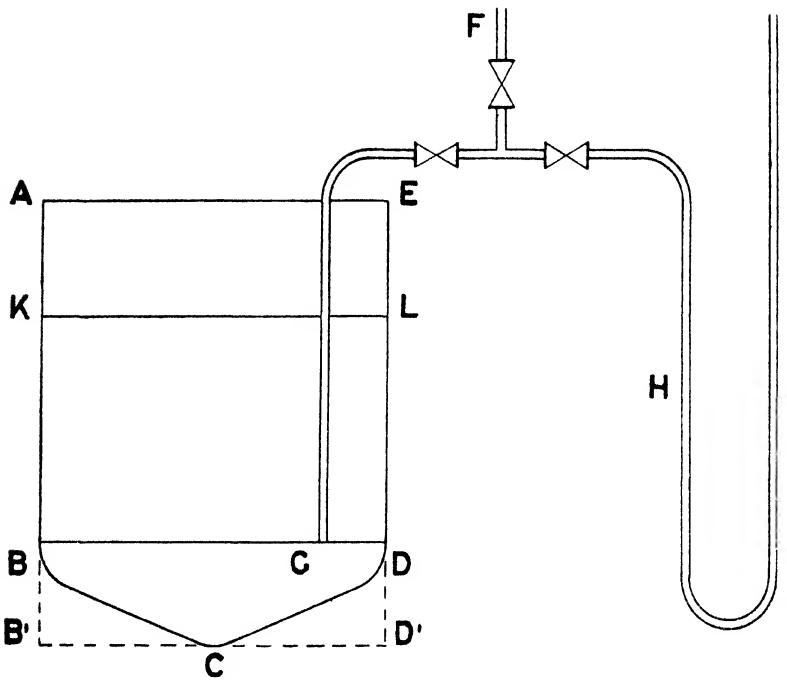
In most cases the bulk of the fatty acids in a pan is supplied by the fats. If the general control in the factory is good the exact amount of fat charged to a pan is known, and the amount of fatty acids obtainable from it determined as just described. When rosin is used the amount of this is usually weighed out to each individual pan. The percentage of rosin acids obtainable from the rosin is rather variable, mostly between 92 per cent and 98 per cent, but is generally fairly constant for any grade,

so that average figures can be employed. Fatty acids may also enter the pan as scrap soap or nigres. In works where due attention is paid to details the scraps are always weighed before returning to the pan, as a check on wasteful cutting and on the production of bad soap. The amount of fatty acids in nigres and crusts left in a pan is determined almost automatically in this process, and thus there is no difficulty in ascertaining the total fatty acids present in a pan at any stage. Caustic soda is readily gauged to the pan from a feed tank. The most convenient type of gauge for the purpose is one of the pneumatic type, which gives correct reading independent of the specific gravity of the liquor. In this case water may be conveniently used for the actual gauge, which can be made in the works at the cost of a few shillings. Brine is similarly gauged to the pan; if solid salt is used it may be weighed, but allowance must then be made for the fact that it may contain well below 100 per cent NaCl.

The Principle of Determining the Amount of Water by Difference.—The same device that is used on the small scale for determining the amount of water may be used, that of weighing the pan contents and arriving at the amount of water by difference. Since in this case it is not possible to weigh the pan with its contents, some method of gauging the latter must be adopted. The pneumatic method is usually applied only to flat-bottomed tanks, and its adaptation to a vessel such as a soap pan, which has a dished bottom partially filled with pipes, makes a certain complication, but this may be overcome, as will be seen, without much difficulty.

In the diagram consider first ABDE as representing a flat-bottomed tank. GFH is a system of tubes, of which H represents an ordinary U-tube water-gauge. F is a branch tube through which air can be led under pressure, and stopcocks are provided on each of the three branches. Liquid in the tank stands at any level, such as KL. If air is blown into the left-hand tube until bubbles emerge, and the tap at F be then closed, the air in the tube will be under a definite pressure due to the head of liquid

between G and KL, and if the tap to the gauge is now opened this pressure will cause the liquid in the gauge to sink in the left-hand and rise in the right-hand arm, and if the liquids are identical, say water, the difference in level between the two arms will be equal to the height



from the bottom of the water in the tank tube to the surface KL. If liquid of some other specific gravity is in the tank a mass of the same weight, although standing at a different level, will show the same pressure on the gauge, and in general for a given tank the weight of liquid, irrespective of its specific gravity, is correctly indicated on the gauge if the scale of the latter is correctly made to apply to the tank in question. This fact makes this type of gauge particularly suitable for substances such as chemical solutions or oils, which vary in specific gravity, as the latter does not have to be taken into consideration

as when the volume is determined by dipping or by a float gauge.

A soap pan may be diagrammatically represented by the complete figure ABCDE. The level of the tube being still on BD, and the surface of the liquid at KL, the gauge will evidently still measure the mass of liquid in the space KBDL. The mass of the liquid in the pan would thus be that indicated on the gauge, plus that of the liquid in the dished portion of the pan. Suppose now the orifice of the tube to be placed at the extreme bottom of the pan. In this case the reading on the gauge represents a quantity of liquid which would be contained in a tank continued downwards to a flat bottom passing through C, that is to say, it is higher than the real amount in the pan, and a certain weight must be subtracted from the gauge reading. Between these two positions there must be one at which no correction need be made, and that is obviously the position at which to place the orifice of the tube. This imaginary plane would include between itself and BD a space equal to the volume of the dished portion of the pan. Below this is a small volume of which the contents do not affect the gauge. One must assume this to be filled with liquid of some definite specific gravity, and add the corresponding weight to the calculated figures for each graduation on the scale. This space, and also the variations in specific gravity of the soap under working conditions, being small, the error possibly caused by this assumption is practically negligible.

For use with full-sized soap pans it is found satisfactory to fill the gauges with mercury. They are not difficult to make, or they can be supplied by instrument makers. Some that the author found very satisfactory cost £5 apiece. These were provided with accurately engraved scales made according to measurements supplied by the customer, and were supplied in well-made cases, fitted with a three-way tap and other refinements. Careful estimates were made of the accuracy obtainable, and if made to careful measurements it is found that the error should not exceed at most ½ per cent. Gauges of the

Bourdon type might probably be found at least as convenient, and probably a good deal cheaper. There is no absolute necessity to have a separate gauge for each pan, but it is hardly likely that two pans could be found so absolutely identical in measurement that the same weight scale could be used for both. Unless they are, it is better to graduate the gauges according to pressure, and read off the corresponding weights from a table made for each pan. By doing this one gauge could be made to serve quite a number of pans.

If the tank tube is left with a plain open end, as indicated at G, two small errors are possible. In the first place, when the tap to the gauge is opened a small amount of air must pass into the latter; the liquid at G will rise slightly in the tube, and the gauge thus read slightly too low. On the other hand, it is possible for a bubble to form at G, which if it is not detached will in effect lengthen the tube and cause the gauge to read too high. It is better therefore to screw on to the end a bell-shaped expansion, which is closed at the bottom, a row of small holes being bored through the sides, as near to the bottom as possible. Any bubbles formed are immediately broken off, and the upper part of the holes forms the true datum-level. In addition the passage of one to two c.c. of air out of the tube causes such a minute rise of the liquid in the expanded tube that the effect cannot be detected on the gauge. Those who construct their own gauges should not omit this small refinement.

CHAPTER IV

THE SOAP-BOILING PROCESS

The soap-boiling process—saponification and the other operations before fitting—the bleaching of soap in the pan.

Soapery Equipment and the Soap-Boiling Process. —The pans in which soap is boiled are either circular or rectangular in plan. Rectangular pans have the advantage of economising space, but are slightly more expensive for a given capacity. Circular pans having no corners, there is not the same tendency for masses of the soap to form backwaters and so hinder perfect mixing, and many prefer them on this account. Ordinary sizes for manufacturing may be from 6 to 15 feet across, and occasionally more. With regard to depth, there seems to be a convention among manufacturers of soap plant to make the depth equal to the width. Apart from the trifling saving in material for a given capacity this is bad practice unless the pans are very large. When the material in a pan separates into two layers, as in the case of soap, there is always an intermediate zone, containing much good soap which cannot be got off free from the lower layer, and this amount is relatively more in a shallow than in a deep pan. Small pans therefore, measuring 6 to 9 feet across, may advantageously be made 9, 10, or 11 feet deep if conditions permit. Pans are almost invariably made of mild steel, and most existing pans are built of riveted plates, but probably modern welding methods make an even better job. A pipe, generally 4 to 6 inches in diameter, which moves on a swivel joint near the bottom of the pan, and has a slot several inches long in the casting forming its free end, serves to remove the upper layer of soap from the pan. Heating is always by steam, and almost invariably by open coils disposed around the bottom of the pan. There may be two to four of these coils, each controlled

by a separate valve. The steam should be trapped near to the pan so as to avoid the entrance of unwanted water. The steam-pressure may well be anything between 60 and 100 lb. In some soaperies a few pans are sometimes provided, in addition, with close steam coils, to use in cases when it is undesirable for steam to condense in the soap, but for most purposes these are unnecessary. The pans may generally with advantage be lagged, the most efficient lagging being probably glass wool, suitably protected with wire-netting and a facing of cement. The opinion was some time held that a pan after fitting should be allowed to cool considerably in order to give good settling, but this idea is exploded. The good soap in a well-lagged pan leaves the sides more completely than in one which may cool rapidly, and in cases in which a really smooth fit is required the settling is much more satisfactory if the soap is not allowed to cool too much.

The materials—fats, caustic soda, brine, and water—should be led into the pan through pipelines, and these generally deliver over the top of the pan. If the water and aqueous solutions are led straight over the side there is a tendency for them to plunge in an unbroken mass right to the bottom of the pan and to take an appreciable time before mixing properly with the contents. A much better arrangement is to fix a shallow cone, 12 to 18 inches in diameter, a little above the middle of the pan, and to lead them over this. They are thus sprayed out into a thin sheet, and enter more quickly into reaction with the mass in the pan.

The First Change: Saponification.—In the small-scale experiment described in Chapter III nothing but fats and alkali solution were put into the beaker in the first instance, but it would have made no essential difference if soap in the form of nigre or scraps had been there to begin with. In large-scale practice this happens more often than not, but unless the amount of nigre is unduly large it tends to help rather than hinder the operation.

The fats are almost always delivered to the pan in a liquid state. Sometimes the whole charge is in the pan by the time it is convenient to start saponification, but the

operation may quite well begin before the whole of the charge is pumped over. Steam is first blown into the pan until the whole mass is in ebullition, and then strong caustic solution is run in. In carrying out the operation the following facts must be borne in mind.

Unless the fats are kept violently agitated they tend to form a layer at the top of the mass, and in this state, since reaction between fat and alkali can occur only at their common surfaces, it can only be slow. Violent agitation tends to break up the fat layer to some extent into small globules, which expose a much greater surface to the alkali, and the reaction can go on more readily. If soap is present in the pan to start with, the solution aids this emulsification, but otherwise the operation will go only slowly until enough soap has been formed to do so. If the fats used have a considerable percentage of free fatty acids the initial formation of soap goes on more readily, as the neutralisation of the free acids by alkali proceeds more rapidly than the decomposition of the glycerides. In order to get the operation well going it is necessary to have soap present in solution, and care must therefore be taken to add the caustic only in small quantity at first. There is always water present in the pan at this stage, and this dilutes the strong caustic used, but if too much is added the solution becomes strong enough to grain out the soap from the solution and it ceases to promote the necessary emulsification of the fat. The old idea that it is necessary to begin saponification with a very weak solution of caustic was correct enough at the time when pans were heated with fire and the operation often started with nothing but fats in the pan, but in modern practice caustic is usually stored at a strength of at least 70° Tw. and it is quite unnecessary to dilute it before use so long as care is taken not to feed it in too rapidly at first.

When the reaction is well under way the alkali becomes more and more quickly absorbed, and the aim of the soap boiler is to feed in the caustic lye so as always to have a slight excess. Familiarity with the changes in appearance of the pan during the operation makes this easy, but a

novice if in doubt should make occasional tests with test papers. Two possibilities of mishap should be guarded against: one due to lack of an excess of caustic, the other to having too large an excess present.

Failure to maintain excess of caustic may bring about the condition known as "balling" or "bunching." When this occurs the contents of the pan begin to thicken, and may in bad cases go almost solid. On the first sign of this happening caustic may be run in and the boiling kept as vigorous as possible. Some addition of salt may help in keeping the soap thin. On the other hand it may happen, especially when the reaction has gone somewhat slowly at first, and there is a possibility of a rather large temporary excess of caustic, that saponification begins to take place too rapidly, generating so much heat as further to accelerate the reaction. This may cause steam to be generated in minute bubbles throughout the mass, and the bubbles being too small to get free of the viscous soap cause the mass to swell rapidly; if this action cannot be checked the pan may actually boil over. This mishap has probably occurred in every soapery at some time or another, but generally the violence of the action can be checked in time. The procedure is to stop the flow of caustic and steam, take steps to cool the pan by tossing the surface soap with a paddle into the air, and by spraying in water, and possibly thin the mass by the addition of brine.

It is not at first an easy matter to learn to control the boiling by proper manipulation of the steam. A chemist who has occasion to carry out experiments on large pans will do well to familiarise himself with the general nature of the process by carefully watching the operations in the soapery on every opportunity, and then, if he has the facilities, carrying out small boils of a few hundredweights unaided. No serious mishaps are likely to occur on this scale, and after one has gained a practical familiarity with the operations it is just as easy to work small manufacturing pans, and after a little further practice to boil pans of any size. The art of the process, after learning how to keep the soap in the pan and yet boil it vigorously, is to become

familiar with the different appearances which the soap should have at various stages, and to detect any appearance which may indicate abnormal conditions.

The operation is completed when the whole of the fat is saponified with no more than the minimum excess of alkali. If this is left to the soap-boiler's judgment by the primitive means of taste and feel of the soap, he may if very skilful carry the operation to the correct finish, but experience shows that mistakes are often made, usually in leaving unsaponified fat in the pan. It is surprising that the use of test papers to indicate the presence of excess alkali, which has been in use for a generation or more, should not have become universal.

In times past, when soap makers were usually ignorant of the alkali requirements of fats, and caustic lyes were of very uncertain strength, any kind of scientific control was out of the question, and this method served its purpose. Nowadays the amount of fat charged to a pan should be accurately known, and the amount of caustic lye required is worked out in a few moments. If this amount is placed in a small feed pan, the soap boiler can draw on it freely, knowing that the whole quantity will be needed to saponify the fat. If there is any doubt of the accuracy of the figure some 2 or 3 per cent less may be measured out in the first instance, but there is generally a sufficient margin, as somewhat more than the theoretical quantity is always required. The advantage of being able to add the caustic freely until almost the end of the operation, instead of having to make tentative additions and frequent tests long before it is finished, is obvious.

When it is decided, in one way or another, that saponification is nearly complete, it is necessary to test the contents of the pan before adding more lye. A sample of the boiling soap is taken on a paddle and grained out with a little salt. If the lye that separates is sufficiently alkaline the pan is boiled up again for a minute or two and again tested; more alkali is added if the alkali previously present has disappeared. When, after repeating this operation as may be necessary, the lye shows a slight

permanent alkalinity it is safe to assume that saponification is complete.

There is no need in these tests to rely on the old method of testing the soap on the tongue. This test is in any case unsatisfactory as the sensitiveness to caustic soda varies with different individuals, but complete reliance may be placed on the reaction of thymolphthalein paper to the lye. This indicator remains colourless at any *p*H value due to the presence of sodium carbonate only, but small additions of caustic soda raise the *p*H value to a point at which the indicator turns blue. Samples of lye which if tested by the ordinary routine method are found to contain 0·01 to 0·02 per cent of caustic colour the paper a faint blue, 0·1 per cent causes an intense blue colour. A reasonable excess of caustic to have at the finish of the operation is shown by a palish blue on the paper.

There may be some who still believe it to be impossible to complete saponification at one stage. An interesting sidelight is thrown on this matter in a recently published book by Hefter & Schönfeld.[1] In the old type of fire-heated pan, in which all the heat was conveyed to the materials through the walls of the pan, the latter were necessarily at a temperature much above boiling-point. Whatever kind of pan is used, when saponification has passed the preliminary stage the soap solution gradually becomes strong, and as it ultimately dissolves the remaining fat the system becomes homogeneous and viscous. Such a solution will stick to the walls of the pan, and in the old fire-heated pans, with relatively hot walls and no steam jets to help to dislodge the soap from them mechanically, the soap, or at any rate the impurities in it, would readily char, and so discolour the product. It was customary in order to avoid this to keep sufficient electrolyte present to maintain the pan in an "open" (two-phase) condition. In this state the soap is mostly in large aggregates, and a large proportion of the water, containing much of the alkali and possibly a little soap, alone wets the walls of the pan, the masses of soap being

[1] *Fette und Fettprodukte.* Vol. 4. Julius Springer. Vienna.

unable to adhere to them. One notices this condition very well when a pan is being grained out. In these conditions, however, the rate of saponification is enormously slower than when fat and alkali are present together in a homogeneous solution, as only that portion of the fat will react with the alkali which is for the time being at the common surface of the soap and the lye. It was quite common in the old days for saponification, instead of being complete in an hour or two, to continue over several days, or even weeks. Each day, after an overnight settling, the lye was withdrawn and the operation started afresh, and thus there was no possibility of completing the reaction at one operation, but this was merely so because the saponification went too slowly to be complete in one day.

In modern practice the necessity of preventing the soap from sticking to the pan walls does not occur, and once the soap formed has made a solution strong enough to emulsify, and finally to dissolve the residual fat, the operation begins to go with great speed. When nearing completion it naturally slows up again as the concentration of the unaltered materials becomes less and less, but evidence has been given to show that the reaction may go on to over 99·9 per cent.

The main argument for a strong change disappeared when these facts became known. It is interesting to note that the manner recommended in text-books for carrying it out consisted in boiling slowly for many hours with the pan in an open condition, a relic of the methods of centuries ago. It was obviously inefficient and in most cases quite unnecessary.

The above should make it clear that to obtain quick saponification it is necessary to keep the pan as far as possible in a close condition. The addition of a little salt to thin the mass may be permissible, but to maintain an open condition any longer than necessary is bad practice.

As soon as the pan is completely saponified it is ready for graining out. The ordinary procedure is merely to keep the pan well boiling, and add salt or brine until the

appearance of the soap indicates that separation has occurred. A sample of the soap on a trowel is seen to consist of masses of curd, from between which perfectly fluid lye will run. As soon as this happens the steam is shut off and the pan left to settle.

Graining out in a casual way, without paying any great attention to the amount of salt used, will bring about separation of the mass into curd and lye, but is unlikely to lead to the best results. The curd under the best conditions always contains a considerable amount of lye entangled in it, and this naturally interferes with the efficiency of the removal of glycerin. However well the curd is settled it is impossible to obtain the soap hydrate entirely free of lye, but careful attention to graining out may help to reduce the amount to a minimum. Experiments, and tests of the lyes and curds from a large number of boils, have shown that the amount of lye entangled in the curd depends very much on the amount of salt used in graining out. There is no definite numerical relationship between the two, but in general it may be said that the more salt used in graining the greater will be the amount of entangled lye. The best results—that is to say, production of curd with the minimum of entangled lye—are obtained when the percentage of salt in the lye is only just sufficient to separate the soap satisfactorily; larger proportions of salt probably modify the physical condition of the soap hydrate and make it obstinately retain more of the lye. To give a general idea of this effect, a certain soap may grain out satisfactorily if the salt in the lye amounts to 10 per cent, and under these conditions the curd may contain 56 to 60 per cent of fatty acids, corresponding to 15 to 9 per cent of entangled lye. If the percentage of salt in the lye is 13, which would not be at all exceptional, the percentage of fatty acids in the curd tends to fall to some such figure as 51 to 54, corresponding to 18 to 22 per cent of entangled lye.[1]

[1] Over thirty years ago Merklen realised that for every kind of soap there was a limiting strength of electrolyte, whether salt or caustic alkali, below which soap would dissolve in appreciable quantities, and he determined these concentrations, using sodium and potassium hydrates, for

This fact does not seem to be generally known to soap boilers, and in many cases far too much salt is habitually used, but when the importance of limiting the amount is pointed out they usually have no difficulty in accustoming themselves to using smaller amounts, and thus obtaining curds considerably richer than before.

The best way to carry out the operation is to measure into the pan the amount of either solid salt or brine which will give the required result. The principle on which this is done is extremely simple. The soap in the pan is assumed to be all in the form of a hydrate containing 66 per cent of fatty acids, and thus the amount of this hydrate is 1·52 times the weight of fatty acid present. After saponification the remaining contents of the pan may be assumed to be water, unless salt is already in the pan, in which case its amount must be allowed for. Glycerin may be regarded as equivalent to water in the calculation. One then merely needs to add so much salt, or salt solution of standard strength if brine is used, as will make with the existing water a solution of the required salt content. It takes only a few minutes in the laboratory to determine sufficiently nearly the minimum salt percentage of the lye, a degree of accuracy within about ½ per cent being sufficiently close, and once this is known for any particular type of soap this figure may be always used. A numerical example will make this quite clear.

Amount of fatty acids in the pan 10 tons, therefore the weight of soap hydrate is 15·2 tons. Total weight of contents of the pan after saponification 20·5 tons. Difference, equal to the amount of water to which salt must be added to make a lye of the required composition, is 5·3 tons. Assuming the required percentage of salt

a large number of soaps made from commercial oils. The importance of not greatly exceeding these values does not seem to have been generally recognised in this country, although a few soap makers seem to have made a practice of graining out with as small an excess of salt as possible, thereby obtaining richer curds and a better removal of colour and glycerin from the soap. From a recent German work one would judge that this matter is given due attention in that country, and if the few examples of analyses of curds, containing over 60 per cent of fatty acids, are to be taken as typical, the results obtained are extremely good.

in the lye is 10 per cent, and that 26 per cent brine is used for graining, the amount of this works out at 3·31 tons. This may be read off from diagram 6. In practice this amount of brine is run into the pan while the latter is boiling briskly, and after a thorough boil-through to mix the solution well the operation is finished. It may be thought well to make a minor correction for the condensation of steam during this final boil, but in general this may be disregarded.

In the above it has been assumed that a sufficient amount of lye is produced by graining out the contents of the pan as soon as saponification is complete, without further addition of water, but it may be that to obtain a good recovery of glycerin a larger amount of lye should be produced. In the above case the weight of the contents of the pan after adding the brine amounts to 20·5 + 3·31 tons = 23·81 tons. If the curd contains 58 per cent of fatty acids, a reasonable percentage, it weighs $\frac{10}{\cdot 58}$ tons = 17·2 tons, and the lye therefore weighs 6·61 tons, which is probably quite as much as is wanted. But had the amount of water used during saponification been less, and solid salt instead of brine used for graining, the amount of lye allowed for might have been too small. In this case water as well as salt is added to the pan to make up the additional amount, the amounts of each being adjusted so as to make a 10 per cent solution.

The quantitative method, although very convenient, is not essential if the problem is merely to grain out the soap with the minimum amount of salt, but when it is required to produce a definite amount of lye, as it is to ensure the best recovery of glycerin, measurement of the correct amounts of water and salt is essential. No amount of skill will enable a soap boiler to run in definite amounts of material into the pan without some appliance with which to measure them.

Second and Later Changes: The Wash.—The amount of glycerin in the lye of the saponification change falls far short of the total present. Its proportion of the whole is

variable, but is usually between 30 and 45 per cent. Most of the remainder of the glycerin, which is left in the meantime in the curd, may be removed by the successive operations called washes. In Chapter VII it will be shown that in order to obtain the highest economic yield of glycerin it is necessary to decide in advance how many washes should be made and how much lye should be produced from each; at present we are concerned merely with the manner in which this amount can be controlled.

Both the principle and the practice of this operation are simple. One begins by assuming that the graining-out is carefully conducted, and that consequently the proportion of lye to soap hydrate in each curd is constant. This will not be absolutely correct, as small variations are bound to occur, but deviations from a reasonable mean value should be small and unimportant. In order to have a uniform figure to work on it will be assumed that each curd contains 58 per cent of fatty acids, this figure being based on the experience of fairly good working.

After the lye has been run off from the saponifying change the curd is well boiled up with steam. As nothing but water and salt are to be added to the pan, and the curds before and after the operation are assumed to have the same weight, the total quantity of water and salt to add will be the amount of lye that it is required to produce. There is a small amount of lye already in the curd, but this will contain water and salt in the same proportions as in the lye to be made, and so the problem is merely the simple one of finding the amounts of water and salt or brine which will produce so many tons of lye.

The water is first added to the pan. If the pan is provided with a gauge this merely means adding water until the total weight of the contents is that of the curd plus the added water required. If there is no gauge the soap boiler must guess the amount of water he adds as best he can—according to his skill he may come close to the required amount or not. It remains then merely to add the requisite amount of brine, either gauged or estimated according to the method used, and after thoroughly

boiling-through the operation is finished. It may be mentioned that even when the method is carried out by measurement there may be a slight difference between the amount of lye provided for and that actually obtained, and without measurement the difference is liable to be considerably greater, but not much harm will be done if the difference is corrected on the next change. One may add that it is good practice to make sure on each change that the lye has sufficient alkalinity to produce a faint blue tint on the test paper, adding a slight touch of caustic if necessary to ensure this.

The Rosin Change.—The incorporation of rosin in the soap charge creates a number of minor problems. These arise from the differences between it and the fats. In the first place, rosin is an acid material and can be converted into its soap by the action of sodium carbonate, unlike the fats, which, being esters, require caustic alkali. There is thus an inducement to use the cheaper soda ash instead of caustic soda. Again, when rosin is completely saponified it cannot be salted out of its solution like soap made from fats. A third problem arises from the fact that, although it yields no glycerin to the lyes, it increases the amount of soap curd at whatever change it is introduced, and is consequently a hindrance to the efficient recovery of glycerin. The additional amount of curd retains a larger proportion of the glycerin if no alteration is made in the amount of lye produced; if the glycerin recovery is not to be affected it is necessary to make additional lye corresponding to the added amount of rosin; this lye being weaker costs more to convert into crude glycerin.

These small problems are solved in various ways and no ideal solution is possible. The last-named difficulty is usually got over by introducing the rosin to the pan at as late a change as possible—preferably the one before the fit. Complete saponification of the rosin with soda ash is impracticable as the solution thickens so much that it cannot be pumped. One practical method which has much to recommend it is to have special pans near (or on) the ground-level, the tops of which are covered with strong

steel grids. The rosin casks are broken on these and the rosin falls into the pan. In this it is boiled with solution of soda ash, the quantity of the latter which is used being insufficient to neutralise the rosin completely. This mixture of rosin and rosin soap can then be salted out. The percentage of salt in the lye is very much lower than in the case of fats and it floats on the rosin soap mixture and can be run away. Only a portion of the colouring matters of the rosin are removed in this lye, but it certainly effects some slight purification and carries away some of the splinters from the casks, which are otherwise liable to cause trouble. The soap mixture is pumped to the soap pan and saponification completed with caustic soda.

Sometimes the rosin casks are brought to the pan-room floor, where they are broken up and the rosin shovelled into the soap pan. When this is done there is a tendency for lumps of rosin to settle between the steam coils, and unless special care is taken they may escape the action of the alkali. It is a definite advantage in this case to gauge to the pan the amount of caustic required by the rosin. When this is all absorbed it is an indication that the whole of the rosin has been turned into soap.

The Strong Change.—The strong, or strengthening, change was necessary in the early days of soap manufacture when circumstances made it nearly impossible to be sure of complete saponification of the fats on the first change. Two arguments in its favour may be found in the literature of soap-boiling. The first is that it is impossible to saponify the last traces of fat except in the presence of a large excess of alkali, such as is not permissible on the saponification change. It is quite possible that certain laboratory experiments may have pointed to this conclusion, but the results may have been due to difficulties in manipulation and not comparable with those obtainable under the more favourable conditions existing in a large pan when properly manipulated. Analyses of the curds of the first change, after saponification has been carried out with care, show that no measurable quantity of unchanged fat need remain. Moreover soap makers are

perfectly well aware that free fat left in a soap is liable to predispose to rancidity, and possibly interfere with the lathering properties of the soap, and the fact that for years past vast quantities of soap have been manufactured without a strong change and have proved perfectly satisfactory seems to dispose of the matter from any practical point of view.

The other argument appears also to be a theoretical consideration unsupported by evidence. It has been stated that the strong change, conducted as described below, removes some, or even all, of the salt from the curd. But practically every hard soap made, with the possible exception of some cold-process soaps, will be found on analysis to contain salt, and there is no reason for supposing that the small quantities usually present, between 0·3 and 0·5 per cent, have any bad effect on the product. When a soap curd is boiled with strong caustic lye some of the salt in the curd passes into the lye, its place being taken by caustic soda, but to talk of eliminating salt by this means is absurd. Under the practical limitations of working conditions only a small proportion of the salt can be replaced in this way, and no advantage would be gained by carrying the reaction further, as the amount of free alkali in the soap would then become excessive.

The actual method of carrying out this change varied greatly in different factories. The commonest method was perhaps to boil the curd gently and add sufficient strong caustic lye to keep the pan in an open state. The strength of alkali became reduced by condensation of steam and by absorption of alkali by free fat if any were present. More strong lye was added so as to open the pan again, and in this way the pan was kept boiling in an open state for the greater part of a day. The pan was then left to settle overnight, preparatory to fitting. This is a relic of the old method, possibly necessary in the case of old fire-heated pans, but inefficient and unnecessary with modern methods of boiling with open steam.

The strong change has certain positive disadvantages. In the first place, the lye run off has to be employed in

saponifying fats in another pan, and this generally involves the nuisance of providing special storage for such lyes. Apart from this the method does not lend itself to exact control, and the strength of the half-spent lye and the alkalinity of the finished soap are liable to be very variable.

Another objection to the process is that, as it presupposes that saponification need not be complete on the first change, it tends to make the soap boiler indifferent as to whether this is carried to a correct finish, through a feeling that any error on the first change is automatically adjusted on the strong change. Since a considerable amount of fat may be left unsaponified on the first change without any marked effect on the appearance of the soap, the process tends indirectly to have a bad effect upon the yield of glycerin.

Bleaching with Hypochlorite Solution.—This is not an essential part of the soap-boiling operations, but as it may form a stage in the process it is best to deal with it here. While certain of the undesirable colouring matters contained in fats are removed by washing, others of them cannot be discharged in this way, but some of these may be oxidised with the formation of colourless substances. Sodium hypochlorite is a substance which has long been used for this purpose and it is very conveniently applied to the boiling soap in the pan. Its application as a bleaching agent is somewhat limited, thus it will not discharge the colour of palm-oil soap nor bleach the miscellaneous assortment of coloured scraps with which most soap makers are burdened. Its chief use is in bleaching tallows and greases of poor colour, and also certain vegetable oils, and for these purposes it is simple, cheap, and effective. The reagent is employed in the form of a dilute solution: 4 per cent of "available chlorine" is a convenient strength. The solution was formerly prepared by agitating bleaching powder with rather over the theoretical amount of soda ash solution, the mixture being allowed to settle and the clear solution of hypochlorite decanted off. The lime in the bleaching powder is converted into a bulky mass of calcium

carbonate, which must be washed to free it of the hypochlorite solution it holds, this weak liquor being used in making up a fresh batch. This process may still occasionally be employed but has generally been superseded, since liquid chlorine has become available in cylinders, by the method of leading chlorine gas into dilute caustic soda solution. The preparation of the solution in this way is a very simple matter, all that is needed being to bubble the gas into a cold solution of the required strength. As a suitable strength of the finished solution is only about 4 per cent of available chlorine, this may safely be done, if the caustic soda solution is cold to start with, without the temperature rising to the point at which the reaction begins to take another course with the formation of sodium chlorate. In practice a suitable amount of caustic soda solution of the required strength is led into a tall cylindrical vessel fitted at the bottom with a gas inlet, and the gas cylinder is connected up with a flexible tube and rests on a balance, so that the operation may be stopped when the required amount of gas has been delivered.

In carrying out the bleach the fats are first saponified as usual and if possible one or two washes are made. If this can be done a good deal of oxidisable material is removed which might use up some of the bleach. The curd to be bleached is boiled up with sufficient water to close it thoroughly. The bleaching solution is then led steadily into the pan, which is kept well boiling all the time. It is best to ascertain the amount that will be required by a preliminary test in the laboratory. The reaction occurs fairly rapidly and the effect on the appearance of the soap in the pan is quite striking. When it appears to be complete it is as well to test a sample in the laboratory with a further small amount of liquor, and add more to the pan if this is indicated. When the bleach is finished the pan is grained out as usual.

When the operation is properly carried out the soap should not tend to go back in colour, and should have no odour of chlorine nor give any starch iodide reaction.

There are other methods of bleaching soap by oxidation but it is doubtful if any of them is as cheap or efficient as that with hypochlorite. In the conditions in which it is used it seems to be without effect on either the glycerin or the unsaturated fatty acids present.

CHAPTER V

THE SOAP-BOILING PROCESS (*continued*)

The soap-boiling process (*continued*)—fitting—accidental and intentional variations in the composition of the neat soap—variations in the composition of the nigre—precision in adjustment of the type of fit—the control of nigres.

The Operation of Fitting.—The final stage in making a boil of soap was doubtless discovered by accident. If soap boiling to-day ended at the stage of making curd soap in a fire-heated pan it would not be long before some experimenter tried the effect of boiling up the curd with water, either with the object of adulterating it or in the hope that the effect would be to reduce the curd to a smoother and more coherent mass. If after this operation had been carried out the pan were allowed to stand for a time undisturbed it would be found to have settled into two layers. The lower layer would, however, in this case not be an ordinary spent lye, but a thin solution of soap, and it would contain much dark-coloured material which the lye had previously failed to remove from the soap. The advantage of such an operation in the refining of the soap is obvious, and in addition an examination of the soap from the upper layer after solidifying would show that it differed considerably in its physical properties from curd soap. The latter, if made from materials which form a fairly hard soap, tends to be crumbly, and is obviously not homogeneous; the fitted soap is tougher and somewhat translucent, and to the connoisseurs in such matters more attractive in appearance. It also contains as a rule a higher percentage of fatty acids, and this, when the soap is fitted under more or less standard conditions, is nearly constant.

The successful finish to this operation was at one time invariably judged by the appearance of a sample of the boiling mass taken from the pan on a trowel, or paddle,

just as when, on the other changes, the soap is examined to see if it is properly grained out. When the curd is boiled up without addition of water the sample from the pan is seen to consist of granular or curdy masses of soap, from between which the lye will separate and flow away as a dark-coloured liquid. As water is added during the operation of fitting such samples are seen gradually to take on a totally different appearance. When the sample is withdrawn and the paddle held at first horizontal the soap remains spread over the surface in a smooth sheet. This is at first opaque, owing to the dispersion of innumerable minute bubbles of steam throughout the mass. In a few moments the soap cools sufficiently for these to condense, and the sheet of soap becomes translucent. If the paddle is now tilted this sheet breaks up into separate flakes, smallish in the early stages of the process, but gradually becoming larger as more water is worked into the pan.

The state of common knowledge of this process, which has now been practised for generations, is roughly as follows. It is known that the addition of water to the pan, followed by vigorous boiling, brings about a change in the nature of the mass which causes it, when left undisturbed for some hours or days, to separate into two sharply defined layers, the lower of which, unlike spent lye, contains a considerable percentage of soap. It is also known that this change is accompanied by one which occurs in the appearance of the soap when examined on the paddle, the successive appearances of the soap being described as "coarse" or "rough," "medium," and "fine" or "smooth." If it is assumed that general knowledge is confined to the matters mentioned in text-books one may say that little or nothing is known as to variation in the nature of the soaps resulting from variations of the type of fit.

It is stated as a fact in several fairly recent text-books that the composition of the neat soap is unaffected by the nature of the fit, but whether this statement is usually believed by soap makers it is impossible to say. In point of fact it is entirely incorrect, and is contrary to the experience of those soap makers who make it a routine

practice to determine the fatty acids in each pan cleansed; and it is contradicted in the same breath by certain of the writers themselves, one of whom says that the soap (alleged to be constant in composition) contains between 62 and 64 per cent of fatty acids, and another that the percentage is between 61 and 63. The fact of such a statement occurring in works of repute does at least suggest that it is an impression commonly held. A similar misconception exists with regard to the composition of nigres. These may contain any percentage of fatty acids up to 40 per cent or over.

It seems probable that a common idea of the fitting process is that it produces soaps which differ from one another in a manner somewhat analogous to that in which the samples on the paddle are seen to differ, that is to say that there are purely physical differences between soaps chemically identical. If this were the case the differences between the products would be relatively unimportant and the rough method of grading by the paddle test would be quite adequate. In point of fact, however, soaps differently fitted do not show marked differences in the solid state, but every addition of water has an effect on the quantity of nigre, and on the percentage of fatty acids in both that and the neat soap, and as all these matters effect the economy of the process, it is necessary, if the best results are to be obtained, to use some method of control more exact than the customary one.

The lack of exact knowledge of the soap-boiling process, and especially of the fitting operation, is due in an indirect way to the simplicity of each operation. It would be difficult to find three simpler chemical operations than the saponification of fat, the salting out of the soap, and the incorporation of water in fitting. Each of these operations can be, and often is, successfully conducted without attention being paid to the quantities of reacting materials, and if the object were merely to make soap of good quality, without regard to the quantity produced, there would in a sense be no occasion for measurement; but fortunately for progress the need for this has arisen from the necessity of obtaining a good yield of glycerin,

and of converting the greatest possible amount of the fats used into soap of the best quality. It is more than likely that progress in the latter respect was definitely hindered by the wrong conceptions just referred to, which tended to make the soap maker think that variations in the type of fit, while affecting in some mysterious way the quality of the soap formed, had no effect on the yield or on its composition. It is worth while pointing out that in soap-boiling the materials concerned in each stage separate into two immiscible liquids which have certain constituents in common. It is quite impossible to determine how these constituents are distributed between the two layers without measurement, and in order to throw light on such matters as the distribution of glycerin between soap curd and lye, and of soap between neat soap and nigre, a series of large-scale experiments were carried through. The practical results of these as regards glycerin recovery are dealt with in Chapter VII; the study of the fitting operation occupies the remainder of this chapter.

The procedure of fitting a pan is extremely simple; the only difficulty in the ordinary process is in deciding from the mere appearance of the soap when the proper amount of water has been incorporated. The curd to be dealt with should be given an overnight settling, and drained as free of lye as possible. Steam is now blown into the pan and usually some indefinite amount of water run in. The soap slowly changes its appearance, becoming "closer" and more viscous, and minute steam bubbles remain entangled in the mass, causing its volume to increase until, in the course of half an hour or so, the surface may reach within an inch or two of the top of the pan. All this time a full flow of steam is maintained so as to agitate the mass thoroughly. This is necessary in order to ensure that the whole of the lye entangled in the curd is well mixed with the water and the resulting solution in turn saturated with soap. When the soap has reached the top of the pan steam may be shut off, and in a few moments it will be seen that the appearance of the soap is entirely different from that of a curd, and when bubbles have ceased to rise and break the surface

the mass will take on the appearance characteristic of a fitted soap. The mass remains in gentle motion and forms on the surface large sheets of soap separated by channels of frothy liquid. As these cool the steam bubbles in them condense, and they disappear edgewise below the surface, fresh soap from below taking their place. This appearance varies slightly with the amount of water that has been added, and some soap boilers judge of the finish of the operation by it, but the variations are too slight to allow it to form a satisfactory criterion of the finish. The usual procedure is to take up a sample of the soap on a well-warmed trowel or wooden paddle and judge of the nature of the fit by the appearance of the flakes that glide off it. No amount of mere written description will enable a beginner to carry out this test so as to ensure a good finish; for what it is worth it is only to be learned by much practice in the pan-room. In any case the new technique, to be explained later, is more exact and perfectly simple to carry out.

As will be evident, the fitting of a pan so as merely to bring about a state in which it will separate into neat soap and nigre requires no particular skill. The real difficulty arises from the fact that there are infinite variations in the amount of water that may be added, and corresponding variations in the composition and the relative amounts of the two layers. The amount of water added is the thing that really matters, and this is not a definite quantity for all cases, but depends upon the amount of entangled lye in the curd, on the nature of the materials of which the soap is composed, and on the desired fatty acid percentage of the neat soap. As the operation is ordinarily carried out the only means by which the soap boiler can judge when the right amount of water has been incorporated is by the appearance of the soap on the paddle, and this appearance varies by imperceptible degrees between the limits of a very coarse and a very fine fit. A further complication is in the fact that different soap bases require a different appearance on the trowel to yield similar results. Thus if a washer soap is fitted so as to give as nearly as possible the same appearance as a

allow rosin soap, in nine cases out of ten the latter will yield a neat soap one half per cent or more lower in fatty acid test than the former, although this may not be the result the manufacturer desires. The difference is due solely to the method of control and not to any specific properties in the soaps themselves making different results impossible; either type of soap can by suitable adjustment of the water yield a neat soap of any test from 63 per cent, or rather over, down to about 60 per cent.

The rational method recommended is exactly the same as that described in the making of miniature boils, the only difference being that instead of weighing a beaker of soap on the scales the soap mixture in the pan is weighed by means of a gauge. The procedure is thus as follows.

Suppose for example the pan is known to contain 10·5 tons of fatty acids, and the curd to be fitted is found to weigh 18·4 tons (corresponding to 57 per cent F.A.). Then we say 10·5 tons of fatty acids yield $10{\cdot}5 \times 1{\cdot}52$ tons soap hydrate = 16·0 tons, and the weight of entangled lye, or free solution, is 2·4 tons. The percentage of NaCl in this may be, for the sake of argument, 10·2, and from a previous boil it may be found that the desired type of fit is obtained by reducing this to 8 per cent. Thus the final weight of free solution will be $\frac{2{\cdot}4 \times 10{\cdot}2}{8}$ tons = 3·6 tons, and the amount of water to add, therefore, 0·66 ton.

To carry out the operation the curd is boiled up in the usual manner; unless the steam is known to be very wet a small amount of water may be added at the beginning to close the soap. When the soap reaches near the top of the pan the steam is shut off for a moment and the contents weighed, and the greater part of the deficit of water is now gauged into the pan. The pan is now boiled hard again in the usual manner and further small quantities of water added until the total weight is correct. After the last addition of water the soap is well boiled up to the top of the pan and the operation is finished. No special skill is required to carry out this process; the reading of the gauge occupies only a few moments, and there is

no need to judge the finish of the operation by the appearance of the soap. It is interesting, however, to do so, and it is found that when normal curds are treated in this way, so as to yield average results, the appearance of the soap on the trowel is one that the ordinary soap boiler would consider good. The author has found that deliberate small variations, made so as to form neat soap with a fatty acid content possibly one half per cent below the average, also produce an appearance on the trowel which most soap boilers cannot distinguish from the normal result, thus indicating the greater precision of the new method. An interesting divergence is noticed in cases when by accident an exceptionally dry curd has to be dealt with. In such instances the addition of a very small amount of water produces the desired fit, and naturally the amount of nigre which will be formed is very small. Such pans settle quite normally, but as they contain less than the usual amount of water the appearance on the trowel is quite out of the ordinary, and liable to confuse a soap boiler trained in the old method; as a rule the soap would either be redissolved and grained out again or else fitted with the addition of caustic or salt. This would naturally produce more nigre, thus lessening the yield of good soap, but no advantage would be gained by doing so. The ordinary test is in fact unsuitable for abnormal conditions such as this, and in general one may say that the appearance on the paddle varies quite considerably according to the amount of water in the pan. It has been recommended to obviate this difficulty by the expedient of always reducing the fatty acid percentage of the pan contents to the lowest figure that could occur in the usual course, but it would be impossible to do this accurately without the aid of a gauge, and in any case it would involve the formation of an excessive amount of nigre on every boil.

Some consideration must be given to the question of free alkali in soap. When a strengthening change was part of the usual procedure a considerable amount of alkali was left in the last curd, replacing some of the salt, and the fitted soap was therefore alkaline, though in the

circumstances the percentage of free alkali varied a good deal. For certain soaps, notably toilet soaps, it is desirable to have some free alkali present, as this guards to some extent against rancidity, but the amount should naturally not be excessive. The relative amount of sodium hydrate, and for that matter of sodium carbonate, which corresponds to salt in graining is readily determined by experiment. Sodium carbonate is much less active than salt, approximately 2·5 parts Na_2CO_3 being in effect equivalent to 1 part NaCl. Sodium hydrate is more active, the relative effect depending on the concentration, but in dilute solutions one may reckon 0·8 of NaOH, or say 0·62 Na_2O, as being equivalent to 1 of NaCl. With the aid of these figures a neat soap can be produced containing any desired percentage of free caustic. Suppose for example the soap if fitted normally would contain 63 per cent of fatty acids and ·36 per cent NaCl, being free of caustic, and that it is required to make the soap to contain 0·1 per cent caustic (as Na_2O). Now 0·1 per cent Na_2O is equivalent to 0·16 per cent NaCl, and the neat soap should therefore contain 0·2 NaCl and 0·1 Na_2O. In the example already given the total salt present is 10·2 per cent of 2·4 tons = ·245 ton, and the amount of caustic required to add must be one-half of this—*i.e.* ·123 ton, or ·49 ton of 70° Tw. solution. The amount of salt equivalent to this is $·123 \times 1·6 = ·197$ ton. The amount of free solution will therefore be the amount of an 8 per cent solution which will contain ·245 + ·197 ton salt, or 5·52 tons. Such an operation evidently increases the amount of nigre formed, but in most cases this is of little importance, as a very coarse fit, producing a nigre weak in fatty acids, is quite permissible.

Intentional Variations in the Composition of Neat Soap

By a study of the conditions which determine the composition of the neat soap it is now possible to a large extent to eliminate the variations which occur from boil

to boil. These are due mainly to variations in the salinity of the free solution, and this cannot be accurately adjusted by the conventional method of judging the end-point of the fit. The method by which this adjustment can be accurately made has been explained, and by this means it is possible to obtain more consistency in results than is possible by the older method.

While unintentional variations are always undesirable, there may be, and in fact are, cases in which a different standard from that usually adopted would be of advantage. It is possible to modify the composition of the soap deliberately by making suitable alterations of the salinity of the free solution. Before going on to explain in detail how this is done some useful applications may be considered.

Genuine soaps sold in bars or tablets are generally assumed to have a fatty acid percentage of 63 per cent. Sometimes contracts specify a percentage of 62–64 per cent, but in either case there is no occasion for the manufacturer to send them out at a percentage much above 63. Practically all bar or tablet soap is exposed to the air for a time so that the surface of the bars may become dry, and thus a considerable loss in weight occurs. This varies according to circumstances, but may often amount to one or one and a half per cent. Thus the average fatty acid percentage of the soap as sold may be approximately 1 per cent higher than that of the soap in the pan, and the obvious thing is therefore to fit the soap as so to be 62 per cent or a little over when cleansed.

Apart from the genuine soaps there is a large trade in soap of a slightly lower fatty acid percentage, say from 60 to 62 per cent. These soaps are generally made by mixing neat soap with silicate or other solutions, but may be equally well made in the pan, as will be shown later. This is not only a neater method of manufacture than "running" a neat soap of the ordinary type with silicate, but generally yields material of better quality.

Results such as the above are obtained by reducing the salinity of the free solution, that is by making a properly

controlled, smoother fit. In normal circumstances this would lead to the formation of more and richer nigre, but the increase in amount, as will be seen, is readily avoided.

On the other hand there are many cases in which a fit much coarser than the normal is indicated. The soap base used for making powder, for example, is sometimes cleansed as an actual curd. For several reasons this is not altogether desirable, but an extremely coarse fit has many advantages. An overnight settling is usually sufficient to bring about a good separation of nigre, the composition of the soap cleansed is very nearly constant, and as the nigre is very weak in fatty acids an excellent yield is obtainable from the pan.

In the making of soap base for flakes a fit coarser than the normal is indicated for two reasons. In the first place the nigre is usually sent away to a pan in which much cheaper materials are used, and it is therefore economical to form a nigre which is poor in soap. A less obvious reason is the fact that if flakes are made to a definite fatty acid percentage, those produced from a smoothly fitted soap will contain more salt than those resulting from a coarse fit. Now since even the finest toilet soaps contain salt it may be taken for granted that salt *per se* is not detrimental, but it is quite possible, and even likely, that amounts of salt above what may be considered as normal may have a bad effect on the texture of the soap, particularly if the charge contains a considerable amount of the higher saturated fatty acids. An illustration may emphasise the difference caused by variations in the type of fit. Sample 2 in the table on p. 87 contains 63·35 per cent of fatty acids and ·435 NaCl. Sample 9, a smooth fit, contains 61·3 per cent fatty acids and ·53 NaCl. To make 1 ton of 76 per cent flakes requires 1·20 tons of No. 2, or 1·235 tons of No. 9. The flakes made from them will contain ·52 and ·65 per cent NaCl respectively. The figures are interesting in view of the somewhat prevalent confusion of ideas connecting smoothness of fit with smoothness of texture in the soap. If either soap tended

to be rough in texture one would naturally expect it to be the second, which is made from the smoother fit.

For similar reasons a coarse fit is to be preferred when making soaps to be run with silicate solution. Apart from the question of a better yield, which is always a matter of importance, the amount of salt in relation to the silicate solution has to be taken into consideration. To a certain extent the addition of salt intensifies some of the properties of silicate solutions, and thus any solution to which salt is added is roughly equivalent to some stronger solution without salt. The result is that the presence of salt in the mixture makes it necessary to use a slightly weaker silicate solution than would otherwise be the case, and if the total amount of salt in the mixture is variable the strength of the silicate solution to use will also vary. When the fit is coarse the ratio of salt to fatty acid in the soap is at a minimum, and also varies less with small variations in the fatty acid content. It is well known that in making silicated soaps it is usually necessary to make a number of trial mixings with varying strengths of silicate solution in order to determine which strength gives the best result. These variations are due partly to the effect of the salt, as just stated, and partly to varying composition of the fatty acid mixture in the soap. By using coarsely fitted soap in all cases one practically eliminates the first of these disturbing factors, and makes the problem of producing a good quality run soap so much the simpler.

In order to fit a soap so as to produce neat soap of any required test it is necessary first to know what percentage of salt in the free solution will be required. This varies considerably according to the nature of the soap charge, the more soluble the soap the higher will be the percentage of salt required. The determination of this is best done by direct experiment, and the way in which this is done depends upon the nature of the problem and the facilities for experiment in the works. If the problem is a simple one, say to reduce by about 1 per cent, the test of the neat soap, when the soap is very soluble, and tends with ordinary manipulation to yield a soap which tests too high, one may

make an arbitrary reduction of the salt concentration on a first boil, making finer adjustments if necessary on later boils. In this case one would determine the percentage of salt in free solution on a normal boil, either by direct measurement as the boil proceeds or from the fatty acid and sodium chloride tests of the finished soap; a reduction of about 2 per cent on this figure should give a result very near to what is required. When the object is to produce a soap at a much lower figure, such as may be ordinarily made by the addition of 3 to 5 per cent of silicate runnings, it is better to be guided by a short series of careful experiments. These may take the form of a number of miniature boils in which the percentage of salt on the free solution is varied to definite extents, but it is better to carry out a trial boil in a small experimental pan if one is available. In this case the pan is first fitted very coarsely and a beaker sample taken; then a small further addition of water is made and another sample taken, and so on. All the samples are allowed to settle in the steam oven and then analysed. An example of the results obtained in this way on an easily soluble household soap is given in the following table.

Sample	NaCl in free sol. %	Neat soap		Nigre Fatty acids
		Fatty acids %	NaCl %	
1	11·0	63·2	·47	< 1
2	10·9	63·35	·435	1·2
3	10·7	63·3	·425	3·5
4	10·3	63·2	·435	9·6
5	10·25	63·2	·44	8·6
6	9·3	62·8	·445	24·0
7	8·25	62·35	·45	32·6
8	7·85	61·85	·48	36·2
9	7·55	61·3	·53	37·2
10	7·25	60·85	·55	39·3

In a series of experiments made in this way the results should be plotted, fatty acids against salt in free solution. It can then be seen at once if any results are inconsistent

with the rest, and, disregarding these, a smooth curve can be drawn through the others from which data can be obtained for using the method on a large scale.

It will be seen that the variations in salinity of the free solution are fairly large compared with those in percentage of fatty acids, and as the salinity can be adjusted with considerable accuracy, the percentage of fatty acids in the soap can be controlled within quite narrow limits. On the large scale this is found in practice to be the case; variations from the mean should not be more than about ·2 per cent in the upper portion of the scale, and slightly more in the lower.

When a very coarse fit is desired, as often happens, this method of control ensures the formation of a nigre very weak in soap, say about 3 to 5 per cent of fatty acids, and its amount will also be relatively small, the result being that only a small proportion of the total fatty acids finds its way into the nigre. On the other hand, if a low-testing soap is required, such as sample 8, the percentage of fatty acids in the nigre will be very high, over 36 per cent in this case, and owing to the additional amount of water that is required to bring about the necessary dilution of the free solution the amount of nigre formed must be much greater. At the first glance these facts seem to make a serious objection to the method, but there is a simple way of overcoming the difficulty. Supposing sample 8 to be made from a fairly good curd, which might contain 58 per cent of fatty acids and 1·5 per cent of salt. It may be shown by application of the rule on p. 93 that the nigre must amount to about 15 per cent of the total pan contents, and that it would contain well over 9 per cent of the fatty acids. This is a large proportion and would be larger still if the curd were wetter. The alternative method to this is first to fit the pan so as to produce a soap as in example 3. In this case the nigre would be only 9 per cent of the contents of the pan, and owing to its being so poor in soap the fatty acids would be only a little over one half per cent of the whole.

This neat soap may now be fitted again, and this intro-

duces a new and interesting problem the solution of which leads to results of great value. Soap No. 3 contains 63·3 per cent of fatty acids, and No. 8 contains 61·85 per cent. If 100 parts of No. 3 could be entirely converted into No. 8 the amount of the latter would be 102·34 parts. The additional 2·34 parts, if consisting of water only, would dilute the free solution in No. 3, which contains 10·7 per cent of NaCl and amounts to 3·97 per cent of the soap, to $10{\cdot}7 \times \frac{3{\cdot}97}{3{\cdot}97 + 2{\cdot}34} = \frac{10{\cdot}7 \times 3{\cdot}97}{6{\cdot}31}$, or 6·75 per cent, a weaker solution than that in No. 8. To make a soap exactly corresponding to the latter, salt must therefore be added in addition to water. The amount of salt in 100 parts of No. 3 is ·425, and that in 102·34 parts of No. 8 is ·491. There is thus to be added ·066 of salt in 2·34 parts of solution, or 2·34 parts of a 2·8 per cent solution.

If the neat soap left in the pan is now actually fitted so as to incorporate just these proportions of salt and water, the whole of it will be transformed into soap No. 8, that is to say, no nigre whatever will be formed. The operation has actually been carried out in this way with complete success, the whole of the soap present being converted into the quality required. There are, however, certain difficulties, such as the formation of water lumps, which make the operation difficult to carry out, and small errors in measurement may lead to the production of soap of poor quality, so that in general a different method will be adopted. It is evident, however, that a soap mixture of this kind could quite well be made in a mechanical mixer. This is a practical process of great value which will be dealt with fully in another chapter.

The above principle applies equally to all cases in which a soap in such a series as the above is made from one higher in the scale. The strength of salt solution required as a diluent varies greatly; it is in general higher with the more soluble soaps, such as those of the washer type, and depends also upon the extent to which the fatty acid content of the soap is reduced, stronger solutions being required as the scale is descended.

It is thus seen that the objection to this method of making the lower soaps, due to the excessive formation of nigre, can be entirely overcome. One may either, as above, fit the pan so as to produce no nigre, or alternatively make mixtures of the same composition in the crutcher, or as a third alternative additional salt and water may be added so as to form a definite small amount of nigre. The first method has the advantage of dealing with the whole of the soap concerned at one operation, and thus saves a considerable amount of labour compared with mixing in the crutcher, and it cuts out the two to four days required for settling when a nigre is formed. To do it successfully, however, the nigre from the first fit must be nearly quantitatively removed, and somewhat more than the usual care is required to ensure the correct proportions of materials in the pan, otherwise the soap may be poor. The method of making the mixture in the crutcher also makes it possible to utilise practically all the neat soap formed on the rough fit, and if any error is detected in the composition of the mixture on the first mixing it can be corrected on later ones. It is the best method to employ when soaps of different grades have to be made from the same pan. The last method, that of making the conventional type of fit and producing a small and arbitrary amount of nigre can hardly fail to produce soap of good quality, and incidentally helps to brighten the soap by removing traces of dirt which may have remained in the soap after the first fit. It is highly suitable in the cases in which all, or nearly all of the soap is made to one fatty acid standard. In fixing the quantities of water and salt required, it must first be calculated what would be required to form a soap without nigre, and then those which will go to form the amount of nigre decided on. Thus in the case of soap 8 for example it may be decided to make 15 per cent of nigre in the pan. This nigre consists of $36{\cdot}2 \times 1{\cdot}52$, or 55 per cent, of soap hydrate, and 45 per cent of free solution containing 7·85 per cent of salt.

An example will make it clear how the data are obtained for controlling the operation. Suppose the pan to contain

10 tons of fatty acids in the form of soap No. 3 from which it is desired to make soap No. 8.

The weight of soap in the pan at the start is $\frac{10}{\cdot 633}$ tons $= 15{\cdot}8$ tons. As 100 parts of soap require ·066 NaCl to make the new soap, 15·8 tons require ·0104 ton on this account.

The amount of nigre being fixed at 15 per cent of the whole, we can, knowing the fatty acid percentages of the initial and final soaps calculate the fatty acid percentage of the pan on fitting from the formula on p. 93. This works out at 58·0 per cent, and the mass on fitting must therefore be $\frac{10}{\cdot 58} = 17{\cdot}25$ tons: 15 per cent of this, or 2·59 tons, is to be nigre. The nigre contains 45 per cent free solution, and this contains 7·85 per cent NaCl; the weight of salt required for the nigre is therefore $2{\cdot}59 \times {\cdot}45 \times {\cdot}0785$ ton $= {\cdot}0918$ ton. Add to this the amount ·0104 and the total amount required for the operation is ·1022 ton.

The fit is conducted in the usual manner, first running in this amount of salt as brine, and then water to make up a final weight of 17·25 tons. The appearance of the soap on fitting will probably seem abnormal, but no account need be taken of this. Pans fitted so finely as this settle somewhat slowly, and it is possible that an additional day will have to be allowed.

Many careful tests of soaps made in this way show them to be just as hard as those of a higher fatty acid percentage. The general appearance is very good; when the charge is one that usually produces a rather rough-looking soap at 63 per cent, this effect disappears at 61 or 60 per cent, but the soaps still have a certain amount of feather.

The Control of Nigres.—The process of fitting greatly improves the appearance and texture of the soap, and also enables the product to be kept fairly constant in composition. These advantages, however, are not gained at the mere cost of carrying out the operation in the pan-

room, but there is sometimes a tendency to disregard the other costs of the operation. In the first place the nigre, which forms the vehicle for removing considerable dirt and colouring matter from the soap, cannot itself be cleaned up by any ordinary methods. One might naturally imagine that a nigre, if passed through all the changes of a subsequent boil, would give up some of its impurities to the lyes, and the remainder to the nigre of the second boil, but in practice this does not happen, and a certain deterioration always occurs when nigre is returned to a second boil of the same soap. In most cases therefore the nigre is passed on to a pan which is otherwise made up of cheaper materials, and the value of its fatty acids is reduced to their level; this difference in values constitutes a real charge on the original operation. Thus it pays to take whatever measures are possible to reduce the amount of fatty acids in the nigre to a minimum. Another aspect of the matter of equal importance, though it is often overlooked, is the effect of variations in the amount of nigre on the yield of good soap from the pan. Apart from the nigre this yield is never quantitative, as there is always a small amount of neat soap that cannot be skimmed off from the nigre, and in addition small amounts of crusts and fob. This loss, fortunately not large, cannot be avoided, and not much can be done to reduce it below about 3 to 5 per cent, but the proportion of the soap retained by the nigre is generally much greater. The latter is, however, under control, and suitable means should be taken to keep the amount and richness of the nigre as low as circumstances admit.

The reduction in the yield from a pan caused by allowing an excessive amount of nigre, or too rich a nigre, is a matter which may have a marked effect on the pan-room costs. Quite apart from the fact that any reduction of the output is a disadvantage in itself, it may cause a considerable increase in the cost per ton of the soap made. If 20 tons of good soap should be cleansed from a pan, but only 18 are actually obtained, all the expenses of making the boil, general charges, wages, steam, and so

on, have to be borne by the reduced quantity, and the manufacturing cost per ton is raised by one ninth; one may put it in another way by saying that ten boils are necessary when nine should be sufficient.

The general causes which lead to the formation of undue wastage of this kind have already been explained, but their importance to the soap maker can only be fully realised when expressed in figures, giving definite measurement of the effects. This is easily done with the aid of a useful formula which is derived as follows.

Let the total amount of material in the pan on fitting be called unity, and the amount of nigre x. Then the amount of neat soap is $1-x$.

Let a be the fatty-acid percentage of the total contents,
b ,, ,, ,, nigre, and
c ,, ,, ,, neat soap.

Now the total quantity of fatty acids in the pan = quantity in nigre + quantity in neat soap, or

$$\frac{a}{100}=\frac{bx}{100}+\frac{c(1-x)}{100}, \quad \text{or,} \quad a=bx+c(1-x),$$

$$\text{and} \quad x=\frac{c-a}{c-b}.$$

Putting this into words, the amount of nigre as a fraction of the whole mass

$$=\frac{\text{F.A. \% in neat soap} - \text{F.A. \% in total mass}}{\text{F.A. \% in neat soap} - \text{F.A. \% in nigre}}.$$

The formula may first be used to determine the amounts of nigre formed when the pan is at different stages of dilution. As the type of fit affects the result two cases are considered: (*a*) is a coarse fit yielding a neat soap of 63 per cent, and a nigre of 18·5 per cent fatty acids; (*b*) a smooth fit yielding neat soap at 61 per cent and nigre at 38·5 per cent fatty acids.

Thus even when the fit is rough it pays to take every care to maintain as high an average percentage of fatty acids in the fitted pan as possible, and above all to avoid

Average fatty acids in pan %	Nigre, percentage of pan contents		Percentage of total fatty acids in nigre	
	(*a*)	(*b*)	(*a*)	(*b*)
56	15·7	22·2	5·18	15·3
54	20·3	31·2	6·98	22·2
52	24·6	35·6	8·80	26·4
50	29·3	49·0	10·84	37·7
48	33·8	57·8	13·02	46·2

making a practice of diluting the pan to a low percentage in order to make the fitting easier.

To aid in studying the effects of varying types of fit the figures quoted on p. 87 have been taken as a basis. These were plotted, the fatty acid percentages of neat soap and nigre respectively against the percentage of salt in the free solution. Smooth curves were drawn as closely as possible through these points, and from these were read off the figures in columns 1 to 3 of the table below. The total mass on fitting, column 4, is that which would be produced by adding water only to the curd to produce the stated dilution in the free solution, the curd being taken in this case to contain 58 per cent fatty acids and 1·45 per cent salt, this being equivalent to a test of 12 per cent in the lye.

Neat soap F.A. %	Nigre F.A. %	NaCl in free sol. %	Total mass F.A. %	Percentage nigre in total mass	Percentage of total F.A. in nigre
63	18·5	9·65	56·35	15·2	4·8
62·5	28·5	8·75	55·52	20·6	9·9
62	33·5	8·15	54·88	25·2	14·6
61·5	36·5	7·70	54·34	28·8	18·1
61	38·5	7·35	53·89	32·0	21·3
60·5	40·3	7·10	53·55	34·4	24·0
60	41·5	6·85	53·18	36·8	26·4

These figures show that even when a fairly rich curd is available the fitting of a pan so as to produce a soap of 62 per cent or lower is liable to cause an excessive

amount of nigre, though as has been shown this difficulty can be entirely overcome by making a preliminary coarse fit. The ordinary method of fitting as practised in most works is probably seldom directed towards producing a soap of any predetermined fatty acid percentage; in most cases the author has observed the tendency is merely to produce a fairly well-defined and pleasing appearance in the soap when finished. With different types of soap this tends to produce different average "pan tests," and thus a kind of natural standard is accepted as correct for each type of soap. Quite naturally strict conformity to these standards on successive boils is unlikely, and this is shown by the fact that most works make a practice, however little use may be made of the laboratory in other respects, of testing each boil before it is cleansed, and probably graining out and refitting the pan if the test comes much more than one-half per cent. below the accepted average. The mere difference in the quality of the finished soap would probably not justify this, but it is probably found that if a low-testing pan of this kind is cleansed the yield of good soap is very low. It should be borne in mind however that the production of a low-testing soap is seldom due to any abstruse causes; nine times out of ten the sole reason is that the percentage of salt in the free solution is too low. The necessity to wait three days or so while the pan is settling before doing the test, can be avoided by examination of the soap on this principle immediately the pan is fitted. The sample is taken as soon as the steam is shut off and immediately tested for fatty acids and salt. The result of these tests gives the percentage of salt in the free solution, which may be read off direct from the nomogram. The standard percentage to give the results required has previously been ascertained from the analyses of the normal product, and any marked deviation from this can readily be detected within an hour and the necessary correction to the fit made without loss of time. Reference to the first two analyses which come to hand show that in two successive boils of the same soap the tests of the fitted soap were

as follows:—No. 1: fatty acids, 53·0 per cent, NaCl, 1·5 per cent; No. 2: fatty acids, 56·0 per cent, NaCl, ·63 per cent. In the first case the percentage of salt in free solution is 7·6 per cent, and the resulting soap tested 62·85 per cent fatty acids. No. 2 contained 4·1 per cent salt in the free solution, but allowance had to be made in this case for ·08 per cent caustic (as Na_2O), raising the effective salt in free solution to 5 per cent. This soap tested 61·35 per cent fatty acids. The variation was in this case intentional, but had it been due to accident the low percentage of salt in the free solution would have indicated that a low test in the soap was to be expected.

In carrying out this test one should be careful to determine both the fatty acids and the salt on the same weighed portion, as the sample taken from the pan is a coarse mixture of neat soap and nigre, and two separate portions are liable to differ in composition.

Before leaving this part of the subject it should be pointed out that the adoption of the quantitative method does not involve any additional laboratory tests. It is of course assumed that the amount of fatty acids introduced into the pan is known, and that the brine used in the pan is saturated, so that its percentage of NaCl may be taken without sensible error to be 26 per cent. The mere weighing of the curds and lyes then gives the information from which the fatty acid and salt contents of the former can be calculated, the results being practically as accurate as those of ordinary routine tests. To control the fit it is of course necessary to know in the first instance what concentration of salt in the free solution will give the required result, and this is best determined by tests of a few samples of satisfactory soap, but once this figure is found it may continue in use so long as the fat charge remains tolerably constant.

CHAPTER VI

SOAPS CONTAINING ADDED MATERIALS

Commercial soaps made by mixing neat soap with solutions of alkalies or salts—the use of salt solution for this purpose—mixtures made with silicate solutions—the correct composition of silicated soaps—"glued-up," mottled, and carbolic soaps.

THE neat soap formed on fitting contains as a rule from 30 to 32 per cent of water. This water is combined naturally with the real soap and the product is often termed a pure or genuine soap.

As so large a percentage of water is in any case present it is not surprising that soap makers in the past strove to cheapen the soap by the addition of further quantities of water. Neat soap will not, however, mix with water to give a satisfactory product. If plain water is stirred into neat soap in a crutcher the soap with which it comes immediately into contact becomes heavily hydrated and much more viscous, to the extent even of forming semi-solid masses, and in these circumstances it is practically impossible with ordinary appliances to form a homogeneous mixture. Even if this can be done the soap when solid is altogether unsatisfactory, and thus early attempts at adulteration in this way were failures.

It was then found that the difficulties in mixing could be got over if moderate amounts of electrolyte, such as sodium sulphate, were dissolved in the water, but soaps made in this way were still very unsatisfactory. In 1835, however, the idea occurred to Sheridan to use weak solutions of sodium silicate for this purpose, and this process was patented and was found to produce much more presentable soaps. At that time, however, sodium silicate was made by a method which was not suitable for large-scale manufacture, and it was not until 1854, when Gossage invented the process at present in use, that this substance

was available to the soap maker at a low price and of standardised composition. Gossage and others now found a large market for silicated soaps, particularly for export to semi-civilised countries, and these products, which were made to standard compositions became a very important trade. Many of the popular varieties contained less than half their weight of ordinary "genuine" soap, but being cheap and constant in composition they suited the requirements of the populations that bought them. Nowadays soaps of this class are largely made in the countries where they are consumed, and export from this country has greatly fallen off.

The makers of these soaps claimed that the cheapening of soap by the addition of sodium silicate solution was justifiable, as this material has detergent properties and is much cheaper than fats; and for many years various kinds of silicated soaps, including the artificially mottled soaps, had a great vogue in this country as well as abroad. As a rule the soaps for home consumption were less heavily liquored than those made for export. There is still a demand for these, but owing to the higher manufacturing costs it is not possible to make a soap of this type to sell as cheaply, on the basis of real soap content, as an ordinary pure soap, and on the whole the public tends more and more to buy genuine soaps, or even to some extent to go a step further and use soap flakes when these are suitable. A pound of the latter, if of a reliable make, contains about as much real soap as $1\frac{1}{4}$ lb. of good bar soap.

Notwithstanding this tendency there is still a demand, which no soap maker can afford to neglect, for soaps which have been let down with silicate or other solutions. Generally speaking these are sold to buyers who are aware of the lower test of the soap and buy it on account of its lower price, or they may reach the public as proprietary articles without any implied guarantee as to their composition.

Although sodium silicate, as will be seen, is not the only material, or even always the best, for producing "liquored" soaps, it is probably more used than any other, its suitability for the purpose being due to the colloidal properties of the solution. If the mixture made in the crutcher is

homogeneous, as it is in the case of most of the soap mixtures containing over 50 per cent of fatty acids, it is doubtful whether silicate solution is better than a salt solution of proper strength; both solutions act in the same way, and the advantage is if anything with the salt solution. Mixtures made to produce the lower-testing soaps are however not homogeneous. If they are allowed to settle for several hours at the temperature of the crutcher they will separate into two layers—similar to neat soap and nigre on fitting. The only way to produce good solid soap from such mixtures is to produce a fine emulsion in the crutcher and to ensure that this does not separate during the cooling of the soap. The silicate solution seems to assist in the stabilisation of this emulsion, and the soap when set is smooth in texture and firm; similar mixtures made with salt solution are quite unsatisfactory.

A study of the nature of the soaps made by mixing limited quantities of salt solution with neat soap is a convenient introduction to the study of liquored soaps in general.

Soaps Liquored with Salt Solution.—The early attempts to make satisfactory soap mixtures of neat soap with sodium chloride or sulphate solutions were unsuccessful. When these salts are added to the water to be mixed with the soap they have the effect of preventing the excessive thickening of the mixture, and it was probably thought they would produce a harder soap than was obtainable by mixing with plain water. Later experiments have however shown that it is possible to get good results only when the amount of saline solution added does not much exceed 20 per cent of the soap taken, and when the strength of the solution is adjusted within fairly narrow limits.

To understand the effect of relatively small admixtures of salt solution one must refer to what has been said with regard to the fitting process, as this method is virtually an extension of that operation.

In the table on p. 87 the first two examples are slightly abnormal; after that it will be seen that the ratio of salt to fatty acid increases on descending the scale. Thus a

mixture exactly corresponding to one of the lower members of the series can be made from one above it by the addition of suitable quantities of salt and water. If this operation is carried out in the crutcher the resulting mixture is indistinguishable from the product made directly by the ordinary process of fitting.

The soaps made by either of these methods down to as low a fatty acid test as 60 per cent or so have all the ordinary characteristics of fitted soaps as generally made; when cold they are equally hard, and apart from a slight tendency to greater smoothness of texture on descending the scale they are indistinguishable except by analysis from the ordinary 63 per cent soaps. Generally speaking they are superior to even the best products made with sodium silicate.

Before making a soap mixture of this kind in the crutcher it must be borne in mind that the object is to make a mixture identical in composition with the neat soap which would be formed on fitting. This contains definite proportions of salt and water, and if the mixture differs from this by more than a trifle the result will be unsatisfactory. If the proportion of salt added is too high there will be a higher concentration of salt in the free solution, a state of affairs which would lead to the formation of a neat soap higher in fatty acids than that required, and a small amount of nigre. The mixture on leaving the crutcher might not have an opportunity to separate into two layers, but it would no longer be homogeneous, and the product when cold would be poor in texture. On the other hand, weakening the salt solution produces a mass which is homogeneous but is in this case more highly hydrated, and such soaps when cold are also poor in quality, being softer and somewhat resilient to the touch. In actual practice mathematical exactness is not necessary, and there is probably rather more tolerance than with silicate mixtures, but as the strength of salt solution required varies very greatly according to circumstances steps should be taken to determine this as accurately as possible.

The best way to do this is to carry out a short series of fitting experiments. If a small experimental pan is available a good plan is to take a suitable amount of newly fitted soap of the type required from a manufacturing pan, and re-fit this in various stages with successive additions of water, taking samples at each stage. Each sample is allowed to settle in a beaker and the percentage of fatty acids and salt in the neat soap determined. If a small pan is not available, sufficiently good results may be obtained from a few miniature boils. It is best to plot the results on squared paper and draw a smooth curve as nearly as possible through the various points. This helps to even out small errors and will show the percentage of salt in the soap of the required fatty acid percentage, and from this there can be worked out what amounts of salt and water are required to make any of the lower soaps from any one higher in the series. The following table was constructed in this way from the results 3 to 10 in the table on p. 87.

Fatty acids %	NaCl %	Wt. of run soap from 100 of 63 %	Total NaCl in run soap	NaCl to add %	Strength of salt solution %
63	·434	—	—	—	—
62·5	·451	100·81	·455	·021	2·6
62	·478	101·62	·486	·052	3·2
61·5	·507	102·44	·520	·086	3·5
61	·542	103·28	·560	·126	3·8
60·5	·571	104·15	·594	·160	4·2
60	·632	105·00	·664	·230	4·6

Any such figures apply to one definite type of soap; in this case one of a very soluble type. With less soluble soaps the NaCl figures are naturally lower and the change with decreasing fatty acid percentage less rapid, and in such cases the strengths of salt solution required may be much less, for example ·4 to ·8 per cent. In all cases, however, the strength of the salt solution increases progressively with the amount of runnings required. For any given soap base which has to be run as a matter of routine to a definite fatty acid percentage the final mixture

will have a definite constant composition as long as the average properties of the fatty acids in the soap remain reasonably constant, but with each fresh boil the tests of the actual neat soap available must be taken into account. Thus in the above table it was assumed that the neat soap taken was 63 per cent. Had it been 62·5 per cent with ·451 NaCl then the total amount of 60 per cent soap from 100 parts taken would be $100 \times \frac{62{\cdot}5}{60} = 104{\cdot}17$. This quantity would contain when mixed $\cdot 632 \times 1{\cdot}0417$ NaCl = ·66, and therefore the amount of salt to add would be ·209 in 4·17 of solution, or 4·17 parts of a 5 per cent solution.

In practice, when a number of mixings have to be made the required strength of salt solution is worked out and a sufficient quantity made up for the whole boil. There is usually no need to carry out any trial mixings. A point to bear in mind is that as the soap mixture when finished is identical with a fitted soap it has no tendency to separate at a high temperature. For this reason it is good practice, apart from the increase in the yield of neat soap obtained by doing so, to fit the pan somewhat coarsely, so that it may be cleansed possibly a day earlier and somewhat hotter than when the fit is smooth and more time has to be allowed for it to settle. Soap mixtures of this type are somewhat thick in the crutcher and a temperature rather higher than usual is desirable. If the mixture is found to be exceedingly stiff it may be an indication that the salt solution is too weak, and it is then sometimes permissible to thin it by a cautious increase in the strength of the salt solution, but this should not be overdone or the texture of the soap will suffer. As these mixtures when properly made are homogeneous there is no occasion to crutch further in the frame. The quantities of salt added should always be worked out as described, but as there is a reasonable amount of tolerance slight errors are of no great consequence.

Since it is difficult to obtain a well-settled fitted soap at a test below about 60 per cent the above method

cannot be followed exactly in making the lower soaps. But excellent soaps at 58 per cent and even lower, have been made on the same principle. From the course of the curve above 60 per cent it is possible to estimate what strength of salt solution will be required to make these lower mixtures, after which a few trial mixings will soon decide whether the salt solution of the strength arrived at in this way, or one a little weaker or stronger, will make the best soap.

Run soaps containing cresols, so-called carbolic soaps, can also be made in good quality by this method. In this case also it is best to use a method of trial and error guided by the above considerations, in deciding upon the best possible mixture.

Very careful comparisons have been made of soaps made with salt solution with the best silicated soaps from similar bases. They are almost invariably found on careful measurement to be slightly harder, quite equal in texture, and generally a shade brighter. The saving in direct cost as compared with silicate is only trifling, but it is a distinct advantage to be able to return scraps direct to the soap pan without introducing any silicate. The method is however only applicable to producing soaps simulating neat soap, and thus definitely not to those liquored below 50 per cent or thereabouts.

Sodium Silicate for Soap Runnings.—Only one of the sodium silicates of commerce is a definite chemical individual; this is sodium metasilicate $Na_2O.SiO_2$, a very soluble crystalline substance, quite different in properties from the commoner products. The latter are manufactured as glasses which are dissolved in water under pressure, the solutions being filtered and then concentrated to such strengths as are required. These form the so-called neutral and alkaline solutions, all actually alkaline in reaction. In the former the ratio $SiO_2 : Na_2O$ is approximately 3 : 1, in the latter approximately 2 : 1. The dilute solutions are mobile, but on concentration they become much more viscous; the commercial 80° Tw. "neutral" and 100° Tw. "alkaline" being thickish liquids. Hydrolysis

occurs in all solutions, which thus have in part the properties of caustic soda solutions; the "alkaline" and "neutral" solutions differ in this respect only in degree. The former are mainly employed in this country in mixing soaps with weak liquor; for making "glued-up" soaps in which strong solutions are used both types of solution are in use.

The amount of silicate solution employed in making a soap of given fatty acid percentage depends only upon the tests of the original neat soap and of that required, allowance being possibly made for any small amounts of solid material added as filling, but the strength of solution required to make the soap of passable appearance and hardness varies enormously, this being dependent on the nature of the fatty acids and also on the degree of dilution required. No general rules have been laid down to determine the strength of solution required for any specific soap mixture, and probably every manufacturer who makes this class of product has laboriously evolved the standards he requires by repeated trials. Even so the standards cannot be adhered to strictly as small variations in the components of the soap base, or in the fatty acid content of the neat soap may necessitate using slightly stronger or weaker solutions than the standard. For this reason it is customary, on cleansing a fresh boil of soap, to make a few trial mixings with slightly varying strengths of silicate, and to judge from the results of these which strength may be expected to give the best result. It is not easy to mix small quantities well by hand, and the samples taken being small, the soap cools much more quickly than the large mass in a frame, and is not always a good guide to the appearance and texture of the latter, but failing anything better this is the method generally adopted. On account of the difficulty in judging in this way what strength of solution is most suitable this method is not as reliable as one might wish, and in most works the proportion of finished soap rejected on account of quality is considerably higher with silicated than with genuine soaps.

An introduction to the study of silicated soaps is provided by the principles of the method by which slightly run soaps are made with the aid of dilute salt solution. These mixtures are all essentially types of neat soap, and are identical with the various grades obtained in the pan by suitable adjustments of the components. Silicate of soda solutions are in one respect comparable with salt solutions; they are all more or less hydrolysed and thus provide an electrolyte which behaves towards soap in a similar manner to salt. We might therefore expect silicate solutions, if of the correct concentration, when mixed in small amounts with neat soap to form lower types of neat soap in precisely the same manner. Again, in dealing with soaps of a fatty acid percentage lower than 50 or so one may conceive the products to be, while still hot, soap solutions comparable, not in this case to neat soap, but to nigre, and as nigres are saturated solutions, those containing the most soap would be made with relatively weak, and those with less soap with stronger silicate solutions. There is no need, however, to theorise as the matter is easily tested by experiment.

The author's own experiments were made by taking samples sufficient to fill a large beaker from soaps in process of manufacture, the samples being drawn from the crutcher when mixing was finished. These were then set aside to settle in a steam oven in the usual way. A note was made of the frames into which the mass of soap was run and this was subsequently examined when ready for sale. In this way one could consider the quality of the soap in conjunction with the phenomena observed in the experiment, and thus determine the conditions for forming the most satisfactory product. It was found that all soaps ranging from 28 per cent, the lowest tested, to roughly 42 per cent, were all of one type. When the quality was good the mass in the beaker separated into two layers, the upper one being however very small in amount. The lower layer constituting the bulk of the material was evidently a soap solution comparable with a nigre and the presence of a small upper layer indicated that it was

saturated with soap. It is obvious that as the mixture cools in the soap frame a further small amount of soap will come out of solution, and thus, in any case, mixtures such as the above, which are found to form good solid soap are never quite homogeneous; but as long as the soap forming the upper layer is only small in amount it appears to disperse satisfactorily throughout the mass, and the dispersion is probably stabilised by the silicic acid and other colloids present. With too weak a silicate solution the upper layer disappears and the solution is probably not quite saturated with soap; on the other hand if the solution is too strong the lower layer is weaker in soap and there is more of the upper or neat soap layer. In the first case the soap when cold is too soft and pasty, in the second the tendency is to roughness in texture. Those who find difficulty in determining which solution is best to employ by inspection of the cooled samples from trial mixings might find it a more reliable criterion to allow the samples made on the small scale to settle in a steam oven and choose the mixture which gives a minimum upper layer of soap, as the one most suited for use on the large scale.

The strength of silicate solution to employ in making a liquored soap of this class depends on the fatty acid standard aimed at, the average nature of the fatty acids in the base soap, which affects its solubility, and to a less extent on the percentage of salt in the soap. If variations in the last two factors can be eliminated it should be possible to make such soaps strictly according to rule. As far as the composition of the fat charge is concerned the majority of soaps of this class are of the tallow-rosin or palm oil-rosin types, and with careful control of the materials used it should not be difficult to ensure fairly constant solubility of the base soaps. The neat soap contains salt and this has the effect of slightly reducing the strength of silicate required, but if care is taken when fitting always to produce a fairly coarse fit the proportion of salt to soap is reduced to a minimum and becomes practically constant.

In the experiments mentioned above the soap mixture was taken from the crutcher at a temperature well below 100°, and separation had taken place before the mass had reached that temperature. Thus the lower layer could be assumed to be saturated with soap, not at 100°, but at some lower temperature, say about 80°. A solution saturated at 100° would contain more soap, and after cooling to 80° or so would separate an unduly large upper layer. In the first attempts to collect practical working data the solubilities of the soap were determined at 100°, but in making mixtures on the manufacturing scale in accordance with these results it was found that the strengths of silicate were somewhat too high. A fresh series of determinations was therefore carried out at about 80°, and these were found to give satisfactory results. The scale obtained for a tallow-rosin soap was as follows:

Fatty acids %	Alkaline silicate solution degrees Twaddell
28	37
30	34·1
32	31·2
34	28·4
36	25·6
38	22·8
40	20

The figures will vary slightly according to the proportion of rosin, the titre of the tallow, and the nature of the fit given to the soap, but any soap maker can make a scale suitable for the soap he uses. If great care is taken to keep the composition of the base soap constant it should be possible to employ such a set of figures on the large scale without carrying out the tedious trial mixings; otherwise three mixings could be made, one with the standard strength and the others slightly stronger and weaker respectively.

Run soaps in the range between, roughly, 40 and 50 per cent are in a different category. When these are heated and allowed to settle it is found that they separate into two layers much less disproportionate in size than in the case of the lower soaps. If one endeavours to make these soaps by reducing still further the concentration of silicate

solution, so as to continue to make simple solutions still richer in soap, the resultant soaps are altogether unsatisfactory. A successful mixture of this class must apparently consist of an emulsion of neat soap and nigre, which is formed by employing a silicate solution too strong to dissolve the soap completely. To secure a good product it is necessary to mix the soap and silicate solution at a lower temperature than is necessary in other cases, and often to crutch the mixture after it has been run into the frame until it reaches a consistency at which there is no risk of separation occurring.

It is interesting to recall that, in fitting a soap, diminishing concentration of the electrolyte leads to the formation of neat soap and nigre which continually approach one another in composition, and might eventually become identical at a fatty acid percentage in the neighbourhood of 47. One might naturally think that such a system would form an ideal soap mixture, but in fact this is not so. The best soaps of this composition are found on examination to separate into two layers, of which the upper forms about 35 per cent of the whole mass and contains about 60 to 61 per cent of fatty acids. There is very little tolerance in this respect and consequently the strength of the silicate solution has to be adjusted with more than the usual precision. It is well known that the soaps in this range are more difficult to make of satisfactory quality than most other liquored soaps.

The lightly liquored soaps offer no particular difficulty if they are regarded as types of neat soap similar to those made with weak brine. It is doubtful if there is any advantage in making them with silicate solution rather than with salt solution, but if silicate is used the general rules for its application are similar to those for salt, that is to say, for small additions of runnings very weak solutions are used, the strength increasing with increase in the amount. If the amount of salt is known which will make a good soap with salt solution a rough idea of the strength of silicate solution required is obtained by assuming 1 part of Na_2O in the silicate to be equivalent to 1·3 parts NaCl.

It cannot be assumed that every soap charge which produces a good genuine soap will necessarily make a good product when run with silicate solution; in some cases it seems impossible to get a good result whatever strength of silicate solution may be used. The fact is well known to soap makers though no satisfactory explanation has yet been given. An instance occurred recently of a somewhat unusual soap charge which produced a remarkably good soap when finished at 63 per cent. When occasion arose to let down some of this to about 60 per cent various attempts to do so with silicate solution were complete failures. Salt solution was then tried, and after one or two preliminary trials the most suitable concentration was determined. On mixing on the large scale this mixture behaved quite normally in the crutcher and the quality of the finished soap was excellent.

Other substances than salt and silicate solution are occasionally used in soap runnings. It is quite usual to incorporate a few per cent of insoluble material such as light magnesium carbonate or one of the refined earths, in some of the more heavily run soaps. Apart from these, various soluble alkaline salts are used to some extent. Amongst them are, sodium carbonate, potassium carbonate and chloride, and occasionally borax. These are mainly used for soaps only slightly reduced in fatty acid content, and the only way to arrive at a satisfactory mixture is by repeated experiments. Soaps of the "White Windsor" type are often made by reducing a toilet soap base to 59 or 60 per cent F.A. with quite strong solutions of potassium carbonate or sodium silicate or a mixture of the two. Such mixtures do not correspond to the ordinary soaps in this range, being rather of the nature of "glued-up" soaps.

"Glued-up" Soaps.—These soaps differ greatly in composition and physical state from the liquored soaps. In many cases the soap base contains a large proportion of rosin, 35 per cent or more, the fats being mainly of the palm-oil or tallow class. A very usual fatty acid percentage is 56 to 58 per cent, but lower qualities are

also made. The runnings are much stronger solutions than those of the liquored soaps, and usually consist of strong silicate solutions, either alkaline or neutral, with considerable amounts of soda ash, or occasionally potassium carbonate. The mixture in the crutcher is never homogeneous, but is essentially an emulsion of neat soap and of soap dissolved in a strong solution of silicate and carbonate. In order to prevent separation in the frame the temperature on mixing should be fairly low, and in any case the mixture in the crutcher becomes extremely viscous, so that a small quantity taken out on a spatula and allowed to fall on to a plate does not settle into a flattish pool before solidifying, but more or less retains its shape. Such soaps will not flow down a shoot but must be dropped from the crutcher, either direct into a frame, or into a movable hopper which delivers into the frames. These soaps sometimes tend to effloresce badly when exposed to the air, and it is curious that this tendency is more marked when they are compounded with neutral than with alkaline silicate. The reason for this is not known, but the fact seems to be well established. The efflorescence, which takes the form of fine needle-like crystals, sometimes $\frac{1}{2}$ in. long, seems to consist in the main of sodium bicarbonate. The neutral solution employed contains about 9 per cent Na_2O, the alkaline solution about twice as much.

Mottled Soaps.—The old-fashioned mottled or marbled was essentially a genuine soap, the mottled appearance being due to streaks of nigre or lye, contaminated with impurities which were always present in the caustic soda used. Its appearance was thus taken as indication that no added water was present, and that the fatty materials were such as to produce a very firm soap; in other words, the crudity of the product was taken as an indication of its value.

When Gossage's improvements in the manufacture of water-glass had made this material available to soap makers in large quantities at a reasonable price, the manufacture of sophisticated soaps by its use greatly

increased, and among other things it was found possible to manufacture soaps having somewhat the appearance of the old mottled soap, but containing considerably less real soap. At least 25 per cent of the product consists of sodium silicate and carbonate solutions, along with small quantities of pigment, such as ultramarine or ferric hydroxide, to produce the desired colour.

The soap bases for these soaps are either white or brownish in colour. In either case the fat charge contains about 25 per cent of nut oil, and no rosin is used. The remainder of the charge may be in the case of the brown base largely or entirely palm oil, in the case of the white base tallow and tallow substitutes, a little cotton oil, and so on. The neat soap, finished very rough, is usually transferred to a special mottling-pan. Gossage invented and used a special type of pan, capable of dealing with 40 or 50 tons at a time. In addition to the usual open steam coils a great length of close coil is provided, and most of the boiling is done with this. A strongly built steel lid, hinged near one side, can be closed and clamped tight when the boil is completed, and the mixture forced by pressure into the soap frames. An ordinary soap pan fitted with close coils serves almost equally well if the frames are not too distant. The base soap is boiled up with the requisite quantities of sodium silicate and carbonate, and frequently hypochlorite, and adjusted so as to contain 47 per cent of fatty acids. Much more exact control is needed than with any ordinary soap-making process, as there is little tolerance in the proportions of real soap, silicate, and carbonate. When the exact composition to make a good product is known, and accurate adjustments can be made, excellent soap can be made even in quite small quantities, but owing to the nice control that is necessary for success much special attention is required, and the process can hardly be economical on any but a large scale.

When the process is properly carried out, and the soap allowed to cool slowly in the frames, its appearance when cut will be that of a white or brownish mass interspersed

with blotches of irregular shape, many of them up to the size of a threepenny-piece. These should have sharply defined margins, and there should be no trace of colouring matter in the spaces between them. If there is any serious mistake in the proportions of the constituents the colouring matter may all fall to the bottom of the frame, or may be uniformly diffused through the mass, or the aggregates be extremely small. All these defects, though without effect on the intrinsic value of the soap, make it quite unsaleable, and any such material must be worked up again.

It is interesting to note that although mottled soaps of a different type may be made with a coconut-oil base so as to contain 20 per cent or less of fatty acids, soaps of the type described can be made successfully only at a test of about 47 per cent, the percentage at which the greatest difficulty occurs in making ordinary silicated soaps of good quality. The physical nature of these soaps is not properly understood, but one may imagine that the mass on the point of setting consists of a two-phase system of neat soap and nigre, the two phases being so similar in composition that they will not separate into two layers by the action of gravity. What type of forces cause the segregation of masses of soap and nigre side by side, and why the pigment may be distributed through one and not the other of them, are questions still awaiting an answer.

Below are given the figures of two mixings, made from the same batch of neat soap. The first is the standard charge and produced a good mottle. In the second there is ·2 per cent additional alkali, as Na_2O, and in this case the mass separated into two layers.

Neat soap	Added materials				
	Silicate sol. 100° Tw.	Na_2CO_3 sol. 68° Tw.	NaCl	Ultra-marine	Water
74	4·12	5·6	0·2	0·2	15·88
74	4·82	6·2	0·2	0·2	14·58

Much smaller variations than these are sufficient to spoil the mottle and make the soap unsaleable.

Carbolic Soaps.—Pure phenol or carbolic acid is used in making certain medicated soaps, but in most so-called carbolic soaps the added material consists of a somewhat crude distillate consisting mainly of a mixture of the cresols. The mixture may also contain pyridine, an undesirable, evil-smelling substance, and naphthalene, which is in itself harmless but of less value than the cresols. Naphthalene is sometimes intentionally added to modify the odour. Qualitative tests for these impurities, made by shaking a few c.c. of the material with sufficiently strong caustic soda to dissolve the cresols, is sufficient to discriminate between good and bad samples. The odour of pyridine develops strongly if more than a trace is present; material developing a strong smell of it should be rejected. Naphthalene is insoluble in the alkali.

Commercial carbolic soaps contain generally between $1\frac{1}{2}$ and $3\frac{1}{2}$ per cent of cresols. The addition of cresols makes the soap softer, and when occasionally soaps have to be prepared containing a much larger quantity this problem becomes a real difficulty. It was at one time thought to be necessary to add caustic soda in amount chemically equivalent to the cresols present, and this may in certain circumstances be advantageous, but plenty of good soap has been made without doing so. Fashion decrees that carbolic soaps should be coloured red, pink, or brown, and this is up to a point an advantage to the soap maker, as it enables him to use up nigres and scrap soap of poor colour; but unfortunately different distributors seem to consider it important to have different tints and depths of colour, varying from the clear pink given by Rhodamine B to dull red. The most usual soap bases for carbolic soaps are those of the washer type; glued-up soaps are also occasionally used.

CHAPTER VII

GLYCERIN IN THE SPENT LYES

Glycerin in the spent lyes—distribution of glycerin between soap curd and lye—the principles which govern the highest economical recovery of glycerin—graphic methods to facilitate calculations—control of the operations in accordance with these principles—examples of yields obtainable in the manufacture of different types of soap.

Glycerin in the Spent Lyes.—When a pan of soap has been well grained out and settled, practically the whole of the soap is in the upper layer, but the glycerin is distributed between the soap and the lye, and generally more of it is in the curd than in the lye. The latter is run off, and when the curd is boiled up with a fresh amount of water, and again grained out, the glycerin which remained in the first curd is now distributed in the same manner as before between the two layers. Thus in the course of a number of operations successive batches of lye remove the glycerin piecemeal from the soap. Each successive batch of lye is weaker than the foregoing and a stage is at last reached at which the lye is so weak in glycerin that it does not pay for treatment and evaporation. At this stage washing should be discontinued, and a certain amount of glycerin will still be left in the soap. Thus it is evident that whereas in the case of the soap the yield of product is very nearly quantitative, in the case of the glycerin only a portion, falling considerably short of the whole, is recoverable in the lyes, and also that this proportion may vary greatly according to the quantity of lye produced.

Now although it is not the best method, soap can be made by the ordinary process without any guidance from outside the pan-room. The indications as to complete saponification, proper graining, and fitting enable a skilful soap boiler to make perfectly good soap without any external aid. But there are no such indications, and no

simple test of any kind, which enable the progress of glycerin removal to be followed, and unless the matter be left to chance, guided only by the vaguest general ideas, in which case no reasonable return of glycerin can be hoped for, some kind of indication must be given to the soap boiler as to the amount of washing the soaps require. Information on this subject in text-books is scanty, and usually of a purely general nature, but it is easily seen that precise figures are necessary if good results are to be obtained. In view of the fact that the value of the glycerin obtained as by-product to a ton of ordinary soap is possibly 10 per cent or more of the value of the soap itself, the recovery of glycerin economically and in good yield is of great importance to the manufacturer.

Most soap makers make a variety of soaps, and the amount of glycerin yielded by the fats from which they are made may vary considerably. The proportion of this glycerin actually obtainable in the lyes, if the extraction is carried to the point at which the lyes are just strong enough to be evaporated with profit, also depends upon the composition of the raw materials, and so in any systematic method of glycerin recovery each type of soap must be considered on its merits. One cannot lay down as a fixed rule that any definite percentage recovery for the soapery considered as a whole is good practice, as this figure depends altogether on the average quality of the raw materials used. In the light of present knowledge, however, all the data are available for determining what yield is practically possible for any given soap. These are, first the percentage of glycerin liberated from the fats, secondly the strength of spent lye with which it is just possible to deal with profit, this being dependent on the value of crude glycerin and the cost of producing it from lyes of given glycerin content, and finally the numerical relationships which exist between the quantities of soap and spent lye and of the glycerin they contain. It is only in recent times that any light has been thrown on the last of these.

The Distribution of Glycerin between the Soap Curd and the Lye.—If a soap is made from a mixture

of fatty acids, so that no glycerin at all is present, and grained out in the ordinary way it behaves in quite a normal manner. Curd and lye separate as usual and might be found to possess such compositions as the following:—

Curd		Lye	
Fatty acids . .	58 %	Sodium chloride .	11·0 %
=real soap . .	62·8 %	Other solids . .	0·5 %
Sodium chloride .	1·4 %	Water . . .	88·5 %
Water . . .	35·8 %		

If we now assume the amount of lye to be in some ordinary proportion to that of the curd, say 0·3 of lye to 1 of curd, then the relative weights of water in the two will be: in the curd 35·8 and in the lye $88{\cdot}5 \times 0{\cdot}3 = 26{\cdot}5$ —*i.e.* 1·35 in the curd for each 1 in the lye. The water in the lye will thus be $\frac{1}{2{\cdot}35}$ of the whole.

If glycerin in known amount is added to the mass before graining out in an experiment such as the above, it is found that the proportions of it in the two layers are the same as those of the water, the glycerin in the lye being in this case $\frac{1}{2{\cdot}35}$, or ·425 of the total glycerin present.

A single experiment on these lines would not be entirely convincing as no very exact method exists of determining glycerin in spent lyes and soap, but the average of a large number of experiments, some made with the use of fatty acids and weighed amounts of glycerin as above, and others with weighed quantities of fat, the ester value of which was carefully determined, confirmed the substantial accuracy of the rule. A further and more convincing confirmation was obtained by following the course of several large-scale boils through many changes, in each of which the curd and lye were carefully weighed. From these data it was possible to calculate what percentage of glycerin should be left on the above assumption in the final curd. These results agreed closely with the amounts of glycerin actually determined in the curd. Since the latter is only a small fraction of the total glycerin under

consideration, and the error on its determination practically negligible in comparison with the whole amount, it could be said that the amount in the lyes was satisfactorily accounted for, and the substantial accuracy of the rule established.

Before going on to study the applications of this rule to practice two other matters connected with glycerin recovery should first be dealt with. First, it is assumed throughout that the glycerin liberated from the fats is not attacked in the boiling process, and that the whole of it is present in either the soap curd or the lye. There seems to be no evidence of any loss, and the conditions in the soap pan would not appear favourable for any chemical reaction to occur, neither are any of the ordinary decomposition products of glycerin to be detected in the lyes fresh from the pan. (Trimethylene glycol, when it occurs, is probably formed only when the lyes have left the pan, and are stored for a while in conditions under which micro-organisms can attack the glycerin.) Apart from this, when very careful account is kept of the quantities of glycerin at all stages of the process, the glycerin in the lyes can in the long run be satisfactorily accounted for, and so for practical purposes one is justified in assuming that all glycerin known to be in the pan apart from that left in the soap is to be found in the lyes, or in other words the glycerin yielded in the lyes may be assumed to be the amount liberated from the fats less that left in the soap.

Some attempt must be made to understand the mechanism of the removal of glycerin from the soap into the lye, and this may perhaps be made clearer by a simple analogy. If an insoluble powder, such as fine sand, is mixed with a solution of a soluble substance in water, and the mixture allowed to settle, a certain amount of the solution fills the spaces between the particles of the solid, and any excess can be poured off. If one mixes, for example, 1 kg. of sand with 500 c.c. of salt solution it will probably be possible to pour away 200 c.c. of the salt solution. In this case, unless the substances are such that adsorption can occur on the surfaces of the

solid, two fifths of the salt are recoverable from the solution poured off and three fifths remain along with the sand. If 200 c.c. more water are now mixed in with the residue and the mixture once more allowed to settle it should be possible to pour off a further quantity of salt solution, weaker than the first, and so on. Now if the quantity of salt originally taken was 1, the amount left in the sand after the first operation would be ·6; on the second operation, starting with ·6, the amount left after washing would be $\cdot 6 \times \cdot 6$, on the third operation $\cdot 6^3 = \cdot 216$, and so on, each successive wash water being weaker, and the amount left in the sand becoming less and less but never entirely disappearing. Such a series of operations is comparable to the washing of glycerin from soap under favourable conditions. Suppose now that the sand, instead of being loose, is made up into a number of small packets each enclosed in a very thin membrane through which salt and water are able to permeate. The solution surrounding the granules of sand can no longer circulate freely among the fresh water, and agitation will not have the same effect as before unless some of the packets are broken. In course of time, however, diffusion will bring about admixture, but the process will be much slower.

An analogy should not be pressed too far, but in the above cases the loose sand may be taken to represent, if not actual molecules, at least very small masses of soap hydrate, representing more or less the state of affairs when the soap in the pan is "close" and the whole of the water concerned seems to mix freely and rapidly with the glycerin, this including not only the solvent water but also that loosely combined with the soap as water of hydration. When, however, the soap in the pan is no longer in the condition that would be described as "close," one may imagine the aggregates of soap to be much larger, analogous to some extent to the packets in the crude illustration, but differing from them in that their surfaces are easily ruptured and will then reunite in other forms of their own accord. Thus one might

expect violent agitation of the soap to assist materially the process of diffusion, but there is no doubt the existence of the soap in large coherent masses must tend to hinder to some extent the removal of the glycerin into the lye. It is therefore advisable when carrying out a wash to add as nearly as possible all the plain water that will be required in the first instance, thus deferring as long as may be the existence of an "open" condition in the pan, and it can do no harm to continue the boiling for a short time after the pan is fully grained out. It also stands to reason that if brine is added to the pan when it is already sufficiently grained the water in it is unlikely to remove as much glycerin as it normally should. With proper attention to these details it will be found that the removal of glycerin will in practice conform to the above-mentioned rule.

In the light of what has just been said it is obvious that the results of experiments on the laboratory scale are liable to be very misleading. While it is quite a simple matter to make a boil of soap in a beaker with a few hundred grams of material, it is difficult to effect sufficiently thorough agitation with steam to ensure conditions in which equilibrium will be attained, and there is a strong probability that the ratio of glycerin concentration in the curd to that in the lye will be higher than it should be. For this reason all experiments designed to check the accuracy of the distribution rule were carried out in actual soap pans in which normal conditions of working were ensured.

Assuming the accuracy of the distribution rule under normal working conditions one can now study the effect upon the removal of glycerin from the soap of variations in the composition of the curd, of the relative amount of lye, the number of changes made, and so on. To begin with, the effect of variation in the composition of the curd will be considered.

In the example given on p. 116 the curd was assumed to contain 58 per cent of fatty acids and 35·8 per cent water, and the lye to contain 88·5 per cent water. For

each 1 per cent of water in the lye there would therefore be ·405 per cent in the curd, and glycerin if present would be in the same relative proportions. Thus if the lye contained 2 per cent of glycerin the curd would contain 0·81 per cent. The figure ·405 is called the partition coefficient for glycerin between the curd and the lye. Curds may, however, vary considerably in the amount of soap they contain, and curds poorer in soap will naturally contain a higher percentage of water and glycerin, and will thus retain a higher proportion of the total glycerin in the system than the richer ones. The following table shows the percentages of water, or water + glycerin, and the partition coefficients of curds ranging between 50 per cent and 60 per cent fatty acids, on the assumption that the lye contains 88·5 per cent water.

Fatty acids %	Real soap %	NaCl %	Water %	Partition coefficient
60	65·1	1·0	33·9	·383
58	62·9	1·3	35·8	·405
56	60·7	1·7	37·6	·425
54	58·5	2·0	39·5	·447
52	56·3	2·3	41·4	·468
50	54·2	2·6	43·2	·488

The value of the partition coefficient comes into consideration in connection with the strength of the final lyes.

To save tedious calculations a nomogram (fig. 7) has been constructed. It shows the connection between the proportion of the glycerin removed in the lye, the amount of lye formed, and the fatty acid percentage of the curd. With the aid of this diagram it can be seen at a glance how variations in the composition of the curd, and of the amount of lye removed, affect the recovery of glycerin; a few examples will be instructive.

1. To illustrate the effect of the composition of the curd. If the amount of lye is ·4 for each 1 of fatty acid the proportion of the glycerin removed in the lye amounts to ·31

if the curd has 52 per cent of fatty acids, and ·36 if it has 58 per cent.

2. To show the additional amount of lye required to overcome this effect. To remove the same amount of glycerin from the curd as in the latter case will require ·52 lye for each 1 of fatty acid—*i.e.* nearly one third more lye. The concentration of glycerin in the lye will thus be reduced by one fourth.

3. If the mass of soap, water, and salt in a pan is so adjusted as to give a more or less definite amount of lye on the supposition that the curd separates at 58 per cent, the accidental production of a poorer curd involves the separation of a smaller amount of lye, as some of the lye which should separate remains entangled in the curd. The weight of a 58 per cent curd is 1·725, that of a 52 per cent curd is 1·925 for each 1 of fatty acid. Consequently, if the amount of lye in the first case is ·4 for each 1 of fatty acid, in the second case it is only ·2, and the recovery of glycerin is seen from the chart to be only ·182 in this case—that is to say, one half of what it should be.

These examples show that it is of great importance to ensure the separation of rich curds by careful graining. This is done by reducing to a minimum the amount of salt used for graining. In order to determine whether any risk of loss of soap is incurred by doing so soaps were grained out with varying concentrations of salt in the lye, and fatty acids determined in the latter. The following figures were from an experiment with a soap of the washer type:

NaCl in free solution %	Fatty acids %
10·5	4·15
10·84	0·18
11·4	0·14
11·7	0·17
12·0	0·17
12·5	0·12

The first sample represents a rough fit. The other figures come sufficiently close, allowing for inevitable small errors in analysis, to show that a concentration of salt about 1 per cent higher than that required for a very

rough fit is quite as effective as higher concentrations in keeping soap out of the lye, while at the same time enabling curds of the right type to be formed.

The amount of lye that may be conveniently produced on one change is limited, and is almost always insufficient to remove the requisite amount of glycerin from the soap. It is easily understood that if a certain total amount of lye is produced in one or more operations the amount of glycerin removed will increase with the number of changes. Such a generalisation is, however, of little practical guidance, but the following figures show how much lye in all will be required to remove a definite amount of glycerin when it is distributed over several changes:

Number of changes	Parts of lye for yield of	
	80%	85%
1	2·47	3·92
2	1·53	2·12
3	1·31	1·83
4	1·24	1·69
5	1·18	1·60
6	1·14	1·54
7	1·12	1·48

The figures show that in ordinary cases it is advantageous to make three or four changes, but that beyond this number the gain is only trifling. If three or four changes can be given an overnight settling it is well to make that number, but little or nothing will be gained by making still more changes if this involves insufficient time for settling, as poorer separation will probably result from this, and will outweigh the advantage gained by the additional change.

In considering the effect of a number of changes one may employ the same calculations, or make use of the chart, for each of them in turn. There is a simpler way of dealing with this which is especially convenient when these considerations are turned to practical use. Suppose

a change to be carried out so as to recover some convenient simple proportion, say ·4, of the glycerin in the lye. Then the proportion left in the soap will be ·6. On a second change ·6 of the glycerin present will be left in the curd, that is to say $\cdot 6 \times \cdot 6$ of the original amount. Similarly the proportion of the original glycerin left in the curd after the third change will be $\cdot 6^3$, after the fourth change $\cdot 6^4$, and so on, always assuming the changes to be exactly similar. Now $\cdot 6^4 = \cdot 1296$—that is to say, practically 13 per cent of the original glycerin remains in the final curd, the yield being thus 87 per cent.

It may be required to know what will be the yield per change if a given number of changes, for example four, produce a given yield, say 82 per cent. In this case the argument is: 82 per cent yield is equivalent to ·18 of the total glycerin left in the soap. The amount left on one change will be $\cdot 18^{\frac{1}{4}}$, which is equal to ·65, and thus the proportion to be recovered on one change is ·35. This type of calculation constantly recurs, and for convenience a nomogram (diagram 8) has been constructed from which the results can be read off. It is quite sufficiently accurate for all practical purposes.

When it comes to the practical application of these principles in the soapery it will be quite obvious that the curds obtained will not all conveniently contain 58 per cent of fatty acids, nor will all amounts of lye be exactly as prescribed. One must therefore allow for unavoidable variations. Dealing first with the composition of the curds it may be said that in a series of changes the result will be that which would be obtained if each curd had the average test. If the curds are on the average poorer than they should be, steps must of course be taken to get better results in future boils, failing which it would be necessary to make allowance in the calculations for a lower standard. When the pan is fitted with a gauge, the determination of the weight of a curd, and hence its fatty acid test, is the work of only a few moments, and thus the work may be checked as it proceeds.

Wrong amounts of lye may be due to the difficulty,

when the pan is not fitted with a gauge, in making the contents up to the right amount on graining. Provided the variations are not too large this is of no consequence if errors on one change are corrected at a later one, there remaining only the final lye which cannot be adjusted in this way. So long as the total amount produced is correct quite large variations in the amounts of separate lyes have only a very small effect. Thus if four lyes of four tons each are required, practically no ill-effect would be produced if the amounts actually removed were, for example, 3·5, 4·5, 4·2, and 3·8 tons respectively. But if the wrong amounts of lye are due to inefficient graining, and the formation of weak curds, it is necessary, not only to take steps to remedy this on future changes, but to make some further allowance on further changes so that ultimately somewhat more than the originally prescribed amount of lye is produced.

Practical Application of the Foregoing Principles.—The first step is to ascertain what is the minimum strength of lye that can be profitably dealt with, and this is easily done. To take any convenient round figures as an illustration, suppose crude glycerin to be worth £30 per ton, and the cost of converting lyes averaging 5 per cent glycerol into crude to be £10 per ton of crude. Then if all glycerin plant costs were in inverse ratio to the strength of the lyes the cost of producing 1 ton of crude from lye of $1\frac{2}{3}$ per cent glycerol would be £30. Actually the cost should be somewhat lower, so that it would just pay to recover lyes of this strength, but other considerations, such as plant capacity, the possible need to work extra shifts, and so on, may make it advisable to fix a rather higher standard. In what follows a strength of 2 per cent glycerol has for convenience been assumed throughout, as being on the whole a reasonable figure.

Now, assuming that the last curd to be produced will have a fatty acid content of 58 per cent, the partition coefficient for glycerin will be 0·4, as near as no matter. Therefore if the lye is to contain 2 per cent of glycerin the percentage in the curd should be 0·8 per cent, and it is

important to note that this should apply to all kinds of soap, whether made of good materials or otherwise. This point is emphasised because in some works it is customary to allow more glycerin to remain in good quality soaps than in those made from poorer materials. If this is done the possibility of securing further quantities of payable lye from the better soaps is neglected, and the general yield is less than it might be. Knowing the total amount of fatty acids to be in the pan at the finish, and from this the weight of the last curd which is 1·725 times this amount, it is possible to say how much glycerin should be left in this curd, and what fraction this amount is of the glycerin taken into the pan. From these figures, knowing the number of changes to be made, the yield per change, and hence the quantity of lye required can be calculated. An example of a simple type of boil, such as making a toilet soap in a clean pan will make the method quite clear.

Example 1. Raw materials liberate 1·11 tons glycerin with 9·5 tons fatty acids all saponified on the first change, and three further changes made before the fit.

Weight of last curd $9{\cdot}5/{\cdot}58 = 16{\cdot}4$ tons; glycerin in last curd $16{\cdot}4 \times {\cdot}008 = {\cdot}131$ ton.

Fraction of the whole left in last curd $\frac{{\cdot}131}{1{\cdot}11} = {\cdot}118$, therefore

Yield in lyes = 88·2 per cent.

Now, 88·2 per cent on four changes = 41 per cent on one change, and

41 per cent on one change requires ·485 lye for 1 of fatty acid, or $·485 \times 9·5$ tons = 4·62 tons per change.

Example 2. If the fats are charged into a pan containing nigres etc. the amount of fatty acids and glycerin in these should be known, at least approximately, and added to those obtained from the fats. The treatment of such a boil, free from rosin, is shown as follows:—

Fatty acids from fats 9·6 tons; glycerin 0·92 ton.

Fatty acids from nigres 1·4 tons; glycerin 0·06 ton.

Total fatty acids 11·0 tons; glycerin at beginning 0·98 ton.

Glycerin in last curd $\frac{11{\cdot}0}{{\cdot}58} \times {\cdot}008 = 0{\cdot}152$ ton, which is 15·5 per cent of 0·98, the yield in four changes being thus 84·5 per cent.

This requires a yield of 37 per cent on a single change, for which the required amount of lye is ·41 for 1 of fatty acid, or 4·51 tons per change.

A large number of soaps contain rosin. Whenever possible this should be reserved for the change before the fit. The amount of rosin must be allowed for in the last curd and the loss calculated in the ordinary way, and from this the ratio of lye to fatty acid on each change. In practice, however, this would necessitate a rosin lye heavier than the others, which would be inconvenient, and it is better to take one of two alternatives. If practicable the best way is probably to arrange to remove the whole of the glycerin it is proposed to recover before the rosin change, that is to say from the fat changes only. In this way the loss in soap is less than when the last curd, increased in amount by the amount of the rosin soap, is allowed to retain the specified percentage of glycerin. The lye obtained from the rosin change, if this procedure is followed, is too weak to work up for crude glycerin, and should either be run away or used for making brine. The other alternative is to arrange to make a smaller amount of rosin lye, and to make up for this by increasing the amounts of the earlier lyes. Thus supposing the first intention to have been to make three tons of lye on each fat change, and four on the rosin change, the rosin acids being one fourth of the total, the last lye can be cut down, say, to three tons, and extra lye made on the fat changes. If this is done the amount to distribute over the earlier changes is not one ton but three quarters of a ton, owing to the lesser amount of curd on these changes. It is necessary to make a fair amount of lye on the rosin change in order to remove colour, otherwise the amount could be reduced still further.

Scraps, which contain very little glycerin, should also if possible be put into the pan at the last change. If they are returned at an earlier stage the soap with which they mix

contains relatively more glycerin than the scraps, and they tend to withhold some of this from the lye, so that more lye must be made to compensate for this; they behave in fact almost like rosin soap. On the last change however their effect is very small, as they approximate closely in composition to the soap which makes up the last curd. Actually as they are fitted soap they contain about one third less glycerin in proportion to fatty acids, and may thus be considered as a mixture two thirds of which is similar in composition to the last curd, and may therefore be disregarded, and one third glycerin-free soap. It is sufficient therefore to take one third of the weight of the scraps into consideration in computing the weight of the last curd.

A matter which introduces further complications into glycerin recovery is the presence of glycerin in the salt used. When the lyes are concentrated in the crude department nearly all the salt separates out and is removed from the solution. As taken from the evaporator this salt is mixed with a large amount of liquor containing anything between 10 and 80 per cent of glycerin, and steps are taken to remove this as well as possible. This is sometimes done by steaming out the salt, and sometimes by washing with treated lyes, but the removal of glycerin is never quite complete, and a greater or less amount is always present in the salt as returned to the pan room. The efficiency with which the glycerin is removed varies greatly; in some instances the amount remaining may be about 1 per cent on the salt or even less, but often it may be twice or three times this amount. It is important to consider what effect this may have upon the output.

100 tons of spent lye may possibly contain 4 tons of glycerin and 11 tons of salt. Upon evaporation the solid salt recovered will actually weigh 11 tons or rather over, since although a small amount remains dissolved in the crude glycerin the solid salt always retains a few per cent of moisture. If this salt contains only 1 per cent of glycerin, this will amount to 0·11 ton out of a total of 4 tons of glycerin, that is 2·65 per cent of the whole. In many cases the results are much worse than this, as the percentage

of glycerin left in the salt is frequently as high as 3 per cent, or even more, and the lyes may contain more salt than the above amount. Thus in a crude glycerin plant the recovery of crude glycerin from the lyes is never quantitative, the yield of this product in the department being reduced by the amount left in the salt and other small losses. The loss of the glycerin left in the salt will be only temporary if provision is made in the pan-room for recovering the whole of this glycerin, but a proper understanding of the method of doing so is essential.

This may be made clear if reference is made to Example 2 on p. 125. In this case the fraction recovered on each change is ·37 of the glycerin present. Now in following the course of the boil it is permissible to consider separately the glycerin derived from the fats and that from the added salt. As far as the former is concerned the recovery may be assumed to go on as usual, giving a yield of 84·5 per cent.

The fate of the glycerin in the salt may be considered in the following way. Suppose 1 unit weight to be included with the salt on each change, *i.e.* 4 units in all. That added in the first change will undergo all the changes, and the recovery from it will be 84·5 per cent, that is ·845.

On the second lot, undergoing only three changes, the yield will be 75·3 per cent (from chart 8), on the third 60·6 per cent, and on the last change 37·1 per cent. Therefore out of the 4 units taken the amount recovered will be $·845 + ·753 + ·606 + ·370 = 2·58$, which is $64\frac{1}{2}$ per cent of the glycerin in the salt used. We see therefore unless the quantities of lye are adjusted to suit the circumstances, the glycerin in the salt will not all be recovered; in this case $35\frac{1}{2}$ per cent of it will be finally lost. Now since salt containing 1 per cent glycerin represents an immediate loss of 2·7 per cent in the crude department, only about 1·8 per cent of this will be regained in the soap pan unless special provision is made to do so by forming additional lye. If larger quantities of glycerin are allowed to remain in the salt, the ultimate loss due to this cause may be of the order of 3 per cent.

If the glycerin in salt is determined at frequent intervals,

as it should be, it is easy with the aid of the charts to ascertain how much additional lye must be produced in order to recover it. As the amount is not large it is generally sufficient to make an approximation by allowing 1 to 1¼ per cent additional lye for each 1 per cent glycerin in the salt.

The Yields Obtainable.—The following table gives an indication of the results that should be obtained from various typical soaps. In each case it is assumed that four changes are made before the fit. In the first three examples, rosin and 5 cwt. of scraps for each ton of raw materials in the charge are added on the change before the fit. The last lye is assumed to contain 2 per cent glycerol.

	Glycerin in raw materials %	Ratio lye to raw materials	Glycerin yield %	Average lye glycerin %
1. Palm oil, rosin 3 : 1 .	6·0	·87	72·2	5·0
2. Tallow, rosin 78 : 22 .	7·8	1·13	78·7	5·42
3. Washer type . .	8·8	1·35	81·1	5·29
4. Soap powder base .	9·2	1·80	84·5	5·42
5. Flake base . .	11·1	1·85	88·2	5·29

The most noticeable point about these figures is the large variation in the amount of lye required in proportion to the raw materials. As any marked departure from these quantities involves either a lessened yield or the production of some quantity of lye weaker than the specified minimum it is evident that good results cannot be obtained by guesswork. The yields also vary greatly according to the type of soap, and this fact shows that it is not safe to base any estimates of cost of particular soaps upon the average figure for the works as a whole.

The figures given above and previously as yields represent the percentage of the total glycerin present in the pan in the first instance which is transferred to the lyes in that particular boil. But when the last curd is fitted, a portion of the glycerin in it passes into the nigre and as such is usually worked up in a later boil. Thus the true yield is higher than

those indicated. For example, soap No. 4 in the above table is that quoted in example 2 on page 125. The boil started, as is commonly the case, with the nigre from a previous boil, and the fatty acids and glycerin in this were allowed for, but no account was taken in the calculations of the glycerin in the nigre, only that in the lyes being taken as the yield from the pan. The glycerin in the last curd, about 15 per cent of the whole, is not actually a total loss, as generally about two fifths of it will pass into the nigre, and of this about 85 per cent, amounting to approximately 5 per cent of the original quantity, is recovered in the lyes of the next boil. Thus we may reckon that only about two thirds of the amounts of glycerin left in the last curd are in reality lost, and the yields in practice obtainable in the lyes are some 5 or 6 per cent higher than those shown in the table.

It may be said therefore that the actual yields in the factory, from fats to crude glycerin, should be approximately 3 per cent above those given for individual boils, that is rather over 5 per cent on account of the amounts obtainable on the subsequent boil, less 2 per cent or a little more for losses which may occur in converting the lye into crude glycerin.

For convenience, the calculations throughout this chapter have been based on the assumption that the last lye should contain 2 per cent of glycerin. This choice of a figure is arbitrary and in no way affects the general principles, but is probably a fair average under existing market conditions. Changing circumstances may however make it necessary at any time either to reduce the average yield, if glycerin prices are unfavourable or the demand poor, or to increase it in the event of a national demand for increased quantities of glycerin. By the adoption of the methods here explained any such change may be made practically at a moment's notice, all that is required being a revision of the amount of lyes to be produced, based on the assumption of a higher or a lower minimum strength of lye. To give a rough idea of the required alterations to produce a given effect one may take

the case of a factory obtaining a yield of 82 per cent on the basis of a minimum lye strength of 2 per cent. Suppose it is desired to reduce this yield to 75 per cent. The yield per boil would in the first instance be 79 per cent, and in the second 72 per cent, the losses in the last curd being respectively 21 per cent and 28 per cent. Thus the percentage left in the last curd, and consequently that in the last lye, will be raised in the ratio 28 to 21, *i.e.* the strength of the last lye would become 2·67 per cent. This is found to involve a reduction in the amount of lye required of about 23 per cent. If on the other hand it were decided to increase the average yield by 5 per cent the amount of lye produced would need to be increased by about 25 per cent, and the strength of the last lyes would be reduced to 1·52 per cent. In the latter case, if it were correct to assume that a lye of 2 per cent was the weakest that could be profitably dealt with, there would be a certain loss in producing the higher yield, but this would be kept within reasonable limits by the methods just described.

CHAPTER VIII

ENRICHMENT OF LYES WEAK IN GLYCERIN

Enrichment of lyes weak in glycerin by returning them to the pan—quantitative study of the effect of doing this—utilisation of the residual alkali and soap in the lyes by a preliminary treatment in the soapery—the economy resulting from doing this.

In the chemical treatment and evaporation of spent lyes to make crude glycerin a large portion of the costs per ton of crude vary in proportion to the amount of the lyes dealt with. Crude glycerin made from 2 per cent lyes therefore costs nearly twice as much to make as that made from lyes of twice that strength. A similar problem occurs in many chemical processes in which material is removed from an insoluble mass by repeated extractions with water, and it is an old device in these circumstances to enrich some of the weaker solutions by using them for the early extractions of a fresh lot of material. A method similar in principle was introduced in soap manufacture some thirty or forty years ago, but in spite of its utility does not seem to have come into general use. The reason for this is probably that any descriptions of the method failed to give any figures by which its advantages could be measured, and manufacturers have been averse from introducing complications into the process without definite measurements of the gain to be effected by doing so.

In its simplest form the operation merely consists in saturating some of the weakest lyes with salt and using the brine thus made for graining out the curd on the first change of another boil. If water and brine are used in the same proportion to the soap as normally, the introduction of an additional small amount of glycerin has the effect of enriching both the curd and the lye on that change. For simplicity the curd may be treated with the necessary small addition of water and ordinary brine to remove this excess of glycerin in the curd on the next change, so that at

the end of this operation conditions are restored to normal. The quantitative effects of this may be studied from such an example as No. 2 on p. 125. The amount of fatty acids in this boil was 11 tons, the initial amount of glycerin ·98 ton, and the lyes, each of 4·51 tons contained respectively 8·06, 5·05, 3·22, and 2 per cent of glycerin. Now suppose that on the next boil of the same soap the brine required for the first change is made by saturating some of the 2 per cent lye with salt. Omitting details of calculation, it may be stated that the amount of brine required is 2·88 tons, and this is made by dissolving ·47 ton of salt in 2·41 tons of 11 per cent lye. Actually of course some indefinite quantity of the lye is saturated with salt, and the brine used as required.

The 2·41 tons of lye contain ·048 ton of glycerin, which increases the amount of glycerin in the pan on the first change from ·98 ton to 1·028 tons. As the quantity of lye produced remains the same the amounts of glycerin in the lye and curd become increased in the same proportion, that is from ·363 and ·617 to ·38 and ·648 respectively. If on the second change the curd is reduced to the same glycerin percentage as in the original boil, this involves the removal of ·648 − ·389 ton = ·259 ton of glycerin, which is just 40 per cent of that present. This will require 5·11 tons of lye, against 4·51 in the first case. The third and fourth changes will be unaffected.

The 2·41 tons of last lye taken from the previous boil may be considered in effect to be taken from the boil under consideration, so that the reduction in the total amount of lye formed is 2·41 − ·6 tons, or 1·81 tons. Since the same total amount of glycerin is removed the average percentage of glycerin in the lyes is increased from 4·58 to 5·07, and the cost of the crude produced will be lessened by nearly 10 per cent.

The above represents the simplest way of carrying out the process. All that is necessary is to set aside rather over one half of the last lyes and saturate them with salt. This separates a small amount of soap from the lye, which has to be skimmed off, but this is the only difficulty, and quite a minor one. The brine made is used up on the first change,

and to allow for the glycerin which this would leave in the soap an additional amount of lye, roughly 12 to 14 per cent of that made on any change, is made on the second change, or better spread over all subsequent changes.

The lye which is to be used again is not necessarily converted into brine; it may be introduced just as it is into the pan when the latter is ready for graining, and will not by itself grain the soap, to which salt will still have to be added in the usual way. In soaperies where salt is used only in the solid form this alternative is the obvious thing to do, and is quite effective, and it does away with the slight complication of an additional brine tank.

While haphazard working is never to be recommended, it may be noted that in this operation any return of the last lye to the first change is bound to have some effect of the kind required, but naturally the best possible results are obtained only when some care is taken to use the correct quantities.

If lyes are returned only to the first change it is impossible to use up the whole of the last lye, but there is no reason why the remainder should not be employed on the second, and even on later changes. There is no need for any great exactness in the way this is carried out. It is possible when the lyes contain about 11 per cent of salt to arrange the quantities so that at the end of each change the glycerin introduced in the returned lye is all removed, leaving a curd with the same percentage of glycerin as that in the normal boil. This has the effect of producing a larger amount of lye but of the same strength as in the first instance. In this way the first two changes may be made to absorb almost exactly the whole of the lye from one change; one fourth of the total lyes is thus returned to the pan, but an additional amount of lye is made on the first and second changes. Since the effect of this operation is greatest when the lye is normally richest it is really better to return as large a proportion of the lye as possible to the pan on the first change. The results obtainable may be worked out as follows, taking a boil such as example No. 2 as a normal standard of comparison.

In this case 4·51 tons of lye are assumed to be formed

at each change, and the whole of the last lye is saturated with salt; 3 tons of this, with the amount of salt, ·608 ton, required for saturation are used on the first change. Some of the salt, ·253 ton, will be retained in the curd, and the amount of 11 per cent lye formed will be the original amount of 3 tons plus the amount which will be formed by the rest of the salt, ·355 ton, *i.e.* 3·23 tons; the total amount of lye will thus be 6·23 tons in all. This is ·567 of lye for each 1 of fatty acid, and will remove ·449 of the glycerin present. This glycerin consists of ·98 ton from the fats and ·06 ton from the lye returned to the pan, total 1·04 ton, and the amount removed in the lye will thus be ·467 ton. On the second change one may elect to produce just enough lye to reduce the fatty acid percentage of the curd to the same figure as in the normal boil, and thus the percentage of glycerin in this lye will be the same as in the first boil, *i.e.* 5·07 per cent. The amount of glycerin in this lye must be that in the first curd less that in the second, that is ·573 − ·389 = ·184, to which must be added ·03 present in the returned lye making ·214 in all. This is 35·5 per cent of the total glycerin now present, requiring ·38 lye for 1 of fatty acid, or 4·22 tons in all. The salt in the returned lye plus that required for saturation amounts to ·47 ton, just less than that required to make 4·4 tons of 11 per cent lye, the deficit of ·014 salt being added as such or as ordinary brine.

The final result is to obtain in the first two changes 6·23 tons of lye at 7·44 per cent and 4·22 tons at 5·07 per cent. These contain together ·467 + ·214 = ·681 of glycerin, which is exactly the same amount as obtained from the first two changes and the last change of the normal boil, viz. ·363 + ·228 + ·090. Whereas the normal boil produced 18·4 tons of lye, the amount in this case is 14·96 tons, a reduction in quantity of nearly 18 per cent, effecting a saving nearly as great in the crude glycerin costs.

In the following table the results of a normal boil and of the one just described are put side by side, the former under the figure 1, the latter under 2. Quantities of glycerin are in this case expressed in pounds.

Change	Initial glycerin		Glycerin in lye		Percentage glycerin				Weight of lye tons	
					in lye		in curd			
	1	2	1	2	1	2	1	2	1	2
1	2195	2229·4	812·2	1046	8·08	7·44	3·27	3·01	4·51	6·23
2	1377	1357·4	511·7	480	5·07	5·07	2·05	2·05	4·51	4·22
3	864·4	864·4	321·9	321·9	3·28	3·28	1·29	1·29	4·51	4·51
4	542·5	542·5	202·1	*202·1	2·00	2·00	·81	·81	4·51	4·51*

* Set aside to go to another boil.

At the present day a large proportion of soaps are of easily soluble types and require some such percentage of salt as 11 per cent for graining out. For certain other types, such as tallow rosin soaps, the lyes are weaker in salt. These lyes when saturated with salt require proportionally more of the latter, and thus more brine is made from a given amount of lye while less of it is required for graining. When the lye contains 8 per cent of salt it is only possible to use it up on the first two changes by making these abnormally large, and generally speaking the saving in the amount of lye produced will be only about three fourths of that in the former case. In such cases the efficiency is higher if a fair proportion of the lye is returned direct to the pan and employed in lieu of part of the water. If the soap in the pan is in a "close" state, as after saponification, a quantity of the lye not saturated with salt may be used up in this way, and will not affect the amount of salt required for graining. When the lye is used up thus on a wash a portion of the water which would normally be required is first used to close the soap, the remainder of the water being provided by the returned lye; brine made from the latter will be used as before for graining. By this expedient a considerable quantity of the weak lye can be returned on early changes.

There are thus innumerable variations in the way of carrying out this process, and exact measurements are not

necessary if common sense is used. The points to remember are to select those lyes which are bound to be weakest for returning to the pan, and to return them as far as possible to changes in which the maximum of glycerin is present.

The method as explained has the effect of obtaining the standard yield in less than the normal quantity of lye, but this has involved a departure from the rule that lyes should be recovered for treatment down to the minimum profitable strength. If one carried the boil a stage further, producing a further lye containing well below 2 per cent of glycerin, this lye might be returned to the pan, leaving the original fourth lye to be sent to the glycerin plant. The result of this would be roughly to recover about one third of the amount of glycerin previously left in the soap, or say an additional 5 per cent. As a set-off to this the nigre under these conditions would be correspondingly weaker, and would yield about one third less glycerin to the next boil, but the net gain on the operation would be of the order of $3\frac{1}{2}$ per cent. Thus if at any time circumstances force the manufacturer to increase his normal yield this process provides a means of doing so without additional expense.

Preliminary Treatment of Spent Lyes in the Pan-Room.—The spent lyes as they leave the pan contain considerable quantities of soap. The bulk of this separates out after a few hours' settling and should be skimmed off and returned to a soap pan; the small quantity which remains in solution may be recovered but is generally lost. Apart from the soap, alkali is also present in the lyes, mainly as sodium carbonate; the amount of this may be more than ten times as much as the combined alkali in the dissolved soap. The greater part of the alkali present in the lyes comes from the changes in which fat or rosin is saponified, the water washes being relatively free, so that the percentage in the average of all the lyes varies according to the amount of washing carried out. The alkali, if not recovered, is not only a dead loss of material in itself, but it requires acid of approximately equal value to neutralise it in the glycerin plant. Its presence is due to two main causes.

Until quite recently, and possibly even to some extent to-day, it was customary for soap makers to produce their own caustic soda from soda ash, by the action of lime. This process is carried out in a dilute solution and is never complete. When the solution is concentrated the greater part of the unchanged carbonate is thrown out of solution, but unless the evaporation is pushed very far there usually remains about 3 to 5 per cent of the sodium carbonate in the liquor as used in the soapery, and this is unaffected by the fats, and passes into the spent lye. Its amount may be quite considerable as may be seen. Ten tons of ordinary fats require approximately ·92 ton of caustic as Na_2O, and the accompanying sodium carbonate may thus easily amount to ·04 ton; if 4 tons of lye are produced the alkali carbonate in this will be 1 per cent. The average will be reduced by the admixture with further lyes comparatively free of carbonate, but in any case the actual loss of alkali is likely to be about that indicated. Careful control figures carried out over long periods indicate however that the amount of carbonate actually found in the spent lyes is considerably higher than that which would be caused by imperfect causticisation. To some extent this is due to carbon dioxide picked up from the air by the caustic in store; this may be a very trifling proportion of the whole in works where large quantities are dealt with but is relatively more in small works. A more important factor is the presence of carbon dioxide in the steam. Practically all boiler feed waters contain free carbon dioxide and carbonates or bicarbonates. Except where treatment with lime is possible, and well carried out, carbon dioxide in some form is found in the feed water, and if this is even in the form of sodium carbonate this substance is dissociated in the conditions which exist in the boiler and gives off free CO_2. Some waters can be quite effectively softened, from the point of view of the reduction of scale, by simple addition of soda ash to the supply kept at boiling-point. If this is left to the boiler-man to do without control there is always the risk of adding excess of soda, and this then finds its way

into the boiler and adds to the amount of CO_2 in the steam. In one works where this was done the author found that the excess consumption of caustic was quite large in spite of the fact that the caustic liquor bought was extremely pure, and was received in quantities which were used up in a few days. Losses due to similar causes may be more frequent than is generally thought.

To whatever causes its presence is due, there is always a considerable amount of sodium carbonate in the lye, and the obvious thing to do with it, rather than be put to the expense of neutralising it in the glycerin plant, is to convert it into soap. Early attempts to do this, using either rosin or fatty acids were unsuccessful, probably owing to the impossibility of bringing about sufficiently intimate contact between the reacting substances, but if steps are taken to distribute the fatty acids in a fine state of division throughout the mass of the lye the reaction proceeds rapidly and is nearly quantitative.

The only appliances required for carrying out the operation are a suitable tank in which the lye can be boiled, and some device for dispersing the fatty acids finely throughout the lye. For the tank nothing is better than an ordinary soap pan; if this is built specially for the purpose it should have the ordinary open coils, and a dry steam coil is also advantageous though not essential. A skimmer pipe is not required as the materials can quite well be removed by the bottom of the pan. A smallish tank mounted near the top of the pan serves to hold the fatty acids. These are delivered by a pipe controlled by a valve to a kind of injector placed near the bottom of the pan. The steam which is blown through this injector converts the fatty acids into a fine spray, which in turn is led into a wide pipe provided with numerous largish holes. This pipe is laid close to the open steam coil, and as the spray of fatty acid issues through the holes it is caught up by the steam from the jets in the main coil and forcibly distributed through the mass of lye.

Various kinds of fatty acid may be used, but rosin is unsuitable. Coconut and palm kernel oils are not recom-

mended, on account of the high solubility of their soaps. Since the soap formed is dark in colour it can only go to a brown pan, and cheap fatty acids are therefore indicated. Palm oil split so as to contain about 90 per cent of free fatty acid gives very good results, and is generally a suitable material for use in the boil to which the soap is sent; probably some of the cheap commercial fatty acids, such as those from hardened fish oil, would answer equally well. For the reason to be given later the fatty acids should contain a small proportion of glycerides, and if those available contain no residual fat a small additional quantity should be added.

The lye to be treated should be allowed to settle for a few hours without cooling too much, and is then skimmed and pumped into the treatment tank. This should not be filled more than about half full, as the evolution of gas during the operation causes the lye to foam strongly, and if there is not plenty of space for the foam it is difficult to boil the contents sufficiently violently. The amount of alkali to be disposed of is worked out from the weight of the lye taken and its percentage of total alkali by test. The amount of fatty acid required is then calculated. As the alkali present is never completely used up, rather less than the calculated quantity might be used, but it appears that a small excess of acid is necessary, and it is probably better in the first instance to allow some 3 per cent in excess of that theoretically required. After some experience of the operation it may be possible to make slight modifications.

The lye, after being sampled and tested, is boiled, with close steam if there is a dry steam coil, otherwise with open steam. As soon as it boils steam is turned on to the injector, and fatty acids fed in. The reaction begins at once, and causes the evolution of much carbon dioxide. Keeping the lye boiling hard, the fatty acids are led in as fast as possible, some control being necessary in order to keep the reaction within bounds, as the foam may easily reach the top of the pan. When all the acid is run in the reaction soon slows down, and a sample may be taken out for testing. If the total alkali is reduced to a low figure,

say about ·05 per cent, the lye may be boiled for a further half hour or so, and the operation is finished, but a rough test should always be made to verify this. If the man in control of the operation is reasonably skilful he may, after taking a sample, cool it somewhat, pipette off 50 c.c., and titrate with decinormal acid, using methyl orange as indicator. Failing this any man may learn to measure off say 25 c.c. in a graduated measure, and an equal quantity of a standard acid provided in another measure, and mix them together with a drop of methyl orange solution, the operation being considered finished if the mixture becomes red. If this fails to happen even after rather longer boiling, a further amount of fatty acid may be added as before. If the standard acid supplied is one sixtieth normal the alkali in the lye tested should be about ·05 per cent or lower. To get the best results it is better for the operator to carry out this test for himself, and thus be personally responsible for the success of the operation.

When open steam is used for boiling the lye, dilution occurs to a small extent. This might possibly lead to some of the soap being dissolved, especially when a minimum of salt is used in graining. This is the reason for having a small proportion of glycerides in the fatty acid mixture; it is found that some 3 per cent of free fat on the total fatty acids is sufficient to make the soap insoluble in a lye containing several per cent less salt than that normally required, and thus one may safely use open steam for boiling and be sure of keeping soap from dissolving in the lye, without the necessity of adding more salt.

As a rule a short time for settling is all that is essential, as the upper layer of soap may remain in the pan for a second operation, and it is not important to withdraw the last drop of lye from it. In this case the soap should be boiled up vigorously while the next batch of lye is being run in, and some of the residual fatty acids in it may thus be neutralised by the fresh lye. It is usually quite satisfactory to carry out at least three or four operations before removing the soap and starting afresh, the actual number depending on the average alkalinity of the lye.

A soap pan 12 feet cube is large enough to deal with about 25 tons of lye at a time, and though one operation per day may be taken as normal, it is quite possible at a pinch to do two. When possible it is better to have two smaller rather than one large pan to cope with the amount of lye to be treated.

100 tons of lye, the alkalinity of which is reduced from ·45 to ·05 per cent would require rather under 4 tons of palm oil acids for treatment, allowing for a moderate excess, thus producing roughly 6 tons of soap, *i.e.* 6 per cent of the soap output of the works if one part of lye is made on the average for one of soap.

Lye treated in this way is much easier to deal with in the glycerin plant. On acidification it forms practically no scum, and the amount of acid required on the first treatment is of course very much less. In addition experience has shown that the amount of ferric chloride necessary is greatly reduced, and there is naturally a corresponding reduction in the amount of press-cake formed. All these things lessen the labour required in the glycerin plant to such an extent that the preliminary treatment of all the lye could very well be carried out by the glycerin plant men if the lay-out of the works made this convenient.

The economy effected naturally depends upon the waste originally incurred. On the assumption that the saving of alkali is as above, *i.e.* ·4 ton on 100 tons of lye, and of fatty acids ·2 ton, the value of the caustic soda saved would amount to approximately £6. 8/-, and of the acid required for neutralising the same amount. The fatty acids recovered even if valued as low as £10 per ton would amount to an additional £2, making a total of £14. 16/-. The steam used should certainly cost less than the odd 16/-, and one may thus safely estimate the net economy, apart from expenditure on plant, to be £14, or, say, 2/9d. per ton of soap. If new plant had to be obtained for the purpose, its cost would be saved in six or seven months' working.

CHAPTER IX

PRODUCTION OF CRUDE GLYCERIN FROM SPENT LYES

Production of crude glycerin from spent lyes—the chemical treatments—filtration—evaporation of the purified liquor—requirements of a good evaporator—composition of crude glycerin—recovery of salt—importance of removing glycerin from salt—glycerin plant losses.

ALTHOUGH glycerin was discovered by Scheele as long ago as 1779, and many applications were found for its use in the century that followed, it was only towards the end of the 19th century, as a result of Nobel's inventions of dynamite and "blasting gelatine" that the demand for it became really large. Before its large-scale use in explosives a sufficient supply was obtained in the process of hydrolysing fats for the production of fatty acids. By the early nineties, however, the demand for it outgrew the possibilities of this source of supply, and soap makers, who had known they were running a valuable material to waste, were now forced to tackle the problem of recovering it from the spent lyes. Many fantastic methods were tried, and patented, for the purification of the lyes, but before long a practicable method was devised, and it is this, with a few refinements, which is in general use to-day.

Three distinct operations are required to convert the glycerin in the lyes into the pure product. First the free alkali, residual soap, and the greater part of the other organic impurities are removed by chemical treatment. Next by evaporation of the water and removal of the salt which separates out on concentration, a product is obtained containing 80 per cent or more of glycerin, together with various organic and inorganic impurities and a little water; this is known as crude glycerin. This material is then distilled under diminished pressure with the aid of steam and practically pure glycerin is thus obtained. Formerly many soap makers distilled their own glycerin using small stills in which batches of five to

ten tons at a time were worked up, but these have now been superseded by large continuous-acting stills which work with much greater efficiency, and the production of distilled glycerin is now practically an independent trade and is in comparatively few hands. The ordinary soap maker's process ends with the production of crude glycerin, which is now a standardised product and under ordinary conditions easily marketable.

A crude glycerin plant is practically an essential in any soap works. Apart from the fact that nearly all the salt used in the soapery is recovered and used again, the value of the glycerin recovered is a considerable offset to the cost of making soap; even at the present low price of £30 per ton the value of the glycerin recovered as by-product to a ton of household soap may be £1. 10/- to £2, only a small fraction of which is likely to be obtainable if the lyes have to be sent to another soap maker to work up.

The Composition of Spent Lyes.—The composition of the lye from any change is materially different from that of those before and after, but a manufacturer whose trade does not vary greatly and who is consistent in his choice of raw materials finds his average fairly constant over a long period, though he has it in his power to vary the degree of washing, and hence the average composition of the lyes, according to the state of the market. As it will be convenient in what follows to have a lye of some specific and ordinary composition for reference, the following figures, which were the actual average for a year in a large factory may be quoted. The yield over the period in question was low, only 72 per cent, but it may be taken as fairly typical of many works in which glycerin extraction is not pushed as far as it might be.

Glycerol	4·57%
Free sodium hydrate (as Na_2O) . .	·05%
Combined alkali (as Na_2O) . . .	·45%
Sodium chloride	11·94%

General Outline of the Method of Treatment and Evaporation. — The general principles involved are

extremely simple. Lyes from the soapery, generally very dark and turbid, are brought into a large tank in which they are treated first with hydrochloric acid and then with a coagulant, usually an iron or aluminium salt. Fatty acids and dirt rise to the surface as a scum and are removed, and the whole liquor is then filtered. The filtrate should be nearly colourless and slightly acid. It is now made very faintly alkaline with caustic soda, which precipitates the slight excess of iron present. This liquor is allowed to settle clear or filtered and is now ready for evaporation. For this purpose a vacuum evaporator is employed. When evaporation of water has raised the concentration of salt to about 26 per cent it begins to crystallise out, and continues doing so throughout the operation. Special devices allow the salt to be removed in small quantities at a time without stopping the evaporation, which goes on until the concentration of glycerin in the product has reached about 80 per cent. The three parts of the process, first and second treatments and evaporation will now be described in more detail.

The First Treatment.—It is convenient to have at least two tanks which should hold between them at least one average day's output. They may be made of cast iron in sections, of mild steel, or of timber lined with "chemical" lead. Steel tanks are somewhat the cheapest but are not altogether satisfactory as they slowly corrode; cast-iron are more resistant but need very careful erection and jointing if of large size; lead-lined wooden tanks are very convenient for erection in confined spaces and are durable but not very cheap. On the other hand the cost of replacing the lead when it does wear out is not high owing to the good scrap value of the metal. Round the bottom of the tank is a perforated coil, preferably of lead, to carry air for agitating the liquor.

For proper control of the operations each batch of liquor in the tank should be gauged. This may be done by dipping, in which case the specific gravity of the liquor must be taken into account, or better by use of a simple gauge of the pneumatic type.

The chemicals required for the treatment are hydrochloric acid and usually ferric chloride. Sulphuric acid, though cheaper than hydrochloric, should be avoided; it forms, with the alkali of the lye, instead of common salt, which has some slight value, a corresponding amount of sodium sulphate. The sodium sulphate separates out almost entirely with the recovered salt, and so increases in amount with each cycle of operations until enough is formed to be definitely detrimental in the graining out of the soap. The same objection applies, to a lesser degree, to the use of a sulphate such as aluminium sulphate as coagulant. Iron in the form of ferric chloride is now generally used for this purpose. This may be purchased either as solid or solution, or may be made by dissolving scrap iron of little value, such as barrel hoops, in hydrochloric acid and oxidising with chlorine; or by dissolving bog iron ore in acid. In the latter case the material used generally contains ferrous iron and lime, both of which are undesirable. They may be easily and quantitatively removed by treating the ore cold with just sufficient acid to dissolve the two bases. A neutral solution of ferrous and calcium chlorides is thus formed which may be run away, leaving practically pure ferric hydroxide to dissolve with the aid of gentle heat in hydrochloric acid.

Spent lyes, if they come direct from the pan room without any preliminary treatment, are very impure, containing some soap in solution and possibly some in suspension, alkali carbonate, suspended solids and colouring matters. In general any batch of lye to be treated will contain a mixture of lyes from various pans of very different composition and an average sample should be taken from which to judge of the treatment required. A tank full of such a mixture cannot very well be mixed by agitation with air owing to the foam produced by the dissolved soap, and thus it is better to take a continuous sample of the lyes as they are delivered, through a pet-cock fitted into the delivery pipe. As a small orifice might block up with particles of soap or dirt this should be of fair size, and the sample, which may be collected in a small

tank may amount to 1 or 2 per cent of the whole batch. When the batch of lye is all pumped in to the treatment tank the sample in the small tank can be well mixed by hand, and small amounts taken out for determination of the glycerin and for a trial treatment.

The success of the purification depends upon the correct adjustment of the quantities of acid and iron solution used, and upon adding the latter to a nearly neutralised solution. As the alkalinity of the lye and the amount of impurity to remove vary from one batch to another, different amounts have to be used at each operation, and to determine the amounts to use it is much the best to make one or two preliminary trials, in each case on a litre or so of lye, using a measured quantity of lye and running in acid and iron solutions from a burette. This may be done either by the man who attends to the plant or by a laboratory assistant. Such tests can be made in a few minutes and determine the amounts of reagent to use on the large scale. After the trial treatment a small amount of the liquor should be filtered off, and the filtrate tested. It should be faintly acid, should form no turbidity when a little strong acid is added, and should form a slight precipitate of ferric hydroxide when made alkaline with caustic soda. It must be remembered in carrying out the test that the iron solution is itself acid, so that the addition of hydrochloric acid in the first instance should be sufficient only to leave the lye neutral or even slightly alkaline—*p*H usually about 7·2.

In carrying out the large-scale treatment the correct amount of acid should first be added and the contents of the tank well agitated. If the lyes have undergone no preliminary treatment with fatty acids a considerable amount of scum will rise to the surface and should be removed. The iron solution may now be added, and after thorough agitation the operation is finished. It is well to filter off a sample and test it as above in case any further additions of reagent should be necessary. The finished liquor may have a *p*H value between 5·0 and 5·5, a point at which methyl red changes from orange to red.

In some works it is the practice, instead of making an acid and an alkaline treatment, to make a single treatment in which the liquor is left very nearly neutral. When this is properly carried out the purification appears to be equally good, but more care is required. There seems to be a tendency in this case to produce a cake which does not filter well, and probably for this reason the double treatment is more generally employed.

Filtration.—The liquor is in most cases pumped to the filter press by a steam-driven reciprocating pump. Steam is generally preferable to electric drive for this purpose since as the press fills up with cake the load increases greatly, and if the pump cannot work well against a high pressure the chambers may not fill well. Filtration may be aided by connecting to the pumping main a largish air vessel which smoothes out the pulsating effect of the pump. Consideration should be given to the following points with regard to the presses. Very thick cakes are not obtainable, and therefore the type with recessed plates is preferable to that with separate frames. The plates should be reasonably large so as to utilise a good proportion of the surface of the cloth for filtration; plates 30 inches square are easily handled by two men. As there is a considerable amount of press-cake, which may contain about 70 per cent of lye, the glycerin it contains may amount to 1 per cent or more of the total, and it is very desirable to use presses of the washing type, which will save at least some of the loss. In the ideal washing press the incoming water would expel before it all the liquor in the cake, but in practice much mixing takes place, so that only a portion of the lye can be recovered, as the solution leaving the press becomes after a time too weak for evaporating profitably. In washing the cake the filtrate should be tested with an hydrometer at frequent intervals, and washing stopped when the liquor leaving the press is reduced to about one half or one third of its original specific gravity.

The Second Treatment.—To the filtrate from the first treatment is added sufficient caustic soda to precipitate

all the iron present as ferric hydroxide. The amount of precipitate is much smaller than on the first treatment, and may be allowed to settle and the clear solution drawn off. It is better however to filter it. In this condition the liquor is usually pumped up to tanks from which the evaporator is fed, but it is good practice to add a very small amount of acid to this liquor, making it very faintly acid. This has the effect of liberating any weak acids present, such as CO_2 and traces of the lower fatty acids. If these remain as salts in the liquor they are not thrown out of solution with the salt but remain in the crude glycerin, thus increasing the total residue. The bases appear on analysis as sodium carbonate and add to the ash, and the organic acids go to increase the organic residue. No detrimental effect upon the metal of the evaporator, even after many years' working, has been traceable to allowing the weak acids to escape in this way with the vapour.

Evaporation of the Liquor.—The most elaborate portion of the glycerin plant consists of the evaporator and its appurtenances. Evaporation is always carried out under diminished pressure, and in almost every case in double- or triple-effet plants. While the latter are theoretically the most economical, in actual practice the economy in fuel consumption is hardly detectable, while the prime cost, expense of upkeep and working costs are higher. While the double-effet plant may thus be considered as the standard there is a good deal to be said in favour of supplementing it with a relatively small single "finisher," as the final stage of bringing a batch of crude up to full strength tends to slow up the action of the evaporator.

In this case the liquor evaporated to about 40 per cent strength is drawn over into the finisher, the contents of No. 1 vessel transferred to No. 2, and No. 1 filled with fresh lye. Evaporation in the main plant thus goes on at full speed while the final small amount of water is being driven off in the finisher. In the case of the lye quoted on p. 144 18 tons of lye are required to make 1 ton of crude, and these contain 14·85 tons of water. Of this ·05 ton remains in

the crude and 14·8 tons must be evaporated. The 2 tons of 40 per cent liquor from which the ton of crude will be produced contain only ·66 ton of water of which ·61 ton has to be boiled off. The extra fuel required to evaporate this proportion, about 4 per cent of the total, in a single vessel is relatively small, and the advantage gained may outweigh this slight loss.

Several engineering firms supply evaporators working on the same general principles but differing greatly in general lay-out and detail. It is not proposed to give any description of these different plants, as full information can be obtained from the makers. The requirements and limitations of the individual soap maker have to be taken into account in deciding what make of plant is likely to be most suitable for his purpose, but there are certain points in design which have a bearing upon efficient working and economical maintenance and may be referred to here.

The most vulnerable part of an evaporator is the steam chest, and particularly the tubes. It is therefore necessary to have easy access for repairs to all parts of this. In particular every single tube should be easily removable from below, and in addition the plant should be designed so as to make it possible to replace the complete steam chest without undue disturbance to the upper parts of the vessel or to the building.

The tubes and tube plates may be made of mild steel, brass or copper. Mild steel is the cheapest but least durable on account of corrosion. It has the additional disadvantage that when the tubes are roughened internally by even slight corrosion, the salt tends to stick to them badly, necessitating frequent stoppages of the evaporation for removing it. Brass is a better material for the purpose, and copper though the dearest probably the best of all. Having the greatest durability and also the highest scrap value it may be the cheapest in the long run.

The boxes in which the salt is allowed to separate from the liquor are generally two in number, except in quite small plants, so that one may be filling while the other is being discharged. The ends away from the evaporator are

hinged to form doors which can be clamped tight; between the boxes and the evaporator are large sluice valves which are kept open while the boxes are filling, and closed when the salt is to be removed. There are two types of box. In one type the salt deposits on a gauze false bottom, and when the box is filled with salt the sluice valve is closed and steam driven through the mass to expel the liquor as far as possible through the filter before removing the salt to return to the soapery. This operation is very simple, but is unlikely to be as efficient in the removal of glycerin from the salt as that in which the salt, removed from its box with the adherent liquor, is washed and then dried on a centrifuge or filter. The boxes used in the latter procedure need no filter but open straight over the vessel into which the salt is removed. Such boxes may conveniently be made with steeply sloping bottoms to assist the removal of the salt. The most suitable position for the bottom of the salting-box determines the height at which the whole evaporator should be erected.

In a well-designed plant there should be no possibility of any measurable loss of glycerin by entrainment. When this occurs it is often due to an incorrect arrangement of the boiling tubes and the large tubes or shafts which serve to return the liquor from above the upper plate to the bottom of the vessel. If the foam from the boiling liquor never extends more than a few inches above the upper plate there should be no occasion for excessive head-room. Baffles or "cyclone" arrangements in the upper part of the vessel should not be necessary, but if present any baffles should be made of a non-corroding metal, as thin sheets of mild steel may soon fall to pieces.

The vapour pipe from the first vessel is sometimes fitted with a suitably large valve. This is a good arrangement as it permits the second vessel being used as a single if occasion arise.

Glycerin is sometimes lost through a bad defect in a tube suddenly allowing liquor to escape into the steam chest. In the case of the first vessel, if exhaust steam is used for heating it is not usually advisable to return the condensate

to the soapery owing to possible contamination with engine oil, but to allow for possible accidents it should always be pumped first into a tank before running to waste. The vapour from the first vessel condensing in the steam chest of the second is usually returned to the pan-room.

The vapour from the second vessel may be condensed in either a surface- or a jet-condenser. Two advantages are claimed for the former. First a portion of it nearest the evaporator may be used as a lye preheater, and incidentally save a fraction of the cooling water, and secondly the condensed water may be used again in the soapery and thus any glycerin going over with the vapour be in part recovered. Against the surface-condenser are the fact that it requires a great deal more cooling water, that if the water is not of the cleanest it is very liable to foul and become extremely inefficient, and that its maintenance is almost certain to be more costly. In most cases the balance of advantages is with the jet-condenser.

The functioning of a double-effet evaporator depends upon the fact that the pressure under which the water is evaporated in the first vessel is much higher than that in the second. Consequently the vapour entering the steam chest of the second vessel has a temperature well above that required to boil the liquor in that vessel at the pressure to which it is subject. These pressures have to be controlled and must be indicated by pressure gauges, which should be of a rational type, that is to say they should indicate directly the pressure inside the vessel. Many gauges register only the difference between the internal and that of the external air pressure, and thus the internal pressure can only be ascertained by deducting the gauge-reading from that of the barometer at the moment, a formality which is often omitted. With gauges of a proper type the actual pressure inside the evaporator is seen at a glance. There should be a tap and also some simple trap and drying tube between the gauge and the evaporator to prevent contamination of the former by vapour and spray.

Thermometers are required to indicate the temperature

of the liquor inside each vessel. They should be of a substantial type with a legible well-protected scale. The latter is fixed to the outside of the vessel, and the bulb is placed where it will be surrounded by boiling liquor. Knowledge of the temperature and pressure inside the vessel are necessary to the intelligent control of the operation.

In evaporators fitted with a jet-condenser a suitable wet-air vacuum pump is usually incorporated in the plant.

Apart from various other pumps, air blower, piping, and so on, details of which vary greatly in different factories, the only other item of importance is the arrangement adopted for removing the excess glycerin from the recovered salt. The simplest device for doing this is the arrangement for steaming out the salt in the salt-box. This has already been described. It is doubtful whether this process as ordinarily worked removes the glycerin as well as some suitable arrangement for washing the salt on a centrifuge or filter. A lay-out which gave good results comprised two centrifuges placed immediately below the salt-boxes, so that the salt mixed with liquor could be discharged directly into them. The bulk of the liquor was first removed and then the salt was well washed with liquor from the final treatment. It was then dropped from the centrifuge and removed with a conveyor and elevator either to the brine tanks or to a railway wagon for conveying to the soapery to use dry. As conveyors and elevators are somewhat costly to work and keep in repair, a modification was made which can be generally recommended. In this the sludge of salt and liquor is dropped directly into a wide cylindrical tank, and stirred in this mechanically with enough treated lye to make the mixture reasonably fluid. A small centrifugal pump delivers the contents of this tank to the centrifugals which are situated directly over the brine tanks, and the salt after washing is dropped straight into the latter. All liquors from the centrifuges are returned to the second vessel of the evaporator. This latter method is very satisfactory; the mechanical agitation of the salt with

liquor breaks up any lumps and the liquor is deposited on the centrifuge in a condition in which it needs very little washing. The salt is very nearly white and its glycerin content very low. Generally speaking it is best to return all salt to the soapery in the form of brine. It rarely happens that the amount of water delivered to the pan in doing so is in excess of requirements, and this means of transport is cheaper and also much cleaner than the handling of solid salt.

The Process of Evaporation.—There is not much that can profitably be written about the control of the evaporator except to indicate a few general principles; the actual manipulation of the controls of steam, flow of liquors, and so forth is best learned by direct instruction on the plant and is not difficult. Attention may however be drawn to a few general rules. The first vessel in a double-effet is not usually provided with a salting box, and if the lyes are not abnormally strong in salt one half of the water can be evaporated in this vessel without separation of salt, but there is not very much margin. Consequently only treated lyes, or any liquors weaker in salt, such as the washings from the presses, should be used to charge this vessel; any returned liquors stronger in salt, washings from the salt, and so forth should go direct to the second vessel. If salt does begin to separate out some of the liquor must be drawn over to No. 2 vessel and weak lyes fed into the first vessel to redissolve it.

The boiling liquor should be watched through the sight glass and care taken that its level does not rise high enough to involve the risk of spray passing over with the vapour.

If there are two salting-boxes to a vessel only one should be allowed to fill at a time, and should be allowed to fill as completely as possible with salt before starting to discharge it. After a box has been emptied the door is closed tight and the air blown out with steam before opening the valve to the evaporator.

Evaporation of the liquor in the second vessel or finisher is allowed to continue until the temperature of the liquor reaches a certain figure which depends upon the

vacuum in that vessel. As the latter should vary but little, apart from the effect of seasonal variations in the temperature of the cooling water, the operator continues boiling until a certain temperature is reached at which it is assumed that the concentration is sufficiently high, and the operation is then stopped and the crude run off into the settling tank. It usually pays to concentrate until the crude after settling tests well over 82 per cent glycerol.

The Composition of Crude Glycerin.—By the rules of sale laid down by an International Committee crude glycerin should contain not less than 80 per cent glycerol, not over 10 per cent ash, and not over 3 per cent "organic residue," these all being determined according to specially defined analytical methods. If the ash or organic residue exceed the figures given certain reductions by way of penalty have to be made from the contract price. The latter refers to glycerin at 80 per cent. If the crude tests 81 per cent or over a corresponding increase of price is made. Between 80 and 81 per cent the crude is invoiced at 80 per cent, while if the glycerin tests below 80 per cent a penalty is exacted. It therefore pays to concentrate the crude to over 81 per cent, the more so as the salt content decreases with increasing concentration of glycerol, and it becomes easier to keep the ash comfortably below 10 per cent. There should be no difficulty with the organic residue, which, given moderately good treatment of the lye, should not exceed 1·5 to 2 per cent. There are two impurities to which glycerin distillers take exception. Arsenic is one of these, but since all the chemicals used by the soap manufacturer are now obtainable practically arsenic-free, and moreover small amounts of arsenic are almost quantitatively removed in an efficient lye treatment, this should occasion no trouble. An impurity which may give rise to more difficulty is trimethylene glycol. This substance may be regarded as glycerin in which the middle hydroxyl group has been replaced by hydrogen. This partial reduction of the glycerin can take place in soap lyes by the action of certain

micro-organisms. It seems that the formation of this undesirable product occurs much more readily in certain soap-works than in others, the reason for which is not fully understood. It is probable that if the lyes undergo the pretreatment process directly after leaving the soap pan, and are not allowed to cool completely before being further worked up, the organisms concerned will have no opportunity of decomposing the glycerin. Trimethylene glycol is similar in its properties to glycerin, but has a much lower specific gravity, 1·053 at 18°, and much lower boiling-point, 214°. Although on distillation in a modern type of still it appears largely in the lower fractions, small amounts of it may pass into the main bulk, tending to lower the specific gravity, thus compelling the distiller who sells refined glycerin on the basis of specific gravity to drive off more of the residual water in order to produce a material meeting the commercial standard. Moreover it is a very undesirable type of impurity in glycerin required for nitration for forming propellant explosives, since although on nitration it forms a dinitrate having similar properties to nitroglycerin these are not quite identical, and it may consequently interfere with the ballistics of the final product. Soap makers should therefore do all in their power to keep down its formation to the minimum. Analytical methods for its determination are based on the facts that it has lower S.G. and boiling point than glycerin, a higher bichromate value and a lower acetin value.

The Recovery of Salt.—Salt is a minor but quite important product of the glycerin plant. Before returning to the soapery it should be made reasonably free of glycerin. It is not correct to maintain that any glycerin contained in it is returned to the pan and is therefore not lost. It is true that the glycerin it contains is recoverable to the same extent that glycerin from the fats would be under similar conditions, but whereas the latter is liberated from the fats as far as possible on the first change and is ultimately recovered in a good yield, only perhaps one-fourth or one-fifth of that returnable in salt returns to the pan on the first change, the remainder in portions at later and later

stages from which the yields become progressively poorer. Any glycerin in the salt returned to the pan-room may or may not be recovered by suitable treatment there, but it is better to remove it reasonably thoroughly in the glycerin plant by washing down to 1 per cent or so. Even this small percentage involves an ultimate loss of about 1 per cent on the total glycerin, unless it is specially allowed for in the pan-room.

Losses in the Glycerin Plant.—In any manufacturing process some loss of material is inevitable. For several reasons the determination of this loss with all possible accuracy is necessary for efficient control of the plant. There may for instance be a steady normal loss; when this is known it may be possible to trace certain causes and correct them to some extent. On the other hand it may happen that a plant develops some small defect, insufficient to indicate its presence to those in control by any abnormality in working, but still capable of causing the loss of a measurable amount of product. A periodical determination of the yield may indicate this and prevent the loss from extending over a very long period. For the latter reason it is good practice not merely to determine the yield over periods of six or twelve months, at the end of which stock is taken with all possible accuracy, but to make an effort to obtain useful monthly figures, even although this does involve greater risk of error owing to the relatively large amount of partially manufactured material in proportion to the output. Apart from these considerations no one will dispute the fact that such control of the operations has an effect on the personnel of the plant tending to encourage careful working and the avoidance of waste.

The one difficulty in determining the yield lies in the fact that no really satisfactory method of determining the glycerin in spent lye has yet been made known. The measurement and sampling of the lye are minor problems which can be overcome but it is doubtful whether any known method of analysis can be applied to spent lye with the certainty of obtaining accuracy within 1 or 2 per cent

of the amount present. For a routine method the bichromate oxidation process as used for crude glycerin, with suitable modifications, is probably as good as any.

The procedure of calculating the amount of glycerin in the lye from measurements of the individual batches of lye and curd in the soap pan was primarily devised to avoid the errors due to analysis. Properly carried out it probably gives the most exact results, but unless careful measurements are taken throughout it is of no value. No short cuts are permissible.

With regard to the output of glycerin, the weighing, sampling, and testing of crude in drums are capable of such accuracy that any errors from this source should be only a fraction of 1 per cent. The error in computing the amount in crude in storage tanks is necessarily somewhat higher, but this amount is unlikely to be any large proportion of a year's output. As to the glycerin in salt, the weighing of the salt recovered, or gauging of the brine, in conjunction with tests of average samples, furnish information as to the amount present in this form. The analytical error in this determination is higher, but as the total amount concerned should be only some 2 to 4 per cent of that in the crude it is not of great importance.

Note that glycerin in salt is not a finished product, but is returned to the soapery, where it may incur a further loss. Its total quantity is of importance in helping to account for the glycerin received, but it is not a finished product and in considering its contribution to the true yield of the plant it is probably better to consider only some reasonable proportion of it, say 60 per cent as being recovered.

There are a few known possibilities of loss in a glycerin plant, all of which are worth investigating. First and most obvious are actual leakages of liquor from pumps, etc. Then a certain amount is inevitably lost in the press-cake, which usually contains about 70 per cent of lye. In a plant in which the cake was washed the washing was estimated to remove about one half of the lye, and the residual glycerin was determined. This was found to be about 0·5 per cent of the total glycerin in process,

and one may therefore assume that about 1 per cent of the glycerin is lost in this way if the cake is not washed.

With a well-designed and properly operated evaporator, loss by entrainment should be negligible. It is well however to test the water which condenses in the second steam chest. A rough test for salt can easily be made with test papers impregnated with silver chromate. The papers are made by soaking filter paper successively in solutions of silver nitrate and potassium chromate of about 1 per cent strength. Such papers become pale yellow when wetted with even extremely weak salt solution; if the test is negative it may be assumed that no glycerin is being lost in this way. If the second vessel is provided with a surface-condenser the condensate may be similarly tested; otherwise it is quite simple to fit the vapour pipe with a small pet-cock through which a minute proportion of the vapour is withdrawn through a laboratory condenser by means of an ordinary small filter pump. If any positive reaction for salt is found in any of these tests a glycerin test should be made on the condensate. These methods should certainly be adopted if there are indications of any abnormal losses.

In plants in which this matter has been very carefully investigated it has usually been found that there is a small loss, of perhaps 1 to 2 per cent, over and above those actually determined. It is therefore advisable in calculating yields of glycerin from any soap charge to allow 2 to 3 per cent loss above that believed to occur in the soapery.

While dealing with the glycerin plant reference may be made to some interesting large-scale experiments on the recovery of fatty acids from the press-cake. In two large works the acids were liberated from the press-cakes and twice distilled, the second distillation, with steam in vacuum, bringing about a rough fractionation. The still residues, which consisted mainly of rosin acids, formed a much larger proportion of the whole than the original rosin in the soap charges, and the lowest fatty acids, caproic to capric, were also present in relatively much greater proportion than the

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