Ramifications of the Oil Industry

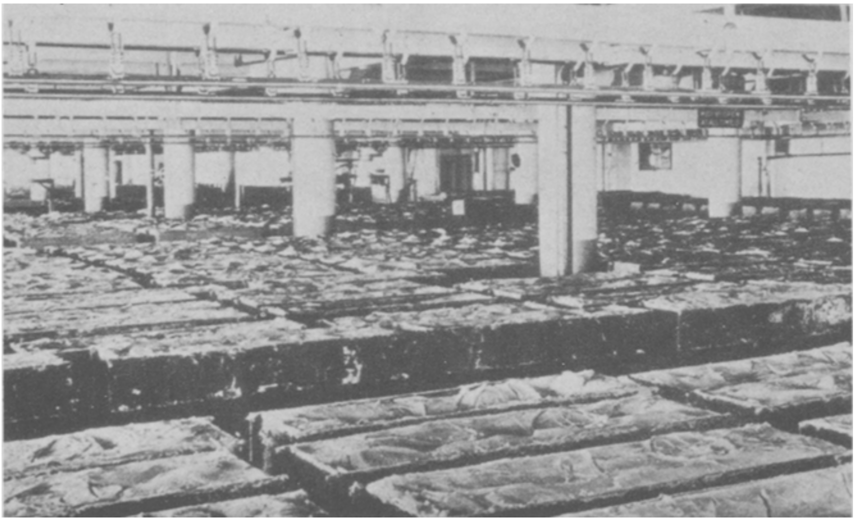
(Part I.) Processes*

BY THOMAS ANDREWS

Boiled and Settled Soaps

In boiled soaps the neutral oil or fatty acid is boiled and agitated with steam in the presence of caustic soda care being taken to see that the excess of caustic is not sufficient to cause the soap to grain, that is to say, that the solution of the soap in dilute caustic must not be impaired by making the solution too strong during the boiling. When the mass in the pan is in a state of chemical equilibrium it should consist of the soda salts of the fatty acids mixed with water, glycerol, excess of alkali, together with the unsaponifiable matter and the impurities in the oils.

The soap, not being soluble in salt solution, is thrown out of solution by the addition of salt to the pan. After settling for some time the soap will be found at the top of the pan as a curd and the bottom layer will consist of the added salt as well as the other matters referred to above. After the removal of this lower layer the soap is brought into solution again by the addition of enough water and is boiled with open steam. An excess of caustic is again added to complete the saponification and boiling is continued until there is no further absorption of caustic. The curd is again thrown out of solution and the bottom layer drawn off after a further settling period. This is repeated, with the addition of resin soaps if desired, and then the soap is closed with sufficient water to form a settled soap and yet be sufficiently open to allow of the discharge of the im-



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Frames in which soap is cooled and hardened

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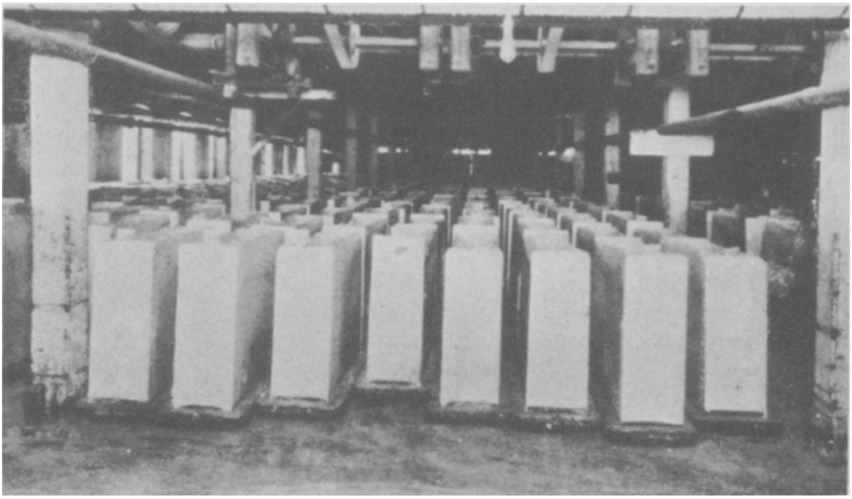
purities. This fitted soap is allowed to remain at rest for several days during which time it settles out into three layers, namely; the settled soap at the top, the nigre or impure soaps at the middle and the foots at the bottom.

The top layer is the true settled soap and consists of about 63% fatty acids combined with about 7% of Na_2O, the remaining 30% being chiefly water.

The nigre is a layer of much diluted soap containing practically the whole of the insoluble soaps, the excess of caustic and the salt. Cooling forms are alkaline layer.

The settled soap is agitated with any medicants, colors or perfumes it is desired to incorporate in the soap until the whole is homogeneous and the mass is then cooled. Until recently the soap was cooled in box like frames, each frame holding about 10 cwt. of neat soap, and the cooling occupied many days. More recently it has become more usual to cool the soap in machines resembling the distance frame type filter press, where the hot soap may be considered as being in the distance frames and the plates are cored to allow of the passage of the cooling liquid, the soap being thus quickly cooled in thin layers. Whether the texture of thin quickly cooled soap can be equal to that obtained by the older method is a point open to discussion. If we are of the school that considers that the 30% of water in the settled soap is in the nature of water of crystallization we shall probably favor the old fashioned type of frame, whereas if we favor the view that the soap is in a colloidal solution we shall favor the quicker cooling machine. Each method has its adherents and such a discussion is outside of our scope herein.



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Stripped frames of soap

If fatty acids are used in the manufacture of the soap then it is possible to dispense with the dearer caustic soda and use the carbonate. Care must be taken, however, to see that the solution and the fatty acids are brought into contact in such a manner that there is no loss through the evolution of the CO_2 from the carbonate. This evolution of gas is such a nuisance that the method is seldom used in spite of the cheapness of the carbonate. In the manufacture of soft soaps some potassium carbonate is intentionally added although there is very little to gain from a price consideration.

A good soft soap will contain all the glycerine in the original oil but there is, as a rule, only about 38% of fatty acids.

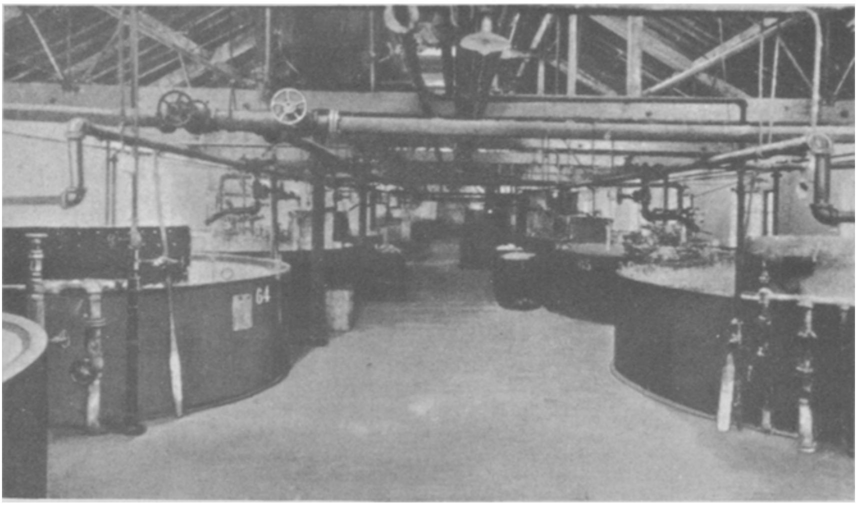
The addition of resin soaps to a settled soap cannot be looked upon as in the nature of adulteration as the alkaline salts of the resins have marked detergent properties and nearly the whole of the laundry soaps and soft soaps, not intended for use in the textile trades, contain some proportion of resin.

The dry soaps are chiefly powdered soap which has been dried and to which has been added some proportion of soda ash. Generally some inert scouring material is also added as well as one of the milder bleaching agents.

Glycerol Recovery

We have noted that after the first boiling together of the fatty matter and the caustic there is removed in the aqueous layer under the soap the bulk of the glycerine that was in the original oil together with the salt, the excess of caustic and the unsaponifiable matter that was in the oil. These liquors are known as soap lyes and are the chief source of our glycerine supply. These lyes may contain anything from 8%-10% of pure glycerol but before anything can be done with them it is necessary to remove the impurities.

The lyes are first treated in such a manner that the whole of the sodium salts (as far as is possible) is converted into the chloride, the fatty acids freed and the mucilage precipitated. This is carried out in practice by adding hydro-



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Kettle room in a large soap factory

chloric acid until the whole of the liquor is neutral or just faintly acid. At the same time, or as a later purification, chemical sand or one of the other albuminoid precipitating agents can be used to remove the mucilage. The liquor after being filtered can be further worked up for the removal of other impurities or may be evaporated to produce 80% soap lye crude glycerine. As the evaporation proceeds the saturation point of the brine solution is soon reached with the result that the salt is deposited within the evaporator. As it is usual to evaporate the solution under vacuum some method is necessary in order to remove the salt which is deposited, before it can seriously interfere with the heating surface of the evaporator. As the modern evaporator is designed to work continuously it is necessary to effect this without the loss of a large quantity of glycerine and without stopping the process. This is done by catching the salt as it falls out upon a grid within a box at the bottom of the evaporator so arranged that it can be isolated from the evaporator proper. When isolated the salt can be washed and the wash waters returned to the evaporator. The washed salt can then be dried with steam and dropped out of the box to be used again in salting out further batches of soap. The isolating valve is then re-opened so that further salt can drop into the box and the operation is repeated.

The further concentration of the glycerine is carried out by distillation in vacuo with the aid of superheated steam. The distilled product is condensed in a special arrangement of fractionating tubes and the fractions may consist of any dilution with water ranging from solid crystalline glycerol to pure water, the fractions depending to a large extent on the skill of the operative. The various fractions are concentrated to about 1.262 gravity and, provided the necessary quality is reached, constitute the dynamite glycerine of commerce.

Sulphonation Products

While on the subject of saponified oils I feel that some reference should be made to the "turkey red" oils. If castor oil is treated with fairly concentrated sulphuric acid at low temperatures in such a way that no sulphurous acid fumes are evolved the product after washing is a sulphoricinoleic acid and is found to consist, commercially, of two parts—a water soluble part and a water insoluble part—the sulphoricinoleic acid being the water soluble part. The two combined have the property of being miscible with water in all proportions and the solution will lather much in the same manner as a soap solution will lather. In this condition it is used for the cleansing of textile goods. The sodium and ammonium salts of the sulpho-acid are used as mordants in dyeing. These are made by adding solutions of sodium carbonate, caustic soda and ammonium hydrate to the sulphonated oil until the solution is just neutral or faintly acid. Those oils to be used in the mordanting of textile goods are generally neutralized with a mixture of soda and ammonia. These are generally sold as a solution in water and their value depends on the percentage of sulpho-ricinate present. The commercial preparations are generally viscid transparent fluids, their color depending on the quality of the oil from which they were prepared and also upon the temperature control that has been exercised during the course of their preparation.

Fat Saponification

In the consideration of the oils for soap making it has been shown that the neutral oils are esters of glycerol and fatty acids. The splitting of the oil into these two parts constitutes a very large part of the oil industry.

There are four methods in use:

1. Splitting the neutral fat by steam pressure either in the presence of bases or not.
2. Splitting the neutral fat with the aid of sulphuric acid.
3. Splitting the neutral fat with the aid of sulpho-aromatic fatty acids.
4. Splitting the neutral fats by the aid of ferments.

In the first method steam at high pressure is blown through the oil or fat with which about 30% of water has been incorporated. During the process sufficient steam is allowed to escape from the autoclave, in which the reaction is carried out, to allow the mixture to be kept in a state of turmoil. If steam is used without the addition of a base a greater temperature will be required and consequently the fatty acids will be darker in color and the loss of glycerine will increase greatly. Moreover it is found that the amount of dissociation of the free fatty acid increases and the time taken to obtain a reasonable split is longer when splitting without a base. Works economy has decided that a split yielding about 98% of free fatty acids in the total fatty matter is the most efficient and this is very difficult to obtain when relying on plain aqueous saponification but occurs at about the eighth hour of steaming with the majority of fats when working with a steam pressure of 120 lbs. per sq.

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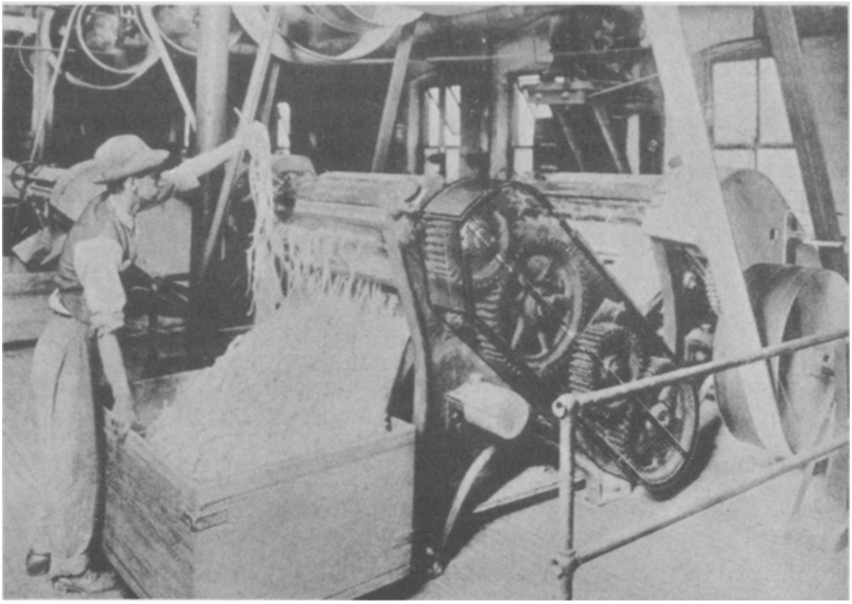
Modern automatic soap-press

in. with 3% of lime as the base. Other bases such as magnesia and zinc oxide have from time to time been used but lime has held its own in the majority of cases. This method is applicable to practically all oils and fats other than castor.

With regard to method number two. It will be remembered that in an earlier part of this paper reference was made to the formation of sulpho-acids by the action of strong sulphuric acid on neutral oils provided conditions favorable for the dissociation of the acids were absent. These sulpho-acids are readily hydrolyzed in the presence of boiling water giving the original fatty acids present in the oils plus some hydroxy fatty acids, some iso-oleic acid and the original glycerol. The sulphuric acid used in sulphonating is recoverable at the end of the reaction. This method of saponification is made use of to a large extent in the candle industry as owing to the formation of the solid iso-oleic acid and hydroxy-stearic acid the yield of candle material is increased. This increase as compared with aqueous saponification is considerable and may rise to as much as 12%.

Method number three is practically a sulphuric acid saponification but it is carried out in such a manner that the actual acid causing the saponification is in such dilute solution that the discoloration of the fatty acids is practically abolished. To revert again to the manufacture of our sulpho fatty acids, if, in the manufacture of them, we had added an aromatic compound such as benzene or naphthalene to the oil prior to the addition of the sulphuric acid we should have formed a mixed sulpho-compound of our fatty acid and the aromatic compound. We should, however, have found that the reaction would have been reversible in the presence of a low glycerine dilution. If on the contrary we had started with a *fatty acid* and an aromatic compound we could have formed the sulpho-aromatic compound in a more or less pure condition. In the presence of water and a trace of mineral acid these sulpho-compounds are capable of releasing nascent sulphuric acid, the reaction being reversible. Therefore if an oil is intimately mixed with one of these bodies in the presence of boiling water and some sulphuric acid we find that the nascent sulphuric acid is capable of saponifying the oil with the formation of the free fatty acid and glycerol. As there is present a comparatively large body of water the acid is liberated in a great excess of water and this affects the fatty acids in two ways. As the acid is dilute no dehydrating effect is obtainable and consequently the color of the oil does not suffer, but on the other hand for exactly the same reason, there is no increase in the "candle material" as no iso- or hydroxy-acids are formed.

With regard to method number four, it is common knowledge that seeds allowed to remain exposed to warmth and moisture give an oil higher in fatty acids than would have been obtained from the same seeds in a fresh condition. This led to the assumption that there was some hydrolyzing agent present in the seed. Research proved that this was the case, the enzyme was isolated and, commercially, it was found that, in particular, castor seed contained a ferment that was capable of splitting oils fairly successfully. The ferment is obtained in various ways from the fresh seed and is capable, on being added to an emulsion of the oil and a dilute acid, of causing hydrolysis, yielding fatty acids and glycerine. The ferment is killed at temperatures of 40°C and over and cannot, therefore, be used in the production of fatty acids of high titre. Moreover the reaction is reversible at high splits making it necessary to remove the glycerine waters fairly frequently. There is a further objectionable feature in that, lying between the glycerine waters and the fatty acids, we find, on settling the whole, a middle layer consisting of an emulsion of fatty acids, glycerine, water and the ferment extract. It is possible to efficiently split castor oil with this process and I have obtained over 90% splits on castor oil, using "activators," on a works scale.



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Milling toilet soap

The glycerine that is obtained by any of these methods is ultimately worked up into dynamite glycerine in a similar manner to the lyes from the soap industry. The fatty acids when of a good color can be worked up into soap but the greater part are used in the manufacture of candles. No process gives a fatty acid that can be used in the candle industry direct owing to the poor color of all such acids, and to obtain the necessary light color and, at the same time, to remove the unsaponifiable matters and other impurities which would influence the burning of candles, the mixed fatty acids are distilled. The fatty acids are fed into a vacuum still and the temperature is raised, generally over an open fire, until the fatty acids are at the desired temperature. Superheated steam is then blown into the hot mass. The distillate consisting of water and free fatty acids is fractionated in a series of tubes. At first the acids distill over freely and are of good color but as the proportion of foots increases in the still the color becomes worse and impurities increase. At this stage the contents of the still are taken out to be worked up with other quantities of foots. These distilled fatty acids consist of a mixture of liquid and solid acids. These are seeded at the right temperature so that crystals of the solid fatty acids lie in a mother liquor of the liquid fatty acids. In this state they are pressed to remove the liquid acids and the solid acids go forward to be used in the manufacture of candles.

Before we are in a position to carry out the various processes mentioned in the preceding part of this paper it is necessary to remove those impurities that will interfere with the process in any way. This calls for a multiplicity of refining processes and it is obvious that what is refining for one class of oil would be an absurdity in another. Just as an example I might quote the refining of an oil for edible purposes and the refining of the same oil for acid saponification. In the one case, that of edible refining, the refining would need to be carried out in such a way that the fatty acids were reduced to a minimum. Were this to be done to that portion of the oil that was to be saponified we should be removing from the oil that part which we require and at the same time we should find that the refining had considerably increased the time that would be taken in carrying out the process. The particular type of refining necessary and the impurities that would injure a given process form the bases of one of the largest departments in an oil works and beyond saying that the refinery often makes or mars the resulting products of other departments I am afraid that I can take this matter no further herein.

I have referred once or twice to the removal of the solid portion from the liquid portion of an oil. This is accomplished by cooling the oil until the solid portion "seeds" or crystallizes out of the liquid portion. The two are stirred together in those cases where the solid portion is a small fraction of the whole and are pumped through a filter press, the solid portion being retained as a cake. In the case of those oils and fatty acids where the solid portion is larger than the liquid portion the seeded material is placed in porous mats between the plates of hydraulic or screw presses and the liquid portion is squeezed out, the pressing being finished hot or cold according to the melting point desired.

Summary

In this paper I have endeavored to show the scope that is afforded by a study of the chief processes used and to give some idea of the many and varied aspects from which the oil industry may be viewed. Incidentally I have tried to show that varied as the processes may appear there are only a few fundamental facts on which the whole industry is based.

I would like to add that the modern oil works is run as a highly scientific co-ordinate whole and to say that it is no unusual business to sell ahead finished oil products, for which the oil seed even is not bought, under close guaranties of cost, quality, and delivery.

(*To be continued*)