Glycerine was first known as early as 1779, and was discovered by Scheele when preparing lead plaster by heating olive oil with litharge. He obtained a soluble sweet-tasting substance, and later, in 1784, he found that the same substance could be obtained from other oils as well as lard and butter. Lead plaster is said to have been known to the Roman physicians, but until Scheele's day nothing was known of glycerine. The substance was more carefully investigated by Chevreul and others, but it was not until 1847, when Sobrero, in Paris, discovered nitroglycerin, and in 1863, when Alfred Nobel demonstrated its value as an explosive, and in 1866 invented dynamite, that the production of glycerine on a larger scale was demanded. It was known at this time that, during the process of soap-making, glycerine was liberated from the fats on complete saponification, but all efforts to recover it by the crude methods then available were unsuccessful.

Slightly before this time the manufacture of stearine candles was undergoing important developments, and numerous patents were granted for processes for the decomposition of the fats and the separation of glycerine. With the increasing demand for glycerine, the soap trade came to the perplexing realisation of the value of the product being daily consigned to the sewer, and the ingenuity of those most interested was industrially directed to its recovery from soap lyes. So that, to-day, the modern soap works has its glycerine plant, wherein is treated not only its own lyes, but also those purchased from competitors less favourably situated in this respect.

The two main, or rather only, sources of glycerine are the soap industry and its allied industry, candle manufacture, and these for the present must be considered separately. I don't propose to go closely into the manufacture of soap, but some slight insight is necessary. The soap stock, either tallow, cocoanut oil, palm oil, or a combination of the lot, is run into pans or soap kettles, and, on the addition of suitable alkali, such as caustic soda, the whole is boiled by means of open steam until complete saponification takes place. The graining process now takes place, that is, the addition of salt or brine, which, after further agitation and settling, causes the soap to separate from the glycerine and float as a thick curd, the glycerine and salt solution remaining at the bottom of the pan. This liquid or soap lye is then run from the soap pan to settling tanks, where any soap which may be present, due to too close running of
GLYCERINE.

the pan, are allowed to settle out, and be skimmed off the surface. This soap lye consists of water containing a solution of glycerine derived from the soap stock, salt which was used in graining the soap, and a varying proportion of free alkali, also soapy, resinous and albuminous matters, some of these latter being held in solution as well as suspension. The lye must now be freed from these impurities, and the recovery of the glycerine and salt as useful products. This purification consists of two treatments; the first treatment consists of neutralising the alkalinity, decomposing the soapy matter and coagulating the albuminous matter. For this purpose mineral acid, either sulphuric or hydrochloric, and sulphate of iron or alum are used. Should the alkalinity be slight, little or no acid is used, the neutralisation being effected by the iron salt. After agitation by air and boiling with closed steam coils, the charge is dropped into receivers, and is then forced by air pressure through filter presses, from which the lye flows to the second treatment tanks, and the impurities remain as solid cakes in the filter press. The lye is now slightly acid, and is treated a second time by the addition of caustic, and again filtered, when the liquid should run clear and almost colourless, and is now ready for concentration.

The concentration of lye may be effected in open tanks provided with closed coils, wherein either live or exhaust steam may be used, but this is the least efficient of all methods, the Foster Evaporator, having two effects, being generally favoured, although film evaporators, having either single or double rolls, are in use. With the Foster Evaporator, the second effect is provided with salt legs and filters, and on concentration the salt is thrown out of solution and swept into these legs. The valve at the bottom of the leg is opened, and the salt and lye is dropped into the salt filter box, where the salt is caught on fine wire gauze and the lye drawn from below the gauze back into the filter. The valve is then shut, and steam is applied to dry the salt, which is then taken from the filter for return to the soap room for further use in graining. This salt does contain a fairly high proportion of glycerine, but as it remains in circulation, the amount does not matter. And so evaporation goes on until the desired amount of concentration is effected, that is 82% glycerine, which is determined by the temperature of the liquid in the evaporator, there being a definite relationship between pressure, temperature and concentration. The liquid or crude glycerine, generally known as “salt crude,” is now run off in tanks or feed heads for distillation.

I will now digress a little to go more fully into the principles of multiple effect evaporation. Pure water at 212° F. boils or gives off vapour of the same pressure as that of the surrounding
atmosphere. At atmospheric pressure the boiling point will rise according to the amount of matter in solution, and will correspondingly increase as the density of the liquor increases from loss of water by evaporation, requiring, therefore, not only a greater amount of heat to raise the temperature of the solution to boiling point, but increasing the heat necessary to maintain the solution at boiling point. Also, in passing into a state of vapour, water absorbs 5.36 times as much heat as is required to raise its temperature from 32° F. to 212°, and this quantity of heat becomes latent. Thus one pound of steam, when condensing to form boiling water, will yield sufficient heat to raise the temperature of 5.36 pounds of water to 212° F. The influence of reduced pressure upon the boiling point of water is also as follows:

Under 5" vacuum boiling point, 195° F.
15" vacuum boiling point, 160° F.
20" vacuum boiling point, 150° F.
26" vacuum boiling point, 120° F.

Other liquids following a similar rule, but with different normal boiling points. These different boiling points of a liquid under different pressures can be directed toward greater efficiency by making the vapour given off in boiling the contents of the first vessel at a certain pressure form the heating agent of the liquid boiling in the second vessel at a lower pressure, and the vapour from this second vessel forms the heating agent for a third, and so on. This principle governs all forms of what are known as “multiple effect” evaporators. The usual limit to this system is four pans, thus utilising the latent heat four times, and reducing the fuel to almost one-fourth that required for a single effect evaporator. With liquids liable to injury by heat, the total variation in temperature available under ordinary conditions is that between the temperature of steam at five pounds pressure (227° F.) and the temperature of a solution at 30° Be, boiling at a vacuum of 26" (131° F.), giving a total of 96° F. With a triple effect evaporator there is steam at five pounds pressure in the drum or calandria of the first vessel, and the liquid in the tubes at atmospheric pressure boils at 227° F., giving off vapour at 212° F. This vapour at 212° F. passes into the calandria of the second effect, and boils the liquid in the tubes of this vessel under a vacuum of 14", giving off vapour at 161° F. This again passes to the third vessel, boiling the liquid under a 26" vacuum at 131° F., assuming this to be a solution of 30° Be. It is a point worthy of note that when the liquid is a solution of solids in water the vapour will always be at the temperature of boiling water at the pressure to which the liquid is subjected at the time,
while the liquid itself will be slightly warmer. While the amount of heat transmitted through the tubes is practically proportional to the difference in temperature, it is evident that the same work is done whether the whole of this difference is in one or several vessels. Or, in other words, a double, triple or quadruple effect can only do the same amount of work as a single effect, but with one-half, one-third or one-quarter the amount of steam respectively.

We shall now consider the candle industry, which is the other main source of glycerine. In the candle industry the separation of the glycerine is mechanically somewhat different, although to the chemist it is much the same. The tallow is run into wooden vats, where it is boiled with an acid chemical reagent known as Twitchell's reagent and water. The boiling is done with open steam coils, and, after one or two boils of varying duration, it is allowed to settle, when the glycerine will be found in the water at the bottom. This aqueous solution of glycerine, generally called "sweet water," is run or pumped to a treating vat, where it is neutralised by the addition of lime and agitated with air, to ensure a thorough admixture of the lime. The neutralised liquid is now passed through a filter press for clarification, and then on for evaporation in any approved form of apparatus. For this purpose a triple or quadruple effect evaporator is used, and, as it contains no mineral salts, and is very free from organic impurities, is much simpler than that required for waste soap lye. A yield of from 10-15% of glycerine is obtained. This sweet water is concentrated in the evaporators in the same way as with soap lye, and is known as "Saponified Crude," but of course the use of salt filters is not necessary.

Various forms of distilling apparatus have been devised, and comprise essentially a vessel for containing and heating the crude glycerine, wherein a high vacuum is maintained; also a series of condensers, with concentrating drums below, and a vessel for expanding and reheating the distilling steam.

Construction of Glycerine Still.

On Sheet No. 2 is shown the layout of the modern glycerine still. "A" is the still itself, which consists of a cylindrical mild steel vessel provided with a closed steam coil ("3"), and with an open steam coil ("5"). Next is the superheater ("B") with its closed coil ("4"). Connected to the still by means of a cast iron pipe and saveall are the condensers. These are simply mild steel cylinders connected one to the other by means of cast iron "U" bends. Below these condensers are the two concentrating drums "E" and "F." After these main condensers
are two condensing towers ("D") with their concentrating drums ("G") and ("H"). On top of the second tower is a further condenser ("J"). This consists of a vessel with two tube plates and vertical tubes, the vapour passing through the tubes while cooling water circulates on the outside of the tubes. Then comes a saveall ("K"), which is a vertical cylinder with a branch on either side and a central vertical gauze baffle; then is the barometric condenser and air pump (Edwards type).

Crude glycerine, either saponified crude or salt crude, is drawn into the still by its own vacuum through the feed pipes marked (1) and (2), and is heated by the steam in the closed coil (3). This steam is at 150 lbs. press. superheated to 400-410° F. This steam, after passing through coil (3) exhausts into the superheater ("B"), where it reheats the steam in the expansion coil ("A"). The steam in this coil is drawn directly from the main, and passes through a 1" pipe and valve, and expands into the 2" dia. coil, which is open to the still through the perforated pipe (5) at from 10 to 15 lbs. absolute. The particular advantage which, properly expanded and reheated, steam possesses in distillation is that the steam expands but slightly, and consequently causes but slight absorption of heat due to such expansion. When, on the other hand, ordinary high pressure steam is used, it expands very much in the still, and absorbs heat from the contents of the still, so that distillation is retarded. Care must, of course, be taken that the temperature of the injected steam is kept below that at which decomposition occurs. This injected steam at a temperature of 350° F. to 370° F. at vacuum of 28" readily distills the glycerine, which, with the steam, passes out of the top of the still, any entrapped crude being caught and returned by the saveall ("N"). The less volatile glycerine is condensed in the first set of condensers and gravitates to the concentrators ("E") and ("F"). These are provided with closed steam coils, and any steam which may have condensed is dried out. These two concentrators provide the finished glycerine, and to empty these the valve above them is closed, the vacuum broken, and the glycerine run off. They are then closed again, the vacuum restored by an outside pump, and are again opened up to the system. The more volatile distillate, consisting of glycerine and watery vapour, passes up the two towers ("D"), which are filled with earthenware pots, the condensate collecting in the containers ("G") and ("H"). ("H") is provided with a steam coil for drying, and the liquid is run off for further distilling in a later charge, while the stronger liquid in ("G") is dried by a steam coil and returned to the still. The vapour then passes through the saveall or separator ("K"), where any condensed glycerine which may
still be held in the watery vapour is trapped by impingement on a wire gauze baffle and returned to the tailings pot for future distillation, the remaining vapours passing to the barometric condenser and air pump.

The distilled glycerine is now carefully tested, and should it prove satisfactory, passes then to be filtered after a thorough admixture with bone charcoal. This filtration is not to purify, but simply to improve the colour of the finished product.

The finished or concentrated glycerine is of a pale straw colour, and has a specific gravity slightly more than 1.262. The glycerine is carefully tested both for impurities and gravity, and is so graded for its various uses. The clear, colourless glycerine of the pharmacopoeia is obtained by double distillation—in fact, often double distillation is necessary before the high standard set by the explosives manufacture can be obtained, a specific gravity of 1.263, with a maximum chloride content of .002 being called for. After nitro-glycerine, the tobacco industry could be regarded as the next big user. Here, glycerine is used as an important ingredient in the preservation of tobacco. The low freezing point of glycerine (40° below) makes it invaluable to the engineer as an anti-freezing medium, and as a substitute for brine in many refrigerating installations. It is also used as a lubricant for certain machinery, to prevent shrinkage in wooden vessels, to impart elasticity to paper, in the preparation of leather, as a solvent for certain aniline colours, in the preparation of certain cements and copying ink, in the manufacture of printers’ rollers, in rubber substitutes, and in brewing. This list is by no means intended to be complete, but serves to indicate the great variety of uses to which glycerine is applied.

DISCUSSION

Mr. R. J. BENNIE referred to the absorbing power of glycerine for water vapour, and said it had been used for the dehydration of town gas. He also referred to the efficient forms of evaporators, giving performances often exceeding those of the multiple effect evaporators, in which caustic lye was used as an absorbent and heating agent. He also mentioned one variety in which the evolving vapours were condensed in the heating coils by means of a turbo-compressor.
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