THE RECOVERY OF CRUDE GLYCERINE

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Composition of Spent Soap Lyes

SPENT soap lyes as they are drawn from the soap kettles consist, in general, of glycerine, sodium chloride and water, with small quantities of caustic soda, sodium carbonate, soap and fatty acids, as well as albuminous and oleaginous matter. When sulphates and sulphuric acid are used in treating the lyes, sodium sulphate will also be present.

The spent soap lyes are cooled to remove soap and are treated to reduce the alkalinity and to remove organic impurities. For the successful recovery of a good quality of crude glycerine the treatment should be as effective in the removal of impurities as is economical.

The lyes should be cooled, treated and filtered as promptly as possible and all tanks should be kept clean and free of sediment to prevent fermentation of the lye. Fermentation causes serious losses of glycerine, with the formation of trimethylene glycol, gas and acid during the decomposition. Furthermore, the gases produced by the bacteria give trouble in evaporation of the lyes and the trimethylene glycol requires separation in the subsequent refining operations.

Treatment of Spent Soap Lyes

One of the most satisfactory and generally used methods of treating spent soap lyes is the double treatment method using ferric chloride may be prepared at the plant in solution by dissolving iron ore or scrap iron in hydrochloric acid. A solution containing about 20% of $FeCl_3$ can be conveniently used. Ferric chloride can be purchased in lump form ($FeCl_3.68_2O$ containing 60% active $FeCl_3$ and 40% water of crystallization.

The treatment is carried out as follows. The settled, cooled and skimmed lye is pumped to the first treatment tank. Ferric chloride is added in the amount determined by experience as being required to give maximum precipitation. In plants using all grades of raw materials, about 0.25% ferric chloride ($FeCl_3.6H_2O$) on the weight of the lye, or 2.5 lbs. per 1,000 lbs. lye, is required. In plants using only the better grades of stock the amount of ferric chloride required may be less.

With lyes produced from mixed and low grades of raw materials, more complete precipitation of impurities may be obtained by the addition of about 0.05% on the weight of the lye, or 0.5 lbs. per 1,000 lbs. lye, of aluminum sulphate $Al_2(SO_4)_3.18H_2O$, with the ferric chloride.

Ferric chloride is strongly corrosive to iron and steel and is therefore dissolved in stoneware crocks or glass lined tanks and added to the treatment tank in solution. Rubber lined tanks are also suitable. A convenient method of dissolving the lump ferric chloride is to place it in a perforated wooden box suspended in the top of the lye tank so that the lye just covers the solid ferric chloride. As the ferric chloride dissolves the heavier solution flows down and away from the container and lighter lye flows in at the top thus giving a natural circulation.

Steel treatment tanks are satisfactory when the ferric chloride is added as described.

The lye in the treatment tank should be well agitated while adding the chemicals and warmed if necessary. Suitable agitation and warming can be obtained simultaneously with a steam ejector placed in the bottom of the tank and arranged to draw in air. This has the objection of adding some condensed steam to the lye, but even so is probably as economical a method of agitation as any, in most plants. Compressed air injected through a perforated coil in the bottom of the tank is also a suitable means of agitation.

After the chemicals are in and dissolved, hydrochloric acid is added to bring the lye just on the acid side. The acid is added slowly, during agitation, so that it is neutralized at once as it mixes with the lye.

Filtered samples of lye are tested separately with dilute solutions of ferric chloride and hydrochloric acid and if the samples become turbid more ferric chloride and hydrochloric acid must be added to the lye in the first treatment tank as required to give maximum precipitation.

With present kettle room practice the amount of hydrochloric acid necessary to neutralize the excess alkalinity in the lye is small. The total Na_2O in the lye should be below 0.2% and it may be less. Before leaving the kettle room the lye may be boiled with fatty acids to reduce the alkalinity. In counter-current soap boiling the wash change brings the spent lye down to neutral or nearly so before it leaves the kettle room for the glycerine plant.

One pound of ferric chloride neutralizes about 0.44 pounds of sodium

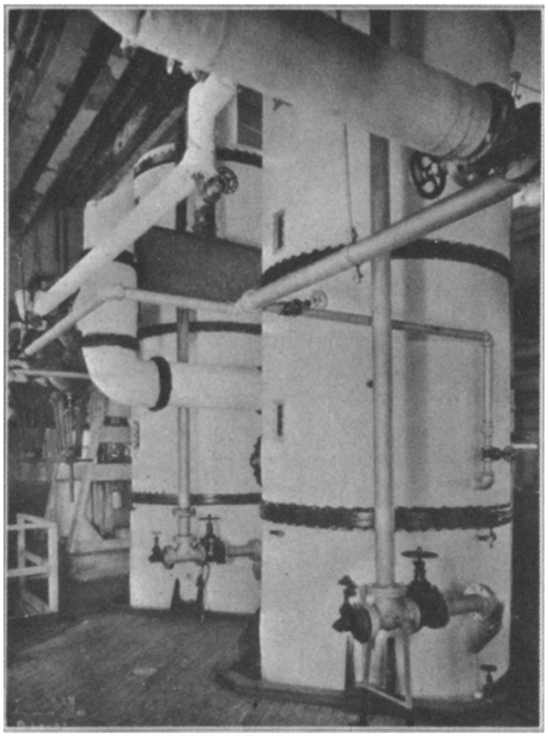

Fig. 1. Wurster & Sanger Double Effect Glycerine Evaporator.

hydroxide according to the following reaction:

$FeCl_3.6H_2O + 3NaOH \rightarrow Fe(OH_3) + 3NaCl + 6H_2O$

One pound of aluminum sulphate neutralizes about 0.36 pounds of sodium hydroxide according to the following reaction:

$Al_2(SO_4)_3.18H_2O + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4 + 18H_2O.$

When the alkalinity in the spent lyes is low, the addition of the ferric chloride and aluminum sulphate alone may carry the lye to the acid side, in which case, of course, no acid is added.

After thorough agitation in the first treatment tank the lye is filtered warm through the first treatment filter press and run to the second treatment tank. Caustic soda of any desired strength is added until the lye is on the alkaline side. A filtered sample of the lye tested with a few drops of a 10 per cent solution of ferric chloride should remain clear. If the sample becomes cloudy, further treatment is given to get maximum precipitation of the organic impurities.

When the treatment is satisfactory, the lye is filtered through the second treatment press and is ready for evaporation. The caustic treated lye must never be filtered through a press which has in it filter press cake from an acid filtra-

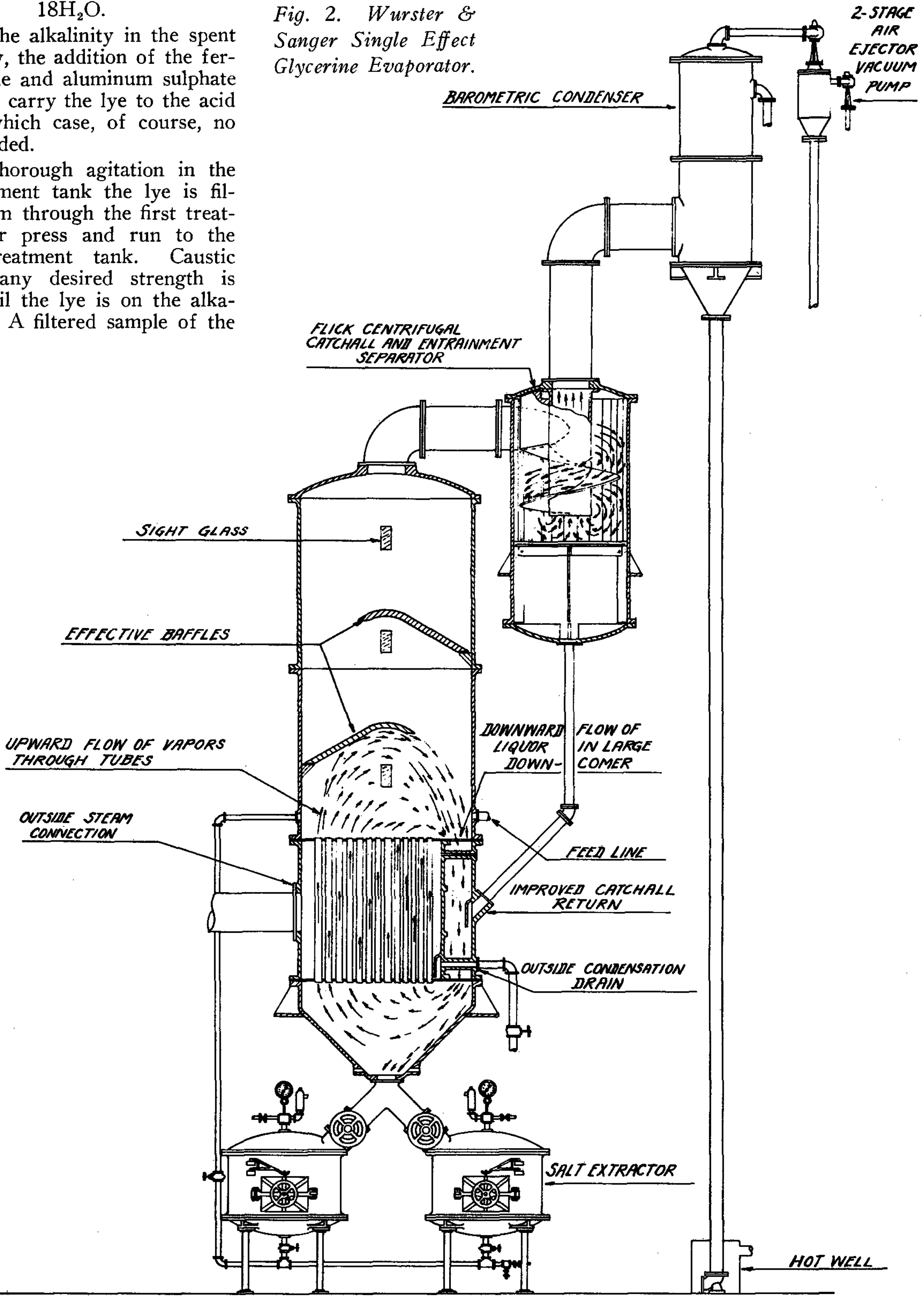

Fig. 2. Wurster & Sanger Single Effect Glycerine Evaporator.

tion, as this would re-dissolve some of the precipitate obtained in the acid treatment, and, vice versa, the acid lye must not be filtered through a press containing the alkaline precipitate.

The ideal condition of a spent lye to give the best quality of crude on evaporation is to have it in such condition that there is present sufficient acid to drive off all volatile fatty acids which can be boiled off in the evaporator. Crude glycerine produced in this way can be distilled to the highest quality of refined gycerine with the least difficulty and expense. The objection to evaporating lyes in this condition is the corrosive action of the vapors on the evaporator. It is a question, however, if this objection is not more than offset by the saving effected in the subsequent refining operation and the higher quality of the refined gycerine.

Other methods of treating spent soap lyes have been previously described in detail.[1]

The glycerol content of treated and filtered spent soap lyes ready for the evaporators will run from 4 per cent to 10 per cent and the salt from 11 per cent to 18 per cent.

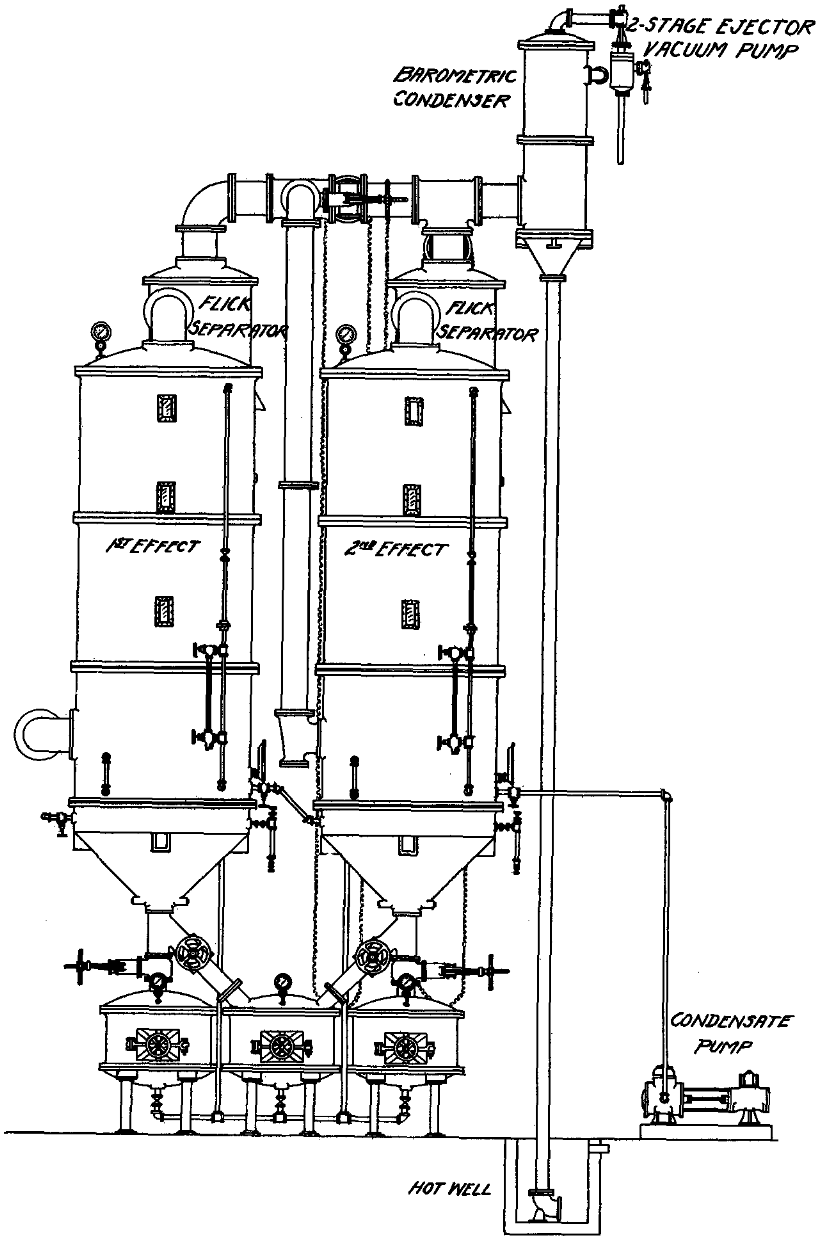

Fig. 3. Wurster & Sanger Double Effect Glycerine Evaporator (Elevation).

Crude Glycerine Evaporators

The glycerine lyes may be evaporated in single effect or in double effect. When evaporating in double effect it is customary to run to half-crude in double effect and to finish in single effect. Single effects are used when exhaust steam is available or when it is desired to have a minimum amount of equipment. When live steam is used it is usual to evaporate in double effect as the steam and water requirements are approximately one-half of the consumption in single effect evaporation.

A single effect evaporator is shown in Figure 2.

A double effect evaporator is shown in Figures 3 and 4.

The design of the evaporators is such as to give maximum efficiency in steam consumption and a high rate of heat transfer so that the equipment will be economical in operation and have a large capacity. The arrangement of the heating tubes and the downcomer of the calandria is shown in Figures 5 and 6. The large downcomer is an integral part of the steam chamber casting and is located opposite the steam inlet. This design produces a definitely directed circulation upwards through the tubes and downwards in the downcomer. Figure 2 illustrates the flow of the liquor. Cross-currents and counter-currents to obstruct the circulation are thus avoided. This rapid circulation results in a high rate of heat transfer. The rapid and directed circulation keeps the tubes free of salt. The salt crystals tend to grow larger, due to the lack of churning, and it is easier to free the salt of glycerine.

A high vapor chamber equipped with baffles is provided to insure separation of the liquor and vapor and prevent liquor from carrying over.

Separators for removing entrainment are provided for each evaporator. The most efficient device for this purpose is the Flick Separator shown in Figures 7, 8, 9 and 10.

The Flick Separator consists essentially of an outer shell, an inner liner with louvers, a helical baffle to direct the vapors and properly located vapor inlet and outlet. The vapors enter tangentially and a circular motion at high velocity is set up. The centrifugal force throws the entrained particles

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[1] See Walter E. Sanger, Recovery of Glycerine from Spent Soap Lyes, Chem. & Met. Eng., Vol. 26, No. 26, June 28, 1922; Oscar H. Wurster, Crude Glycerine, Modernizing Its Recovery, Soap, Vol. 5, No. 1, September, No. 2, October, 1929.

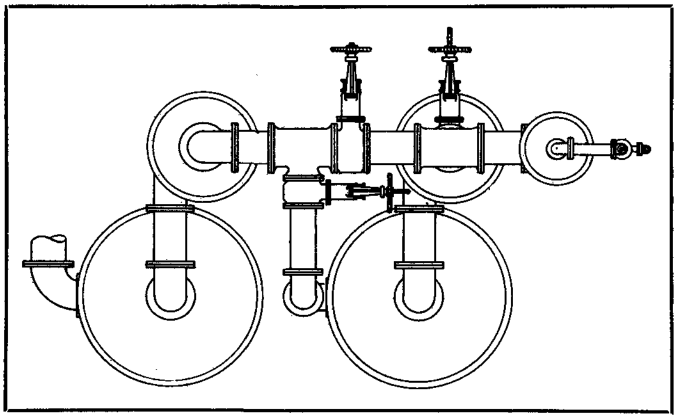

Fig. 4. Wuster & Sanger Double Effect Glycerine Evaporator (Plan).

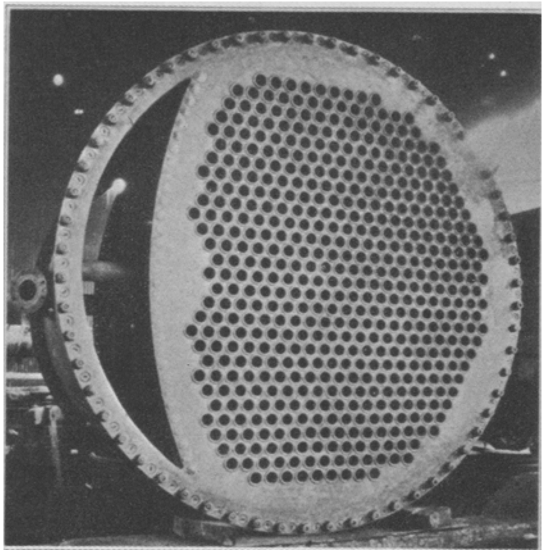

Fig. 5. Wurster & Sanger Calandria with 1,350 Sq. Ft. Heating Surface.

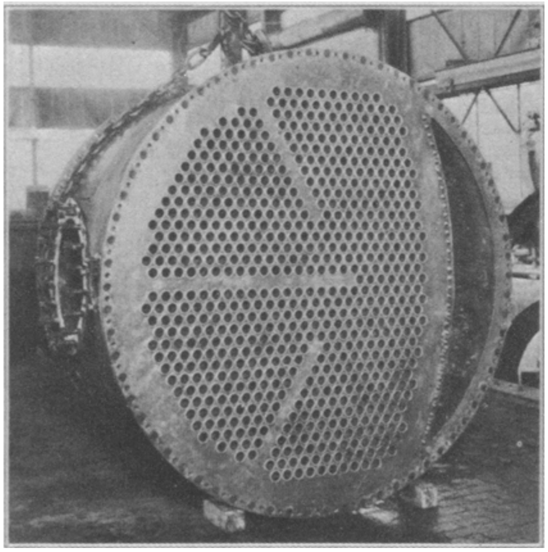

Fig. 6. Wurster & Sanger Calandria with 1,800 Sq. Ft. Heating Surface.

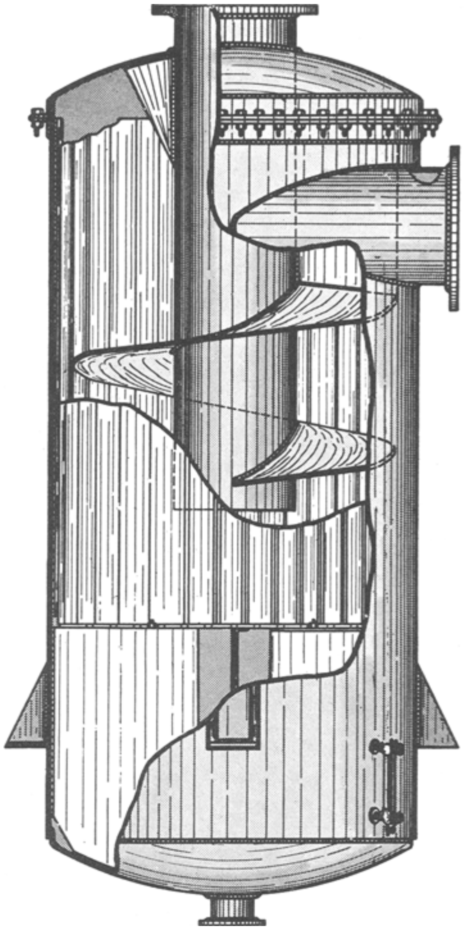

Fig. 7. Flick Centrifugal Catchall and Entrainment Separator.

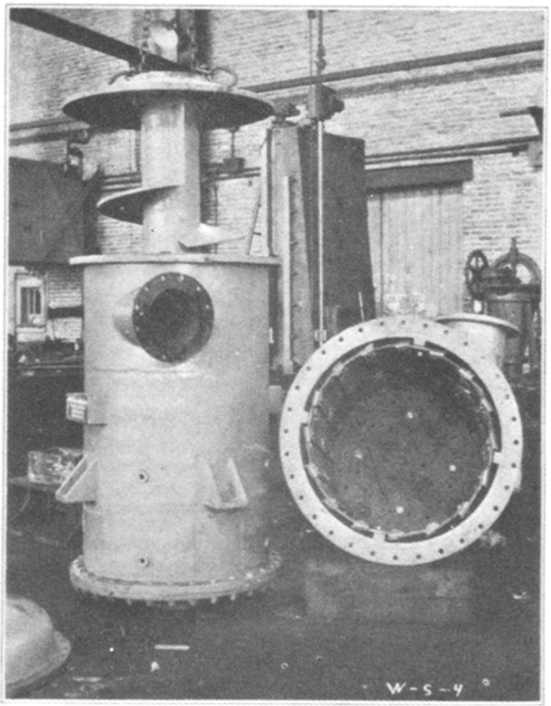

Fig. 8. Cast Iron Flick Separators for Glycerine Evaporators Being Assembled in Shops.

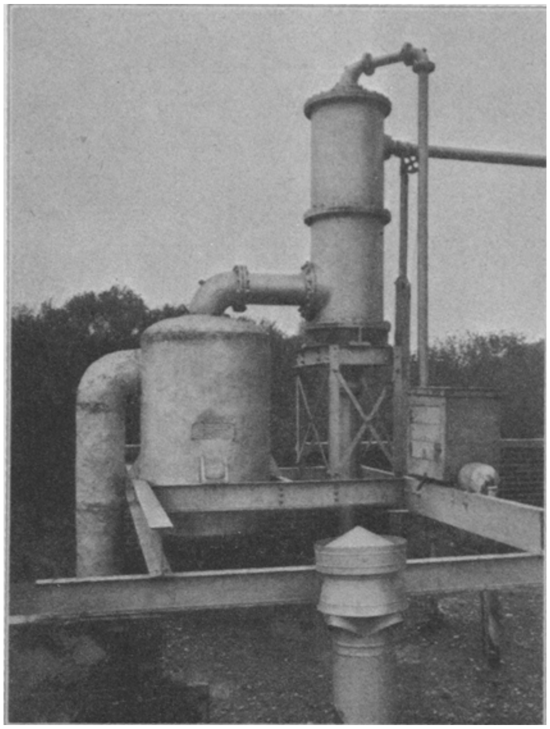

Fig. 9. Flick Separator and Barometric Condenser on Single Effect Glycerine Evaporator. Mounted on Roof Above the Evaporator.

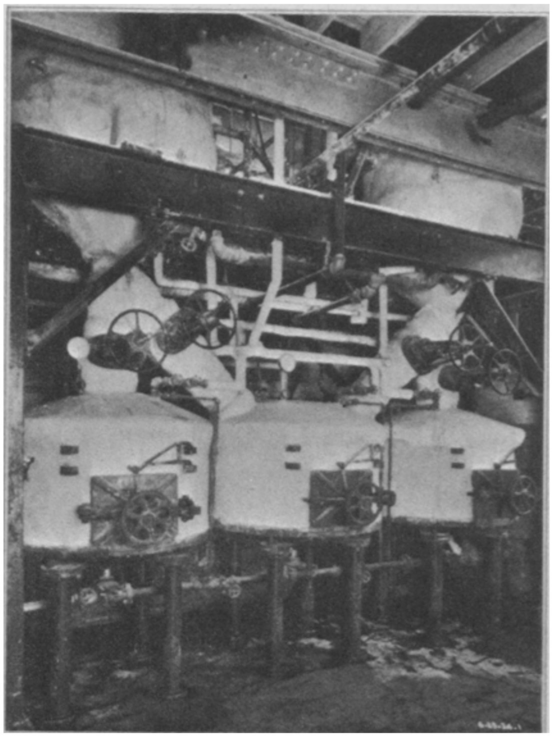

Fig. 11. Wurster & Sanger Salt Extractors on Double Effect Glycerine Evaporator.

against the spaced staves of the inner liner and through the vertical louvers. The liquid particles in the quiet space between the inner liner and the outer shell flow down to an isolated chamber in the bottom of the separator and out through a drain to be returned to the evaporator. The effectiveness of the Flick Separator is due to the centrifugal separation of the entrained particles and the complete removal of the separated entrainment from the path of the vapors.

The vapor piping of a double effect evaporator may be arranged (1) so that the unit can be operated as a double effect only, (2) that, in addition to operating as a double effect, the second effect may be operated as a single effect for finishing, or (3) that, in addition to operating as a double effect, either or both effects may be operated as single effects. Figures 3 and 12 show the third arrangement.

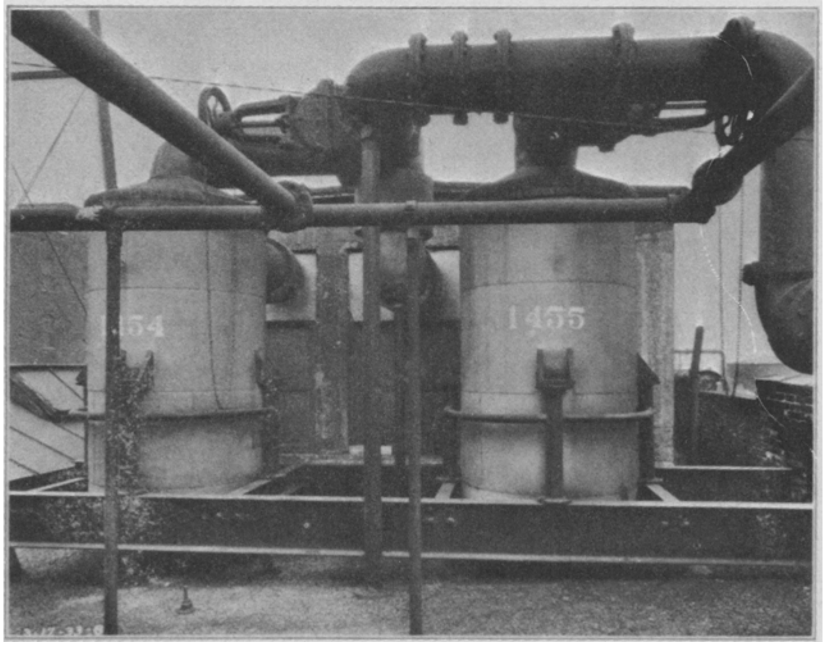

Fig. 10. Two Flick Separators on Double Effect Glycerine Evaporator.

The vacuum equipment usually consists of a barometric condenser and two-stage steam ejector, as shown in Figure 9. For the successful operation of a steam ejector the steam pressure must be uniform and preferably not less than 90 lbs. per square inch, gauge pressure. When the steam pressure is low and fluctuating, reciprocating steam driven vacuum pumps are used. Steam ejectors may be operated condensing or non-condensing. The exhaust steam from either ejectors or pumps may be used for evaporation when the vacuum equipment is designed for a suitable back pressure, which is usually about 5 lbs. gauge.

A low level jet condenser may be used in connection with a reciprocating, steam driven, wet vacuum pump on small installations.

Water jet condensers and barometric heads may also be used, thus condensing the vapors and producing the vacuum with one piece of equipment. For this

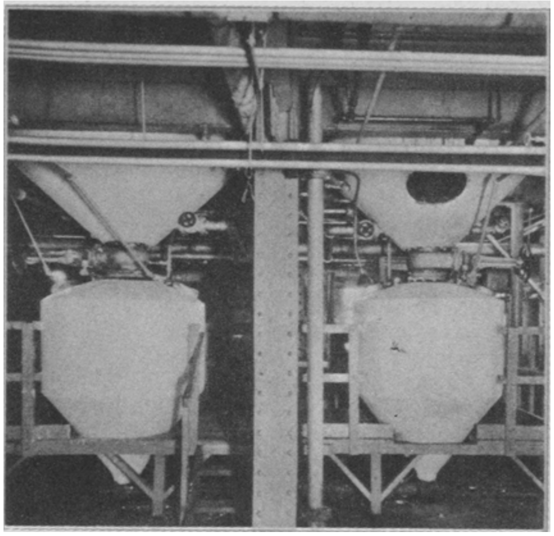

Fig. 13. Salt Drums on Wurster & Sanger Double Effect Glycerine Evaporator.

arrangement the water must be clean to prevent clogging the nozzles and the water must be under pressure. The water consumption is somewhat greater than with a standard barometric condenser. With this type of vacuum equipment precautions must be taken to prevent flooding the evaporators with condensing water.

The design of the equipment also varies with reference to the method of removing the salt. Figures 2, 3 and 11 show salt extractors. Figures 12 and 13 show salt drums. The different methods of operating this equipment will be described later.

The Operation of a Double Effect Evaporator

It is not difficult to run a double effect evaporator and produce crude glycerine, but to operate the unit at its highest efficiency and maximum capacity, to save steam and time, requires careful attention to numerous details.

Equipment Required

A double effect evaporator for the evaporation of spent soap lye to 80 per cent soap lye crude glycerine consists of a first and second effect, each with calandria and vapor chamber equipped with baffles, salt drums or salt extractors on each effect, a separator on each effect, barometric condenser, vacuum pump, condensate pump and the connecting piping. Auxiliary equipment required with the salt drums is a salt sludge tank and centrifuge or continuous filter. This equipment is shown in Figures 3 and 12.

Testing the Equipment

After the equipment is erected and the piping is in place the evaporator unit is ready to be tested for leaks. It is, of course, important that all bolts on equipment flanges be drawn up tightly during erection, all threaded joints made tight and all valve stems properly packed.

The valves on all outside openings are closed, valves on lines connecting parts of the equipment are opened and the vacuum pump is started, venting the exhaust steam to the air. A small amount of water is turned on the barometric condenser. A vacuum of 25-in. to 28-in., referred to 30-in. barometer, is pulled on the equipment. The steam to the vacuum pump or ejector is then turned off and the valve on the vapor line to the pump,

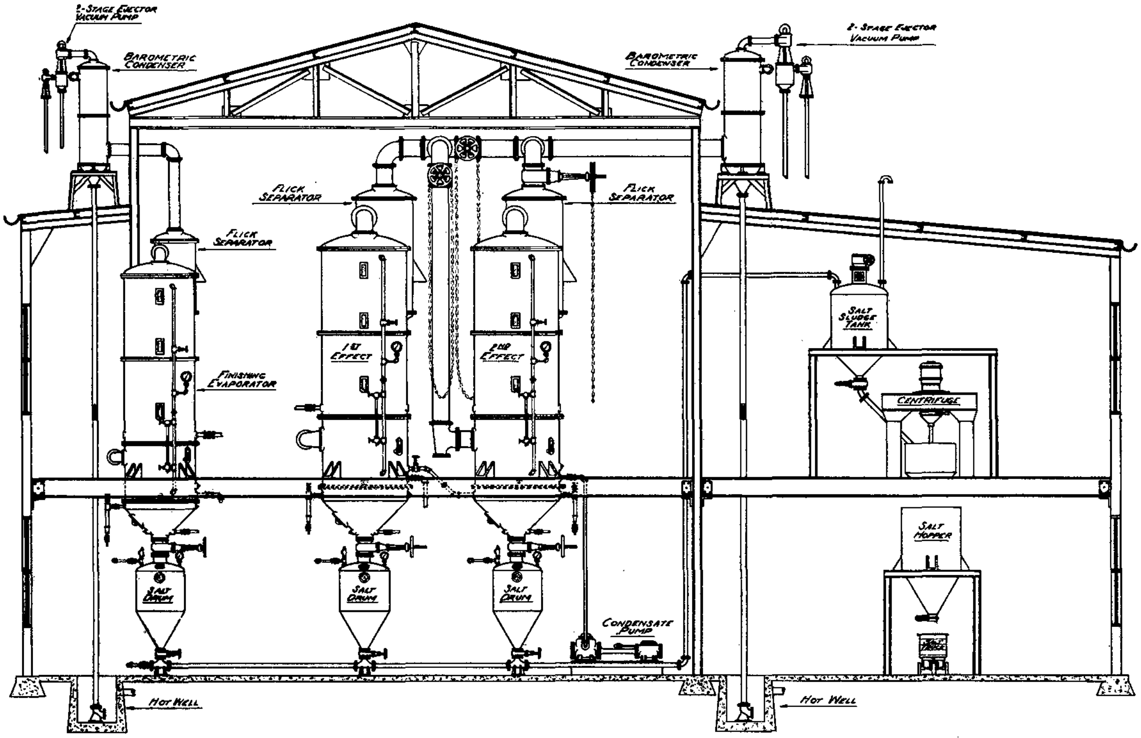

Fig. 12. Wurster & Sanger Glycerine Evaporator Plant. Double Effect Evaporator to Run to Crude Glycerine and Single Effect Finishing Evaporator. The Salt Recovery Equipment Includes Salt Drums and Centrifuge.

or the valve on the exhaust line from the second stage ejector, is closed thus sealing the entire unit. The condensing water is turned off. The vacuum on the system should not drop more than 1 in. per hour. If there are leaks, it is necessary to go over the entire equipment and draw up all joints.

Another method of testing the equipment, which shows where the leaks are, is to fill the entire unit with water and put on a water pressure up to 25 lbs. per square inch. All leaking joints must be marked and drawn up after relieving the pressure. If no leaks appear within two hours after the final drawing up, the equipment is tight and the water may be drained out.

It is preferable not to insulate the equipment until it has been tested and made tight.

After the evaporator has been in operation a few days it is advisable to go over the equipment carefully and draw up all bolts, as they can usually be taken up after the equipment has been heated.

Starting

In starting up the evaporator as a double effect, the valves on the vapor lines are so set that steam will enter the calandria of the first effect and the vapors from the vapor chamber of the first effect will pass through the first separator and into the calandria of the second effect. The vapor line from the second effect is connected to the second separator and then to the barometric condenser and vacuum pump.

The condensate from the calandria of the first effect is removed through a steam trap. The condensation drain from the calandria of the second effect is connected to both the condensate pump and to a steam trap. The condensate is removed by the condensate pump when operating as a double effect (when the steam chest is under vacuum), and by the steam trap when operating as a single effect (when the steam chest is under pressure).

The calandria of the second effect is vented near the top into the vapor chamber of the second effect to take off non-condensable gases which may accumulate in this part of the steam chest. In starting up, this vent line valve is opened wide, so as to pull a vacuum on the first effect. When operating as a double effect, the valve on this vent line is always kept slightly open to prevent fouling of the heating surfaces in the top of the calandria by non-condensable gases. However, in normal operation the valve on this vent line must not be open so far as to draw vapor through the line and increase the vacuum on the first effect.

The salt valves at the bottom of the evaporators are closed and the valves on the feed and discharge lines and on the vacuum breakers are all closed.

When starting operation of the double-effect evaporator, steam is turned on the vacuum pump and the condensate pump is started.

A small quantity of water is turned on to the barometric condenser. In regular operation the water in the discharge leg of the barometric condenser should have a temperature of 100° to 115° F., depending on the vacuum. The tail-pipe temperature is controlled by the amount of cold water run into the barometric condenser and must have attention throughout the run.

With a 2-stage ejector with inter-condenser, water must also be run to the inter-condenser in sufficient quantity to condense the water vapors. An excess of water must be avoided, for this will flood the ejector unit and interfere with its proper operation. A non-condensing ejector, of course, requires no water.

A small quantity of cold water is run continuously to the condensate pump to seal the valves and keep the pump cool.

Care must be exercised to draw only water and non-condensable gases to the condensate pump. If the pump is operated at a capacity considerably above that required to remove the condensate, steam may also be drawn to the pump, resulting in a steam loss. This is indicated if the pump becomes hot.

When the evaporators are under a vacuum of about 15 inches, or a vacuum sufficiently high to pull in lye, treated and filtered lye from the feed tank is run into both evaporators. In subsequent operation, any liquor remaining in the first effect from a previous run is first drawn into the second effect. Fresh liquor is then fed to the first effect only and the second effect is fed from the first effect. In this way the proper balance of operation is maintained. In starting a run, the feed is shut off when the liquor level shows in the gauge glasses, or when the calandrias are ⅓ to ½ full.

When the vacuum in the second effect reaches about 23 in., steam is slowly turned into the calandria of the first effect. The exhaust from the vacuum pumps may also be turned into the first effect calandria. When the liquid in the first effect begins to boil, the vacuum therein will drop.

The vapors pass from the vapor belt of the first effect into the calandria of the second effect, where they are condensed and are withdrawn by the condensate pump. The condensate pump also removes non-condensables heavier than steam, while the non-condensables lighter than steam pass out through the vent line at the top of the calandria. As the vapors are condensed and the non-condensables removed, the vacuum in the first effect again rises.

The liquor in the second effect soon starts to boil from the heat of the condensing vapors. The vacuum first drops slightly and then rises as the vapors are condensed in the barometric condenser.

The starting of the evaporators should be done sufficiently slowly that there will be a minimum drop and subsequent rise in vacuum.

Attention must be given to the water supply to the barometric condenser as the evaporation increases. As stated above, the temperature of the tail-pipe water is usually between 100° and 115° F., depending on the vacuum in the 2nd effect.

When the liquid boils in the first effect, more steam is turned on until there is a positive pressure on the gauge connected to the condensate drain. The liquor level in each effect is so maintained that the tubes are continually wet.

The vacuum on the second effect will generally be from 26 in. to 27 in. Some installations are made for slightly lower or higher vacua for special reasons, but the usual limits are 25 in. to 28 in. The vacuum on the first effect may be as high as 20 in. at the start and gradually drop as the concentration in the second effect increases. If the concentration in the second effect is carried to 80 per cent crude, the vacuum in the first effect will drop to zero. When operating to semi-crude in double effect, as is the usual practice, the difference in vacuum between the two effects is about 10 in. or 12 in.

Operation

Under the above conditions the evaporator is operating at normal capacity. As the liquor level drops in the second effect, more liquor is fed from the first effect and fresh lye is fed to the first effect so as to keep the liquid levels in each effect constant. It is important for the smooth and uniform operation of the plant that feed to each effect be regular and steady rather than than that the level be allowed to drop and then a large charge fed in. With a little practice and care, the feed valves can be set so as to feed at the required uniform rate. Liquid level regulators can be used, but the salt content of spent soap lye is so high that these devices are not entirely reliable on soap lye evaporators. Liquid level controllers for the first effect are fairly satisfactory, but when used on the second effect they require so much attention that manual control is usually used.

Steam to the first effect is regulated as required to show a positive pressure on the condensate drain.

Water to the barometric condenser is adjusted to maintain a uniform vacuum in the second effect and uniform temperature in the tail pipe. The greatest amount of water will be required at the start of the run. As the concentration of the liquor increases and the rate of evaporation decreases, less condensing water will be required.

Separation of Salt

In concentrating spent soap lye to crude glycerine about 11 to 15 lbs. of salt is separated from each 100 lbs. of lye, the exact amount depending upon the amounts of salt and glycerine in the spent lye and on the concentration of the finished crude. As soon as the liquor in either effect reaches the salting point, salt will begin to crystallize and drop to the bottom of the evaporator. The presence of salt may be observed in the liquor which is thrown against the sight glasses on the vapor belt. After salt begins to crystallize out, the lye has no further value in dissolving any salt remaining on the tubes from a previous run, as it is then a supersaturated salt solution, and it is time to start removing the salt from the evaporators.

Methods of Recovering Salt

There are three generally used methods of separating the salt from the glycerine.

(This paper will be concluded in the November issue of OIL & SOAP.)

THE REFRACTOMETRIC DETERMINATION OF IODINE NUMBER IN FLAXSEED OILS

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INTRODUCTION

As linseed oil is used primarily in the manufacture of paints, varnishes, and linoleum, the rapidity with which a given sample of oil will oxidize is usually the most important single factor governing its quality. Although it is true that the drying time of low-quality linseed oils may be materially shortened by the addition of chemical "driers," oils that have low initial drying times nevertheless produce paint films of better quality.

Iodine number as a measure of the total degree of unsaturation of the oil may be considered a quantitative measure of the quantity of oxygen the oil is potentially able to absorb. The rate of oxidation, however, depends not only upon the total degree of unsaturation but upon the relative proportions of the various unsaturated fatty acids in the glycerides of the oil. As the iodine number does not differentiate between these various unsaturated fatty acids, it may not be considered as an exact measure of the drying time of the oil. Rapid-drying raw linseed oils, however, are high in linolenic-acid content and show a high iodine number. Conversely, slow-drying linseed oils are relatively low in linolenic-acid content and have correspondingly low iodine numbers. The iodine-number determination may therefore be considered a good practical (though not exact) method for determining the relative drying times of untreated raw linseed oils, and as such is used extensively in commercial practice. The iodine numbers of linseed oils from different lots of commercial flaxseed range from about 150 to 200 or over. Oils having iodine numbers below 165 are generally considered to be of decidedly inferior quality whereas iodine numbers of 185 or over usually indicate superior drying properties.

The importance of iodine number in the linseed-oil manufacturing industry has greatly increased during recent years, because of the fact that large quantities of flaxseed have been marketed, the oil of which has possessed very inferior drying qualities and correspondingly low iodine numbers. The production of these large quantities of low-quality flaxseed has been due partly to drought conditions and unseasonably high temperatures in the principal flax-growing regions of the United States over a period of years; and partly to the introduction of new varieties of flax that have been bred for high yields and disease-resistant qualities, but which inherently produce low-quality oils.

Since such a wide variation exists in the iodine number of oils prepared from different lots of flaxseed, the linseed-oil industry should be benefited by a simple method for determining in advance the iodine number of the oil that could be pressed from a given lot of flaxseed.

Relationship Between Iodine Number and Refractive Index

It has long been known that in the case of animal and vegetable oils in general, a positive correlation exists between refractive index and iodine number. Lewkowitsch (4), however, after accumulating data on a large number of different oils concluded that no definite relationship existed between these two factors. Niegemann and Kayser (5), on the other hand, report-