May 6, 1958 J. M. AVERY 2,833,644

RESOLUTION OF ALKALI METAL AMALGAMS

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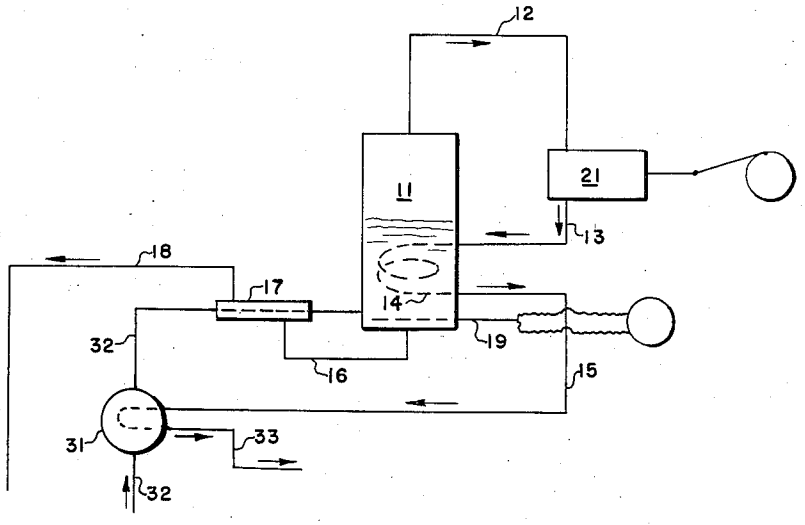

FIGURE 1.

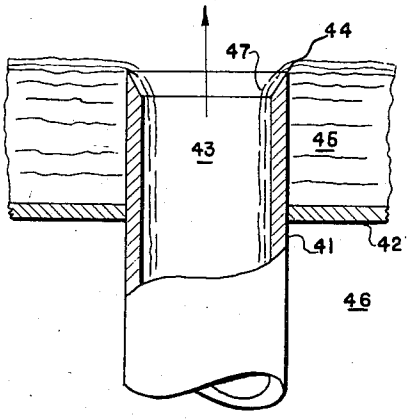

FIGURE 2.

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RESOLUTION OF ALKALI METAL AMALGAMS

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5 Claims. (Cl. 75—66)

This invention relates to the resolution or separation of the components of dilute alkali metal amalgams. More specifically, the invention relates to a new and novel process for the separation of dilute sodium amalgams into fractions including a fraction greatly enriched in sodium metal, and a separated mercury enriched fraction having appreciably lower sodium metal content than the initial amalgam.

The manufacture of the alkali metals, especially sodium in a form suitable for use for their metallic content as such (as opposed to the manufacture of caustic aqueous solutions (has been a problem which has intrigued the chemical industry for some time. At the present time, sodium metal is made almost exclusively by the electrolysis of fused salt systems. The leading process example is the electrolysis of sodium chloride in fused salt cells of the Downs type such as is disclosed in U. S. Patent 1,501,756. Mercury cathode cells on the other hand are well known as permitting a highly effective process for forming amalgams of the alkali metals by depositing from aqueous solutions the metal cations of the ionized salt. In such operations, the cathodic product is a very dilute amalgam of the sodium metal—by dilute meaning appreciably below one weight percent concentration, usually of the order of about 0.2 to not over about 0.3 weight percent in the case of sodium. Because of this extremely low concentration, the cathodic product from such cells has heretofore been employed only in subsequent reaction with aqueous liquids to form a high grade of aqueous caustic solution. Unfortunately, the inherent economies of the electrolysis itself have not been realizable when sodium or an enriched sodium fraction is desired as the end product. Accordingly, a very definite need exists for an economical and feasible method of resolving or separating such dilute amalgams into two streams, one concentrated in the alkali metal content and the other concentrated in the mercury content and available for return to the electrolysis operation for re-deposition of additional alkali metal values. A sodium enriched fraction is suitable, for certain purposes, as a replacement for pure sodium metal, which finds numerous applications in chemical processing as a strong reducing agent. For example, amalgams are effective for the preparation of high molecular weight alcohols by reduction of fatty acid derivatives such as glycerides, and the production of metal alcoholates by reaction with a suitable anhydrous alcohol.

It is therefore an object of the present invention to provide a new and highly efficient method of accomplishing the foregoing resolution into a sodium enriched stream and an amalgam greatly denuded of sodium content. Hereafter, for clarity, this denuded stream is to be referred to as the mercury enriched stream. It will be understood that, throughout the discussion following, all the streams of the process normally contain appreciable weight percentages of mercury and that the terms enriched and denuded are of relative significance. A further object is to provide a process which accomplishes

the above described resolution but which does not employ an additional electrolysis step, as has been suggested on occasion for a separation as provided by the present process. An additional object is to provide a sodium enriched amalgam product stream which, because of its enrichment lends itself particularly effectively to further electrolytic separation of a pure sodium fraction. Yet another object is to provide a particularly effective continuous operation, which is extremely effective in energy utilization for providing such resolution.

The foregoing objects are readily obtained by the present process which comprises, in its broadest terms, the vaporization of a mercury rich fraction from a dilute amalgam feed, the heat involved in said vaporization being derived by the liquefaction of the same mercury rich vapor stream after compression to a more elevated pressure. This compressed stream is recondensed in indirect heat exchange relationship with the boiling liquid from which the mercury rich vapor is vaporized. This boiling liquid, as will be apparent from the description hereafter yields the enriched sodium fraction and is withdrawn from the vaporizing chamber for subsequent usage and processing in various ways. As described in more detail hereafter, the highest degree of economies, obtainable in the most effective and preferred species, ar provided by supplementing the above described main operation with further indirect liquid-liquid heat exchange relationships, and in addition a small amount of direct heat is frequently provided to the system as is described hereafter, and particularly during start up operation. The sodium enriched stream may contain, in theory, up to about 25 percent by weight sodium. However, this limitation is not easily attained for practical reasons, and in fact, a more realistic top level of concentration is to provide enrichment up to about 15 weight percent sodium. Further, in practice, the preferred range of concentration of the sodium enriched product stream is from about 3 to about 5 weight percent sodium. This corresponds to, for a feed amalgam having 0.25 weight percent sodium, removal of 91 and 95 percent of the initially present mercury, respectively.

Although the above described operation is susceptible of numerous different and highly effective embodiments, in general it is preferred that the vaporizing operation be carried out as a single stage vaporizing step. In addition, a highly preferred embodiment involves an entirely pressurized system which, surprisingly, is particularly effective. Another type of embodiment is especially effective for low pressure operation and employs a particular contacting technique for providing the advantages of the high pressure operation.

The details of the invention and of the best modes of its operation will be readily appreciated from the detailed description and working examples given hereafter, and from the accompanying figures wherein:

Figure 1 is a schematic representation of a typical apparatus set up suitable for carrying out preferred embodiments of the process, and

Figure 2 is a diagrammatic detail portion showing details of the construction of a vaporizing chamber particularly suitable for performing certain embodiments of the process.

The mode of operating the process in the broadest form is most readily described with reference to Figure 1, which illustrates schematically the main units of apparatus and their interrelationship for most embodiments of the process. Referring to Figure 1, the principal units are a vaporizing chamber **11**, a compressor **21**, and a heat transfer coil **14** within the vaporizing chamber **11**.

The vaporizer **11** can assume a variety of forms as discussed in more detail hereafter. In all instances, a vapor line **12** is provided for discharging vapor from

this space to a compressor 21. A supplemental heater 19 is provided to heat the vaporizer liquid charge with electrical energy, when required. The compressor 21 supplies by either positive displacement or centrifugal force, increased pressure to the vapor, the compressed vapor being discharged through a high pressure vapor line 13, which feeds a heat transfer coil or exchanger 14 which is positioned within the vaporizing space 11 in such a manner as to be in contact with and provide heat to liquid therein. In giving up heat to liquid in the vaporizer 11, the compressed vapor is condensed in the coil and discharged through the hot condensate line 15. In the most effective forms of the process, the sensible heat content of the hot condensate is utilized in a heat exchanger 31 to preheat fresh amalgam feed to the operation, the fresh feed being introduced through a line 32 to the heat exchanger 31. The condensate so cooled is discharged through line 33 and is then available for recycling to the electrolysis operation. Preheated feed amalgam after leaving the heat exchanger 31 passes through a line 32 to an additional heat exchanger 17. A liquid line 16 from the body of the vaporizer 11 is provided to lead a sodium-rich phase, at the boiling temperature thereof, from the vaporizer 11 to the heat exchanger, wherein additional preheating of the amalgam feed is provided. The thus cooled concentrated enriched sodium phase is discharged from this supplemental heat exchanger 17 through line 18 and is available for subsequent operations.

To further illustrate the process, the following examples describe typical continuous operations at various conditions. The first example illustrates a low pressure embodiment, that is, approximately 1 atmosphere pressure.

Example I

An amalgam feed of 2,520,000 parts by weight is fed at a uniform rate through feed line 32 and the heat exchanger 31. The amalgam contains 0.25 weight percent sodium. The initial temperature is a nominal or ambient temperature of about 70° F. After preheating in the heat exchanger 31, the amalgam is at a temperature of about 680° F. The heated amalgam then passes to the body of the vaporizer wherein a boiling concentrated amalgam is maintained, having a 3.5 weight percent sodium concentration. The vaporizer 11 operates with a boiling temperature of about 755° F. and a pressure of about 1 atmosphere, plus minor pressure differentials necessary to overcome fluid flow friction restrictions. The vaporizer converts to the vapor phase 2,346,000 parts by weight of the mercury, there being substantially no vaporization of the sodium content. The vaporized mercury then passes through line 12 to the compressor 21, and is there raised by a compression ratio of about 2.5, to an absolute discharge pressure of about 35 pounds per square inch absolute. This compressed mercury then passes through the heat exchanger line 14 and condenses at the higher pressure and at a temperature of about 1300° F. In addition to being liquefied, the mercury discharged from the coil 14 is subcooled to about 770° F., or 15° F. above the boiling amalgam in the vaporizer 11. In addition, heat is supplied by the electrical heater 19. After passing through the heat exchanger coil 14 in the vaporizer, the temperature of the condensate is about 770° F. This hot mercury stream then passes through line 15 to the heat exchanger 31 and is reduced in temperature therein to about 78° F.

In the operation of this example the heat and work inputs are as follows:

	B. t. u. per pound mercury vaporized
Work by compressor	9.7
Heat by heater	7.8
	17.5

The actual work input to the compressor and heat input to the heater will be somewhat higher than these values, dependent on the efficiency of operations.

From the foregoing example it is seen that approximately 93 percent of the original mercury component of the amalgam feed is separated and the concentration of sodium in the product sodium enriched stream is increased by a factor of 16, thus providing a chemical material having a sodium concentration effective for use as such in supplying sodium values for chemical reaction.

The efficiency of the low pressure operation as described above is limited in the gross aspects because of the relative low boiling temperature at atmospheric boiling pressures. This arises because of the great density of the amalgam feed and the sodium enriched amalgam product, which limits the allowable depth of boiling liquid within the vaporizer to a level such that the temperature elevation at the lowermost point of the boiling liquid approaches the temperature of the condensing compressed mercury vapor. This is found to reduce the average temperature differential and, by decreasing the thermal driving force for heat transfer, results in an increase in the heat transfer area necessary for a given rate of production. Thus, for example, in an installation operation according to the above conditions described in Example I, a heat transfer area of about 1.5 sq. ft. per 1,000 pounds of feed per hour is required, the mean temperature differential in the vaporizing heating coil being about 75° F.

The deficiencies of low pressure operation indicated above can be circumvented by an elevated pressure operation as illustrated by the examples below.

Example II

The procedure of Example I is repeated, the same feed composition and sodium enriched fraction being obtained but with the following changes in conditions. The temperature of the boiling system is increased approximately 200° F. to about 965° F. The boiling pressure is about 85 pounds per square inch gauge, and the mercury vapor is compressed to about 140–145 pounds per square inch gauge, the compression ratio being about 1.6. Operations under these conditions reduce the work input via the compressor to approximately 4.8 B. t. u.'s per pound of mercury vaporized. In contrast to the results of Example I, however, the process provides excess heat to the extent of about 2 B. t. u.'s per pound of mercury and this can be employed for providing process steam through various heat recuperating heat exchangers.

Example III

The procedure of Example II is again repeated, except that in this instance, the compression step is altered to provide a compression ratio of 1.66 to 1, the pressure of the compressed mercury vapor being 150 pounds per square inch. In addition, the condensed mercury, in being discharged through the vaporizer coil 14, is cooled to only 972° F. thus increasing the final temperature differential to 15° F., the overall mean temperature differential being about 587 F. In this instance, a heat transfer area of about 1.6 square feet, per 1,000 pounds of feed amalgam per hour is required. Thus, although the mean temperature differential is decreased more than 20 percent from Example I, the heat transfer area increase in Example III is only 6 percent.

Example IV

The procedure of Example II is repeated, except the compression ratio is again increased to about 1.85:1, the discharge pressure from the compressor being 170 pounds per square inch. In this case also, the condensed mercury is subcooled to only about 987° F. before being discharged from the vaporizer heating coil 14, or to a temperature of 30° F. above the temperature of the boiling liquid in the vaporizer. In this case, the work input by

the compressor is about 7.1 B. t. u. per pound of mercury vaporized but the heat input by the supplemental heater is reduced to less than 0.2 B. t. u. per pound.

From the foregoing examples it is seen that a higher pressure operation provides marked advantages in not only reducing the work input required to compress the mercury vapor, but also in appreciably reducing the amount of direct heat which must be added to supplement the operation. The benefits from increase in pressure of the vaporizing operation are surprising, in that it is well known that in all liquid-vapor systems, the enthalpy of vaporization decreases with increases in pressure. Thus, in Example II, where the compressor discharge pressure is about 60 pounds greater than the vaporizing pressure, it would be expected that the enthalpy of condensation at the higher pressure would be so much lower than the enthalpy of vaporization of the mercury from the vaporizer, that extremely large heating coil surfaces would be required. This would be considered necessary to allow recuperation of some of the sensible heat of the condensed mercury. Actually, it is found that the vaporizing and condensing operations at higher pressure levels are much more efficient and provide relatively lower heat exchanger requirements than at the low pressure ranges.

The foregoing discussions in the examples are directed to the most effective embodiment of the process, i. e., a single-stage vaporizing operation, conducted either at low pressures, or preferably as described, at pressures of at least 85 and preferably about 100 pounds p. s. i. a. Numerous other embodiments of the process will be highly effective, and in some situations will be preferred for specific installations. For example, if desired, a plurality of sequential vaporizing stages can be employed. These can include what are hereafter termed as forward feed or, alternatively, backward feed systems. The characteristics of the forward feed system are that in the forward feed system, a plurality of vaporizers, say for example three, are employed wherein the liquid phase from a first stage is transferred to the second stage and, the liquid from the said second stage is transferred to a third stage. Concurrently vapor from the first stage is condensed in a heating coil used to supply vaporizing heat in the second stage, and vapor from the second stage is employed in the third stage condensing coil, vapor from the last stage being compressed and returned to condense in the first stage. In contrast, in a backward feed system the sequence of liquid and vapor flows is reversed. Thus in a three-stage system, the vapor from the third stage is condensed in the heat transfer coil in the second, vapor from the second stage is condensed in the heat transfer coil from the first stage, whereas the liquid sequence flow is the same as in the forward feed system. The following illustrates the relative merits of the several systems, the comparison being on the basis of a maximum vaporizing pressure of 100 pounds. In a single stage system, the work input, as already shown, can be in the order of about 4.8 B. t. u.'s per pound of mercury evaporated. In a two-stage backward feed system the work input can be about 4 B. t. u.'s per pound of mercury, and in a three-stage backward feed system the work input can be as low as 3.2 B. t. u.'s, whereas if the forward system is used the work input is slightly higher at about 3.4 B. t. u.'s. The foregoing data apply when the system is operated to provide at least a minimum temperature differential between the boiling liquid and condensed mercury vapor of about 8° F. Generally, although as indicated above, multiple-stake systems result in appreciable reduction of work input for a given amount of separation, in practice a multiple-stage system has severe disadvantages in that, in a three-stage system a compression outlet temperature of over about 1200° F. is required and this temperature level puts a strain in available materials of construction. In the case of a double effect system, it is feasible to operate with a compressor outlet temperature below 1200° F., but in such instances the pressure of operation of the highest pressure stage is necessarily not over about 50 p. s. i. a. or 35 pounds p. s. i. g. It is found that in such instances the conventional type of vaporizing operation is highly undesirable because the high density of the boiling amalgam liquid system results in appreciable boiling point rise if any significant liquid depth is encountered in the space. Accordingly, the preferred conditions for operation of a multiple-stage unit are a two-stage vaporizing system with the vaporizers operating at not more than about 35 pounds p. s. i. g.

However, it is to be understood that if it is desired to employ a multiple-stage system or a single-stage system under conditions which would ordinarily result in a compression outlet temperature above 1200° F., a technique which can be used to alleviate the problem of compression outlet temperatures being above 1200° F., is to feed liquid mercury to the compressor inlet in amount not greater than that necessary to take up the sensible heat of the overhead mercury vapor going to the compressor. A still further technique which can be employed is the use of external cooling of the overhead mercury vapor to compensate for such sensible heat.

Any of various types of compressing devices can be employed to provide the necessary increase in pressure of the mercury vapor. It is preferred to employ rotary, single-stage compressors for this purpose, although positive displacement machines are also employable.

As mentioned above, one of the limitations on the process, particularly in multiple-stage operations, arises because of the high density of the amalgam feed and the mercury rich product stream. It is found that, in the vaporizing operation, the boiling actually occurs at the interface of the liquid-heat exchanger surface. If the heat exchange surface is submerged an appreciable depth below the level of the boiling liquid, the density of the liquid results, in effect, in the boiling step itself being at appreciably higher temperature than the temperature corresponding to the pressure of the vaporized mercury discharged from the vaporizer. This result, in turn, reduces the effective temperature differential available for heat transmission in the vaporizer. This feature is overcome as illustrated by the examples, by conducting the vaporization at an elevated pressure, preferably of the order of about 85 to 100 pounds per square inch gauge. In such instances, a liquid depth of up to about one foot above the heat exchange surface can be tolerated. It is found that this liquid depth, at a vaporizing pressure of 100 pounds, absolute, reduces the mean temperature differential only about 5° F. In contrast, when the vaporizing is carried out at substantially atmospheric pressure, a liquid depth of 1 foot above the heat transmission surface results in a loss in mean temperature differential of 31° F., or more than 6 times the temperature differential loss at the elevated pressure level.

The disadvantages or limitations attendant in lower pressure operations can be circumvented, at least in part, by a special technique which avoids the necessity for a pool of boiling liquid. Instead, a moving film of the boiling liquid is passed over the heat transfer surface, the film being of the order of about $\frac{3}{32}$ or $\frac{1}{16}$ of an inch in thickness or less. Suitable apparatus for implementing this embodiment is shown in Figure 2.

Figure 2 is a segmental sectional view of a portion of a typical vaporizer for providing vaporization from a thin film of liquid. In this instance, a heat transfer tube **41** is mounted in a tube sheet **42**. The upper end **43** of the heat transfer tube **41** projects above the tube sheet **42**, preferably having a sharp edge **44** forming a weir for retention of liquid amalgam **45** on the tube sheet. The space **46** defined by the underside of the tube sheet **42** and the outside wall of the heat transfer tube **41** is the condensing chamber for compressed mercury vapor.

In operation, fresh amalgam feed is passed to the pool **45** on the tube sheet **42**, and generally is heated to near

its boiling point while supported thereon. The liquid then overflows the weir 44 into the interior of the heat transfer tube 41, as a thin film 47. In flowing down the tube wall, the desired amount of mercury is vaporized from the amalgam and is discharged overhead as a moving vapor. The liquid, sodium enriched, fraction collects in an appropriate collector, upstream at the bottom of the vaporizer. Further heat can be recuperated as described in preceding examples.

It is apparent that the procedure or techniques discussed above will avoid any limitations otherwise arising because of the disadvantageous effect of a substantial liquid depth above the heat transfer surface. Hence, this mode of operation will be particularly beneficial in low pressure operation and also in multi-stage operations.

In starting up installations of the process, the vaporizer body or bodies are charged with the appropriate amount of amalgam and it is brought up to boiling temperature by heating with the immersion heater such as the immersion heater indicated in Figure 1. During continuous operation, the immersion heater is employed as necessary to provide the appropriate heat balance.

Having fully described the process of the invention and the manner of its operation, what is desired to be claimed is:

1. The process of resolving a sodium amalgam comprising feeding a dilute amalgam to a boiling, sodium enriched amalgam in a boiling zone, the boiling amalgam being heated by indirect heat exchange with a condensing mercury rich vapor, boiling an enriched mercury vapor from said boiling liquid, compressing said vapor and returning said compressed vapor for indirect heat relationship and condensing adjacent the boiling liquid.

2. The process of claim 1 further defined in that the boiling is conducted at a pressure of at least about 100 pounds per square inch absolute.

3. The process of claim 2 further defined in that the boiling, sodium enriched amalgam contains from about 3 to about 5 weight percent sodium.

4. The process of claim 1 further defined in that the boiling, sodium enriched amalgam contains up to about 15 weight percent sodium.

5. The process of resolving a sodium amalgam into a sodium enriched liquid and a mercury rich liquid comprising passing a film of said amalgam in out-of-contact heat exchange relationship with a condensing mercury rich vapor, and vaporizing a mercury rich vapor from said film of amalgam, then compressing said mercury enriched vapor and returning the compressed vapor for out-of-contact condensation heat exchange with the film of amalgam.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,833,644

May 6, 1958

Julian M. Avery

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 60, Example III, for "587 F." read -- 58° F. --; column 5, line 68, for "multiple-stake" read -- multiple-stage --; column 5, for "condensing" read -- condensation --.

Signed and sealed this 22nd day of July 1958.

(SEAL)

Attest:

KARL H. AXLINE

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Commissioner of Patents