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FUSED BATH ELECTROLYTIC PROCESS OF PRODUCING ALKALI METAL VAPOR

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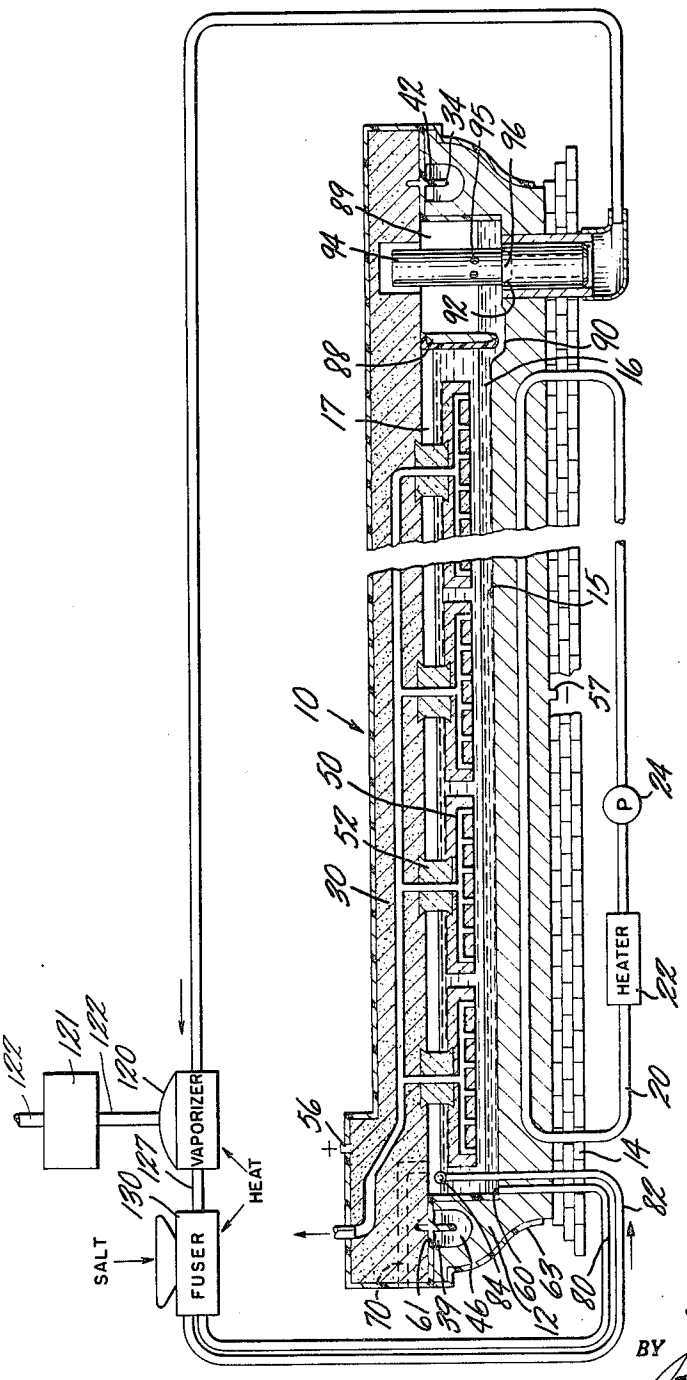


FIG. 1.

INVENTOR.
JOSHUA SZECHTMAN
BY Riggs T. Stewart
ATTORNEY

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FUSED BATH ELECTROLYTIC PROCESS OF PRODUCING ALKALI METAL VAPOR

Joshua Szechtman, Byram, Conn., assignor to Chlormetals Incorporated, New York, N.Y., a corporation of Delaware

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This application is a continuation-in-part of application Serial No. 699,979, filed December 2, 1957, now U.S. Patent No. 3,104,213, and application Serial No. 22,160, filed April 14, 1960, now abandoned.

This invention relates to the production of alkali metal vapors and is more particularly concerned with the production of alkali metal vapors at low cost through the direct electrolysis of alkali metal salts.

Alkali metal vapors are very useful industrially for various purposes. For example, sodium vapor has been extensively employed in chemical processing, e.g. in metallurgy. In addition, alkali metal vapors, such as sodium vapor, are used for the formation of numerous compounds by reaction with various organic and inorganic substances. However, the production of alkali metal vapors, e.g. metallic sodium vapor or metallic potassium vapor, has presented a substantial problem and has involved high costs in that the alkali metal must first be produced in metallic form and then it must be raised to a sufficiently high temperature to vaporize it. In the production of sodium vapor, it has heretofore been necessary first to produce the metallic sodium by one of the conventional methods, such as from sodium chloride in a Downs type electrolytic cell, or from sodium hydroxide by the Castner process, and in all of the existing processes the sodium is collected in its fused or solid state. Then it has been necessary to vaporize the sodium. In the production of potassium vapor, it has heretofore been necessary first to produce the metallic potassium by even more elaborate and costly processes, generally requiring the fusing of potassium chloride and the release of the potassium metal by the substitution of fused sodium metal, inasmuch as it has been impossible to electrolyze fused potassium chloride in an electrolytic cell of the Downs type because of the explosive reaction which would result from contact of the released potassium with the graphite anodes in the presence of air. However, in all of the existing processes the potassium is collected in its fused or solid state, and, as in the case of metallic sodium, it has then been necessary to vaporize the metallic potassium.

There is, therefore, an important need for a process which can effectively produce alkali metal vapors from readily available alkali metal salts directly in vapor form.

It is accordingly an object of the present invention to provide a process for producing alkali metal vapors which avoids the drawbacks and disadvantages of processes heretofore employed.

It is a further object of the invention to provide a process of the character indicated by means of which alkali metal vapors can be produced without first producing the free alkali metal followed by the total vaporization of liquid or solid alkali metal.

In accordance with the invention, a readily available alkali metal salt in molten form, e.g. molten potassium chloride, is electrolyzed in the presence of a molten stream of lead flowing below the anode or anodes of an electrolytic cell, whereby the liberated alkali metal, e.g. potassium, passes downward and away from the anode, and combines with the lead to form a lead alloy. The lead alloy is then removed from the electrolysis zone at the high temperature prevailing in that zone and is passed into a vaporizing zone where the alloy is further heated

a relatively slight amount to effect vaporization of the alkali metal, e.g. potassium. Such vaporization of the alkali metal from the molten lead may also be effected by creating a partial vacuum in the vaporizing zone. The alkali metal vapor may then be conducted directly to other areas for immediate use as required.

It is a feature of the invention that an alkali metal vapor can be produced directly from a readily available alkali metal salt without the need of producing an intermediate solid metal from which the vapor is eventually produced.

It is a further feature of the invention that substantially pure alkali metal vapors can be produced directly from a readily available alkali metal salt without the need for separating contaminants and without the need for complex primary processing of the alkali metal salts to form an intermediate compound from which the alkali metal is eventually produced.

It is another feature of the invention that substantially pure alkali metal vapors can be produced in substantially quantitative yields from the alkali metal salt.

Other objects and features of the invention will be readily apparent from the following detailed description of illustrative embodiments thereof and from the accompanying drawing wherein,

FIG. 1 is an elevational view, partly in section, of an apparatus system particularly suitable for carrying out the process of the invention.

Referring to the drawing, there is illustrated an electrolytic cell designated generally by the reference numeral 10. It will be understood, however, that the invention is not limited to any specific cell construction and that any cell capable of producing an alloy of the alkali metal desired upon electrolysis of the corresponding salt may be employed. For example, there may suitably be used the cell described in my co-pending application Serial No. 699,979, filed December 2, 1957, now U.S. Patent No. 3,104,213, dated September 17, 1963. Such a cell is particularly effective for use in accordance with this invention since it produces a high quality lead-alkali metal alloy from which a substantially pure alkali metal vapor can be directly produced. Also particularly suitable for use in connection with this invention is the improved cell 10 shown in the accompanying drawing which embodies all of the advantages of the cell of my said patent and, in addition, has further advantageous features. The cell body 12 of the cell 10 is suitably formed from metal, and is supported upon an insulating support 14, indicated in the drawing as refractory blocks or bricks, but it will be understood that any other convenient insulating base may be employed. As seen in FIG. 1, the cell 10 defines a sole surface 15 upon which the liquid cathode 16, e.g. molten lead, is adapted to rest and to flow from left to right. Thus, the elongated cell body 12 is formed with an elongated channel of which the sole 15 is the bottom and which provides the electrolysis chamber 17. The sole 15 may be horizontal or it may slope slightly toward the right. The slope of the sole may vary but a slope of 1° or less is preferred.

When the cell is operated at elevated temperatures for the electrolysis of molten salt, the molten salt and the liquid lead cathode are introduced into the cell at temperatures of about 810 to 830 C., in the case of the electrolysis of molten sodium chloride, and the temperature prevailing in the electrolysis chamber is about 850°. These temperatures will, of course, vary in the case of other alkali metal salts, depending upon the melting point of the salt and the boiling point of the alkali metal. Potassium chloride has a melting point of about 776° C. but the boiling point of potassium is about 760° C. Consequently the melting point of the potassium salt is suitably lowered, e.g. to about 720° C. or below by add-

ing to it suitable quantities of another salt, such as calcium chloride, and those amounts that do decompose are not absorbed by the lead. The amount of the added salt to be used will, of course, depend on the temperature to which the melting point is to be lowered and can be readily determined by routine test in each case.

Any convenient means for heating the cell body and maintaining it at the elevated temperature desired may be employed. Particularly effective is the heating means shown in the drawing wherein the cell body is formed with a plurality of longitudinally-extending conduits 20 (one shown) which form a closed circuit with a heater 22 and a pump 24. These conduits are suitably filled with molten lead which is maintained at the desired temperature by the heater 22 and is then circulated through the cell body by means of the pump 24. Actually, the electrolysis reaction is exothermic but the heating means is provided in order to bring the cell to operating temperature when operation is begun and to minimize heat loss during operation so that the desired operating temperature is always maintained.

Closing the cell is a cover 30 which extends completely across the cell body 12 and also extends from one end of the cell body to the other. This cover is formed from an electrically-conductive material and, most suitably, it is formed from graphite. As seen in the drawing, the cell body 12 is formed with a circumferentially-extending channel 34 which extends continuously around the side and end walls of the body 12. Channel 34 is adapted to be filled with a fluid which is liquid at cell-operating temperatures and, most advantageously, this fluid is lead and the channel 34 communicates by means of suitable conduits (not shown) with the circuit which includes the conduits 20, the heater 22 and the pump 24. Depending from cover 30 into the channel 34 is a circumferential flange 42 which is embedded in the cover 30 and which extends downwardly a sufficient distance that its lower end will be immersed in the liquid 46 contained in the channel 34 in order to form a hydraulic seal. The flange 42 is suitably formed from a material which is a non-conductor of electricity.

The cover 30 directly supports the anodes 50 and such support is effected by means of anode stems 52. While in my Patent No. 3,104,213 I show a conduit communicating with the electrolysis chamber for the removal of chlorine generated in the cell during electrolysis, provision may be made for withdrawing chlorine from the cell through the anodes and through the cover. Thus, as seen in the drawing, the stems 52 are received in slots formed in the cover 30 and in the blocks 50 so that these parts are removably interconnected, or the stems may be removably connected only with the cover or only with the anodes, or all parts may be integrally interconnected. The anode blocks, the anode stems or supports, and the cover are provided with inter-communicating apertures and channels or passageways through which evolved gas is led from the site of evolution to a point exteriorly of the cell with minimum contact with contaminating surfaces.

The power connections are indicated diagrammatically at 56 and 57, but it will be understood that any conventional means may be employed to attach the power conductors, and a particularly suitable system is shown in my Patent No. 3,104,213. Similarly, the cover is suitably electrically insulated from the body of the cell and, since it is a conductor of electrolysis current, it is advantageously covered with electrical insulation, as shown in the drawing. In addition, an insulating lining 60 is provided along the interior walls of the cell in the electrolysis chamber 17, and an insulating sheet 61 completely overlies the top edges of the wall of the cell body 12, being interrupted only by the flange 42. An auxiliary outlet channel 70, which may be stoppered to prevent ingress of air, is provided in cover 30 to permit venting of the electrolysis chamber above the level of the electrolyte.

The manner in which the electrolyte and the liquid cathode are introduced into and removed from the cell form no part of the present invention but the manner described in my Patent No. 3,104,213 is particularly suitable especially since it insures against entrance of air or oxygen with the electrolyte and the cathode into the electrolysis chamber. Thus, as seen in the drawing, the liquid cathode, e.g. molten lead, and the electrolyte, e.g. molten alkali metal chloride, are introduced at the left-hand end of the cell body, the molten lead being introduced through a conduit 80 and the molten salt suitably being introduced through a conduit 82. The conduit 82 extends upwardly into the electrolysis chamber 17 and discharges through a self-regulating float valve, indicated diagrammatically at 84, and suitably of the type described in FIG. 5 of my Patent No. 3,104,213. At the right-hand end of the cell body 10, there is provided a transverse wall 88 extending between the side walls of the cell body and engaged by the cover 30 to define the downstream end of the electrolysis chamber proper and to define an end compartment 89. The cell bottom slopes downwardly in the vicinity of the transverse wall 88 in order to form a well 90 into which the wall can extend to form a liquid seal against passage of the lighter electrolyte into the end compartment as long as the liquid level of the cathode is maintained.

The end compartment 89 is formed with an outlet opening 92. A tall cylindrical sleeve 94 is provided with apertures 95 and with a nose 96 normally disposed in outlet opening 92, the cathode level being maintained by the apertures 95 through which the alloy formed in the cell is discharged. The upper end of the sleeve 94 extends into a recess in cover 30 and it may be lifted, e.g. by electro-magnetic means, to permit emptying of the cathode from the cell, as described in my Patent 3,104,213. Suitable electrical insulation (not shown) prevents contact between sleeve 94 and cover 30.

From the cell outlet, the lead-alkali metal alloy is conducted in molten form to a vaporizer 120, which may be of any desired form but is suitably a simple distillation unit conveniently heated by means of gas, oil or the like, in conventional manner. As indicated previously, vaporization of sodium or other alkali metal may be effected without further application of heat to the molten alloy by reducing the pressure in the vaporizer 120. This is suitably effected by connecting the vaporizer to any conventional vacuum source. An entrainment eliminator 121, e.g. a separator containing baffles or a cyclone-type separator, is advantageously associated with the vaporizer to remove any trace of particles of lead which may be mechanically entrained when the alkali metal is vaporized from the alloy. The alloy arriving at the vaporizer is already at an elevated temperature, i.e. at about 850° C. in the case of a sodium-lead alloy, and only a slight additional amount of heat needs to be added to effect the desired vaporization, i.e. to raise it to a temperature of about 890° C. in vaporization at atmospheric pressure, for example. In the case of a lead-potassium alloy, the alloy will come from the cell at a temperature in the neighborhood of 720° C. and it will have to be heated only to about 760° C. to bring about the desired vaporization of potassium at atmospheric pressure. The alkali metal vapors enter the vapor conduit 122 and may be conducted to a further operation employing alkali metal vapors.

It is not, of course, necessary to vaporize all of the alkali metal from the alloy and, indeed, it is not desired to do so, but it is readily possible to vaporize at least about 25% of the alkali metal content of the alloy and, preferably, not more than about 50% of the alkali metal content. After the cathode stream has passed through the vaporizer and has had a large proportion of its alkali metal content vaporized away, it is suitably conveyed through the conduit 127 to the fuser 130 wherein the salt to be electrolyzed is liquefied so that it will flow into the

cell. The fuser is suitably heated by any convenient heating means, e.g. gas or electricity, and the molten lead further assists, by heat transfer, in the melting of the salt in the fuser through which conduit **127** passes as it merges with the conduit **80** which leads from the lower portion of the fuser.

The fuser can be a simple kettle heated by gas or other means, as mentioned, into which the alkali metal salt is charged at the top and from the lower portion of which the molten salt is withdrawn. Thus the molten salt passes into conduit **82** substantially free from air and moisture. The molten lead is similarly substantially free from air and moisture.

Electrolysis is also carried out in the absence of air and moisture, sufficient current being supplied to effect the desired electrolysis reaction.

The alloy subjected to vaporization may have any desired content of alkali, and alkali metals such as sodium and potassium form alloys with lead of a wide range of proportions, but preferably the alkali metal content is at least about 10% and such an alloy can be readily produced by the process of my Patent No. 3,104,213 and by the process described below.

In a typical operation in accordance with this invention, molten sodium chloride at 820° C. is supplied to the electrolysis chamber at the rate of 12 pounds per minute and the lead cathode at the same temperature is introduced at the rate of 45 pounds per minute. Electrolysis is carried out with D.C. current of 150,000 amperes at 4.5 volts and sodium combines with the lead cathode at the rate of 4.5 pounds per minute to form an alloy containing about 10% sodium by weight. This alloy having a temperature of about 850° C. is withdrawn from the cell at the rate of 49.5 pounds per minute and is heated in the vaporizer to a temperature of 890° C. to form sodium vapor at the rate of about 2.25 pounds per minute by evaporating about 50% of the sodium content from the lead to leave an alloy containing about 5% sodium for return to the cell.

Similarly, corresponding conditions and quantities are employed in converting molten potassium chloride into a lead-potassium alloy. In the case of the making of a potassium alloy, the temperature in the electrolysis zone is of the order of 720° C. and the alloy leaves the cell at about this temperature and, as previously mentioned, it will have to be heated only to about 760° C. to bring about the desired vaporization at atmospheric pressure.

As previously indicated, lead-alloys of varying alkali metal content may be employed but generally they will have an alkali metal content of about 10 to 50% by weight of the total alloy for best results. The content of the alloy can be regulated by the current applied in the cell. Thus, a lesser current will produce a lower alkali metal content and a greater current will produce an increased alkali metal content. Such variation in currents will be readily understood by persons skilled in the art.

It will also be understood that various changes and modifications in addition to those indicated above may be made in the embodiments herein described and shown in the drawing without departing from the scope of the invention as defined in the appended claims. It is intended, therefore, that all matter contained in the foregoing description and in the drawing shall be interpreted as illustrative only and not as limitative of the invention.

I claim:

1. The process of producing a vapor of metallic alkali metal which comprises melting alkali metal salt in a salt-fusing zone to provide a body of fused alkali metal salt, introducing a stream of said fused alkali metal salt and a stream of fused lead into one end of a horizontal air-free and air-tight electrolysis zone, said stream of fused lead being introduced along the bottom of said electrolysis zone and said stream of fused alkali metal being introduced at a level spaced upwardly from said bottom to maintain a pool of said fused salt in said electrolysis zone at said level, said stream of salt and said stream of lead being introduced under air-free and moisture-free conditions, electrolyzing said fused alkali metal salt in the presence of said fused lead by causing said fused salt and fused lead to flow through said horizontal electrolysis zone from said end of said electrolysis zone while said lead is electrically connected with the negative side of an electrolytic current, the heavy fused lead flowing along the bottom of the electrolysis chamber and serving as the cathode, with the lighter fused alkali metal salt floating on top of the lead and serving as the electrolyte, whereby to form a molten alkali metal-lead alloy from said fused lead, withdrawing the molten alloy from the other end of said electrolysis zone and introducing said molten alloy into a vaporization zone, evaporating the alkali metal from the lead alloy as a vapor of metallic alkali metal in said vaporization zone to remove at most about 50% of the alkali metal from said alloy, recovering the portion of the molten alloy remaining after vaporization of said alkali metal while in heated condition, passing said portion of molten alloy through said salt-fusing zone to utilize the heat thereof to fuse said salt, and returning said portion to said one end of said electrolysis zone along the bottom thereof to form said cathode.

2. A process as defined in claim 1, wherein said alkali metal salt is a sodium salt.

3. The process of producing a vapor of metallic alkali metal which comprises melting alkali metal salt in a salt-fusing zone to provide a body of fused alkali metal salt, introducing a stream of said fused alkali metal salt and a stream of fused lead into one end of a horizontal air-free and air-tight electrolysis zone, said stream of fused lead being introduced along the bottom of said electrolysis zone and said stream of fused alkali metal being introduced at a level spaced upwardly from said bottom to maintain a pool of said fused salt in said electrolysis zone at said level, said stream of salt and said stream of lead being introduced under air-free and moisture-free conditions, electrolyzing said fused alkali metal salt in the presence of said fused lead by causing said fused salt and fused lead to flow through said horizontal electrolysis zone from said end of said electrolysis zone while said lead is electrically connected with the negative side of an electrolytic current, the heavy fused lead flowing along the bottom of the electrolysis chamber and serving as the cathode, with the lighter fused alkali metal salt floating on top of the lead and serving as the electrolyte, whereby to form a molten alkali metal-lead alloy from said fused lead, withdrawing the molten alloy from the other end of said electrolysis zone and introducing said molten alloy into a vaporization zone, heating said alloy in said vaporization zone to evaporate the alkali metal from the lead alloy as a vapor of metallic alkali metal in said vaporization zone to remove at most about 50% of the alkali metal from said alloy, recovering the portion of the molten alloy remaining after vaporization of said alkali metal while in heated condition, passing said portion of molten alloy through said salt-fusing zone to utilize the heat thereof to fuse said salt, and returning said portion to said one end of said electrolysis zone along the bottom thereof to form said cathode.

4. The process of producing a vapor of metallic alkali metal which comprises melting alkali metal salt in a salt-fusing zone to provide a body of fused alkali metal salt, introducing a stream of said fused alkali metal salt and a stream of fused lead into one end of a horizontal air-free and air-tight electrolysis zone, said stream of fused lead being introduced along the bottom of said electrolysis zone and said stream of fused alkali metal salt being introduced at a level spaced upwardly from said bottom to maintain a pool of said fused salt in said electrolysis zone at said level, said stream of salt and said stream of lead being introduced under air-free and moisture-free conditions, electrolyzing said fused alkali metal salt in the presence of said fused lead by causing said fused salt and fused lead to flow through said horizontal electrolysis

zone from said end of said electrolysis zone while said lead is electrically connected with the negative side of an electrolytic current, the heavy fused lead flowing along the bottom of the electrolysis chamber and serving as the cathode, with the lighter fused alkali metal salt floating on top of the lead and serving as the electrolyte, whereby to form a molten alkali metal-lead alloy from said fused lead, withdrawing the molten alloy from the other end of said electrolysis zone and introducing said molten alloy into a vaporization zone, reducing the pressure in said vaporization zone to cause evaporation of the alkali metal from the molten lead alloy as a vapor of metallic alkali metal in said vaporization zone to remove at most about 50% of the alkali metal from said alloy, recovering the portion of the molten alloy remaining after vaporization of said alkali metal while in heated condition, passing said portion of molten alloy through said salt-fusing zone to utilize the heat thereof to fuse said salt, and returning said portion to said one end of said electrolysis zone to form said cathode.

5. Apparatus for producing a vapor of metallic alkali metal which comprises means defining a salt-fusing chamber for melting alkali metal salt to provide a body of fused alkali metal salt, means defining a horizontal air-free and air-tight electrolysis chamber, first conduit means for introducing a stream of said fused alkali metal salt from said salt-fusing chamber into said electrolysis chamber and second conduit means for introducing a stream of fused lead into one end of said electrolysis chamber, said second conduit means being connected to supply said stream of fused lead along the bottom of said electrolysis zone and said first conduit means being connected to supply said stream of fused alkali metal salt at a level spaced upwardly from said bottom to maintain a pool of said fused salt in said electrolysis chamber at said level, said conduits being effective to introduce said stream of salt and said stream of lead under air-free and moisture-free conditions, means for supplying electrolytic current to said electrolysis chamber to electrolyze said fused alkali metal salt in the presence of said fused lead while said lead is electrically connected with the negative side of an electrolytic current, the heavy fused lead flowing along the bottom of the electrolysis chamber and serving as the cathode, with the lighter fused alkali metal salt floating on top of the lead and serving as the electrolyte, means for withdrawing the molten alloy formed in said electrolysis chamber from the other end of said electrolysis chamber, means defining a vaporization chamber, means for introducing said molten alloy into said vaporization chamber, means for passing the molten alloy from said salt-fusing chamber to utilize the heat thereof to fuse said salt, and means for introducing said alloy into said second conduit means for returning said alloy to said one end of said electrolysis chamber to form said cathode.

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