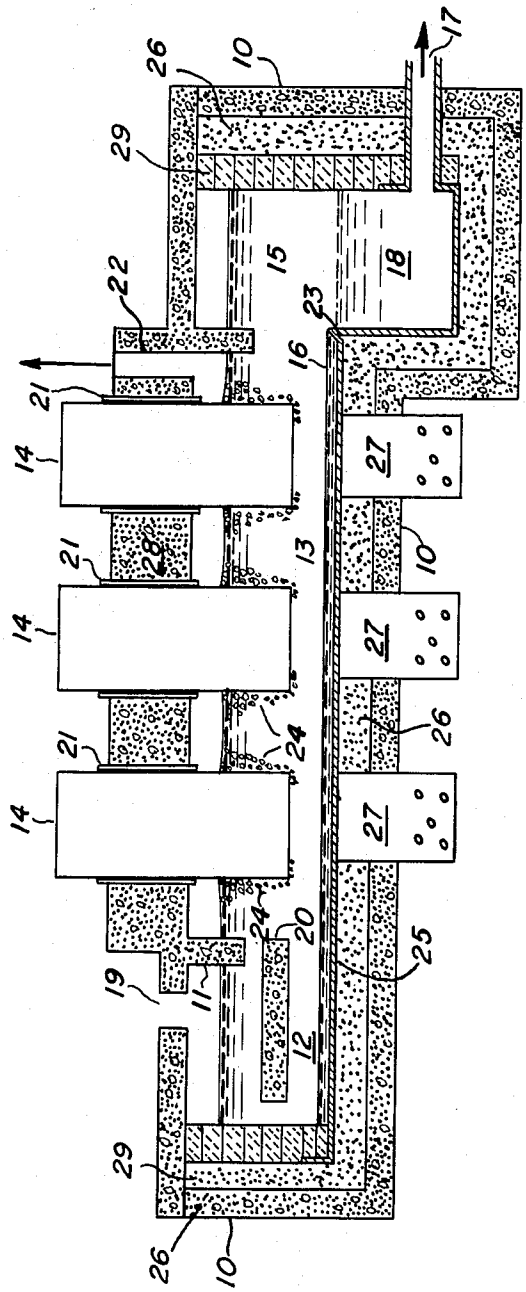
April 17, 1956 F. L. PADGITT 2,742,418

ELECTROLYTIC CELL FOR ALKALI-LEAD ALLOY MANUFACTURE

Filed Aug. 28, 1952



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United States Patent Office 2,742,418 Patented Apr. 17, 1956

2,742,418

ELECTROLYTIC CELL FOR ALKALI-LEAD ALLOY MANUFACTURE

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Application August 28, 1952, Serial No. 306,757

1 Claim. (Cl. 204—247)

This invention relates to the preparation of the alloys of alkali metals and lead. More particularly, the invention relates to the manufacture of lead-alkali metal alloys by the electrolysis of fluid alkali metal halides and the deposition and alloying of the alkali metal with a fused lead which functions as a cathodic receiver.

The alkali metal alloys of lead are significant commercial materials, the sodium-lead alloys being extensively used, for example, in the manufacture of the tetraalkyllead compounds. More specifically, tetraethyllead, a highly effective antidetonant, is produced from the interreaction of monosodium-lead alloy and an ethyl halide, ethyl chloride being commonly used.

In the preparation of alkali metal-lead alloys, such as the above mentioned sodium-lead alloy, it has heretofore been considered necessary to mix together, batchwise, separate portions of pure sodium and pure lead to the desired proportions. Although basically a simple operation, in practice on commercial scale, this manufacture becomes relatively complex. Thus, for example, Fisher et al. 2,276,031 patent points out that the heat of alloying is a very important matter with respect to thermal srains induced in the manufacturing pots. In order to avoid such hazards to steady operation, Fisher provides a sequence of addition of sodium and lead, whereby a heat absorbing capacity is provided by a portion of the metal feeds themselves, to prevent undue temperature rises. The Fisher method is intended for batchwise processing. As an illustration of the relative overall complexity in these alloy manufacturing methods, Amick et al., in Patents 2,043,224 and 2,091,801, disclose the apparatus and overall procedure for a manufacturing operation wherein the Fisher mixing technique is suitable.

As heretofore mentioned, it has been the commercial practice to employ commercially pure alkali metal and lead for the preparation of such alloys. This presents a surprising situation in the manufacture of tetraalkyllead compounds, inasmuch as the end product mixture from such operations includes not only excess metallic lead but also alkali metal compounds corresponding generally in quantity to the alkali metal content of the alloy used in the reaction. Illustrative of this condition is the following equation for the manufacture of tetraethyllead:

$$\underset{\text{Monosodium lead alloy}}{4NaPb} + \underset{\text{Ethyl chloride}}{4C_2H_5Cl} \longrightarrow \underset{\text{Tetraethyl-lead}}{Pb(C_2H_5)_4} + \underset{\text{Sodium chloride}}{4NaCl} + \underset{\text{lead}}{3Pb}$$

It will be seen that, when the tetraethyllead is removed from the product mixture, the residue already contains the sodium value and a large portion of the lead needed to supply the ethylation step. Despite the thus available presence of metal values in the reaction product mixture, it has been the general practice to recover only the metallic lead component of such a reaction mixture. This has been done by leaching out the bulk of the sodium chloride present, which is ditched, and drying the water insoluble components. This dried residue includes substantially all the available metallic lead plus minor quantities of lead compounds (e. g., lead chloride and lead oxide). A

furnacing operation serves to melt the lead content of this residue, the leading being pigged and returned to the conventional alloy making process. It will be seen that although no sodium metal appears in the end product, yet approximately four atoms is irretrievably consumed in producing one mole of the desired tetraalkyllead. The reason for not attempting recovery of the alkali metal values heretofore has been that no economically feasible method was available for the joint recovery of lead and alkali metal values when the latter was in the form of an alkali metal halide.

The object of my invention, generally, is to provide a new and improved process for the production of alkali metal alloys of lead. Another object is to provide a continuous method of producing alkali metal alloys of lead in the molten form and in a purity and composition suitable for direct usage in the manufacture of tetraalkyllead compounds if desired.

A more specific object of my invention, in its preferred embodiments, is to provide apparatus and a process for concurrently and jointly recovering the lead and alkali metal values of a tetraalkyllead-free product mixture and also alloying the so-formed metals into a directly usable alloy. A further object is to provide a process and apparatus for the concurrent recovery of sodium and lead values from a reaction mass which is relatively free of tetraethyllead, and also alloying sodium and lead to provide an alloy of the desired composition for manufacture of tetraethyllead. A further object is to provide such a recovery-electrolysis-alloying process as utilizes the heat of formation of the alloy proper and the fluid forces developed in an electrolysis zone to mutually aid the respective functions cited. A further object is to provide apparatus and a process for minimizing the consumption of alkali metal halide in the manufacture of tetraalkyllead compounds.

The method of carrying out the process will be fully apparent from the description given hereafter and from the accompanying figure, the figure being a cross sectional elevation view of the apparatus for the process.

Generally, the process comprises feeding an alkali metal chloride, or chlorides, to a pretreating zone. Concurrently a supply of lead metal is fed to the pretreating zone, and there is established therein a lower layer of molten lead metal and a surmounting layer of fused metal chlorides including the alkali chloride feed. These layers are passed to an adjacent connected electrolysis zone wherein the alkali chloride is electrolyzed and the alkali metal is deposited in the lead layer forming an alloy therewith. Chlorine, generated by the electrolysis, is separately withdrawn from the lead alloy product is also withdrawn from the electrolysis zone.

In the preferred forms of my process, as will be amplified hereafter, the electrolyte is continuously circulated from the electrolysis zone to the pretreating zone and functions therein as a solvent for dissolving the alkali chloride feed and for facilitating the formation of the molten lead layer. Such circulation is accomplished by utilizing the hydraulic forces generated in the electrolysis zone or by an external propulsion means, or both, when desired.

To further illustrate the operation of the process, reference is made to the figure. The description following is given with reference to production of a sodium-lead alloy, the sodium being obtained from sodium chloride, but it will be understood that the other alkali metals can be thus formed and alloyed with lead. Referring to the figure, a generally rectangular space is compartmentalized by an inverted weir **11** into a pretreating zone **12** and an electrolysis zone **13**. A plurality of anodes **14** are suspended by means not shown above the electrolysis compartment **13**, and project through the top of the roof

or cover **28** into the contents of the electrolysis zone.

The contents of the electrolysis zone **13** includes, as above mentioned, an electrolyte **15** comprising a molten layer of fused salt floating on a molten metal layer **16**. The molten metal layer, in the pretreating zone **12**, is predominantly lead metal, and varies in composition through the electrolysis zone **13** wherein it receives the alkali metal formed by electrolysis. In operation, the lead layer moves continuously or intermittently from the pretreating zone **12** through the electrolysis zone **13** and thence to a discharge port **17**. A collection sump **18** is usually provided for the sodium-lead alloy.

The pretreating or feed compartment **12** is provided with a charging port **19** in the top thereof for admission of the feed materials. A partitioning wall **20** may be provided in the pretreatment zone **12**, said wall being either horizontal or inclined downwardly away from the separating weir **11**. A steel plate shell **25** provides the bottom of the pretreating zone **12** and the electrolysis zone **13**. The walls of these zones comprise refractory brick layers **29**. The next layer **26** outward of these inner surfaces is preferably insulating material such as expanded mica. Lastly, the outermost layer **10** is formed of insulating refractory concrete. Steel lugs **27**, welded to the shell or bottom plate **25** provide means for electrical current flow to the molten lead-alloy cathode **16**.

In operation, the sodium chloride and lead are introduced through the charging port **19**. In some embodiments it will be found desirable to introduce at least part of the lead in the molten state. For example, when the process is used in conjunction with the manufacture of a tetraalkyllead, a make-up supply of molten lead metal may be fed to the pretreating zone in conjunction with the reaction residue comprising an intimate mixture of finely divided lead and finely divided sodium chloride. Concurrently with such feed, a stream of fused electrolyte passes into the pretreating chamber from the electrolysis chamber **15** by flowing under the separatory weir **11**. In the pretreating chamber, the fused electrolyte is blended with the fused sodium chloride feed, and at the same time the lead metal descends and augments the layer of lead **16** at the bottom. Owing to feed of lead in the pretreating compartment and withdrawal of alloy from the electrolysis zone by overflow over the lip or weir **23**, a continuous flow of lead occurs through the apparatus, the lead picking up the sodium generated by the electrolytic decomposition occurring in the electrolysis zone and forming alloy of the desired composition.

The anodes **14** projecting through the shell roof **28** are sealed by gaskets or packing **21**. The anodes, constructed of impervious graphite, are situated in a vertical disposition such as not to make direct contact with the lead-sodium alloy, but approach within several inches of this liquid level.

The electrolysis process is of course accompanied by the evolution of gaseous chlorine. The rise of this gaseous product **24** adjacent the anodes results in vigorous mixing of the electrolyte components and also in the establishment of a slightly higher liquid level in the electrolysis zone. This hydraulic action of the electrolysis step is used to great advantage in that it provides the impelling force, at least in part, for circulation of the electrolyte to and from the electrolysis zone. Accordingly, the fused electrolyte, owing to the lifting action of the chlorine adjacent the anodes, causes the electrolyte, or bath, to flow under the weir **11** to the pretreating zone **12**. The bath is circulated back to the electrolysis zone **13** from the pretreating zone by the above described action within the apparatus. As the pretreating treatment includes a solution or blending of fresh alkali chloride in the electrolyte, this circulation provides a continuous replenishment of the concentration of alkali chloride in the electrolyte in the electrolysis zone.

Example

To illustrate generally the manner of carrying out the process, the following describes the preparation of a ternary alloy of potassium, sodium and lead. The apparatus shown in the figure was used in this operation, except that the pretreating zone **12** did not have a horizontal partitioning wall **20**.

A molten lead layer was first established in the apparatus by pouring in molten lead, the amount being fixed by the height of the overflow or discharge weir **23**, which provided a depth of about several inches of molten metal. A surmounting layer of fused chloride electrolyte was then provided, by introducing solid metal halides into the pretreating zone **12** and melting therein. The electrolyte so provided contained about 50 weight per cent sodium chloride, 40 per cent potassium chloride and minor amounts of sodium fluoride.

Electrolysis was then started by supplying direct current to the electrolysis section. The initial voltage applied to the cell was about 10 volts, but normally a cell voltage of about 7 volts is fully adequate to obtain good electrolysis, this voltage including the voltage drop at the contacts of the electrical supply line with the anodes and the cathode lead layer.

During an extended operation, the temperature of the cell interior was maintained at about 1250° F. Operation proceeded smoothly and the alloy product removed from the collecting sump **18** consisted of a ternary alloy containing approximately 89 per cent lead, and 11 per cent alkali metal, the alkali metal consisting of about 90 per cent sodium and 10 per cent potassium.

Chlorine evolved during the electrolysis was collected at the top of the electrolyzing zone **13** and removed through the discharge port **22** under a slight vacuum.

The feed streams to the apparatus consisted of periodic additions of molten lead and a solid mixture of sodium chloride and potassium chloride in the proportions of about 9 parts of sodium chloride to 1 part of potassium chloride. The current efficiency was about 79–80 per cent.

The embodiment of the foregoing example has peculiar and significant utility in conjunction with the manufacture of tetraalkyllead compounds. In particular, it has recently been discovered that a ternary alloy of lead, sodium and potassium when ethylated at an elevated temperature, in the presence of a lead alkylating catalyst, provides substantially higher yields than heretofore obtained. Further, it has been found that such increase in yield is accompanied by a substantial repression of gaseous by-product. As such by-products are evidently derived from the dehydrochlorination of ethyl chloride by the action of alkali metals, repression of by-product formation results in an increase in economy of utilization of ethyl chloride as well as of the metal values.

The product mixture, derived from the above described ethylation of the lead of such a lead-sodium-potassium alloy includes tetraethyllead, unreacted lead, excess ethyl chloride, and sodium chloride and potassium chloride. After removal of the tetraethyllead and ethyl chloride components of such a reaction mixture, a typical composition of the residue is approximately 70 per cent lead, 25 per cent sodium chloride, and less than 5 per cent potassium chloride. This mixture forms a suitable feed to the present process. According to the efficiency of the ethylation process and variations of the alloy composition desired, the metals containing residue will have from about 20 to 50 per cent by weight of sodium chloride, 2 to 10 weight per cent potassium chloride and 78 to 40 per cent lead.

It will be seen that the processing of a lead-sodium-chloride-potassium chloride mixture by the present process, in combination with the manufacture of tetraethyllead, affords unusual and significant advantages. Thus, not only is the manufacture of tetraethyllead substantially benefit-

ed, but in addition, the presence of a portion of potassium chloride in the electrolyte bath in the electrolysis operation provides the highly desirable function of providing a lower melting electrolyte bath. Thus, although the melting point of sodium chloride is 1470° F., by the presence of a relatively small amount of potassium chloride, it is possible to electrolyze at a temperature of about 1200°–1250° F. as demonstrated in the foregoing example.

It will be readily apparent that the preparation of a ternary alloy of lead, sodium and potassium is the preferred embodiment of the process, particularly in combination with the manufacture of tetraethyllead. However, the process is by no means confined to such a product. Thus, in some cases it may be desired to obtain solely a binary alloy, of, for example, lead and sodium, lead and potassium, or lead and lithium. In those instances, the feed components and the average electrolyte bath composition are appropriately altered. Thus, if a sodium-lead alloy is desired, for example, a suitable electrolyte would contain small proportions of calcium chloride and sodium fluoride in addition to sodium chloride.

As heretofore indicated, the process is applicable when the lead is intimately mixed with the alkali chloride feed, as, for example, when processing the solid product components from a tetraethyllead process. In such instances, the circulation of fused electroylte to and from the pretreating step is particularly important. The action of the fused electrolyte not only dissolves the alkali chloride components of such intimate mixtures, but also serves as a flux in removing any surface impurities on the lead particles, thereby facilitating the melting together and segregation of the lead content.

A large part of the heat requirements for the pretreating operation is provided by excess heat generated in the electrolysis zone, and made available as sensible heat of the electrolyte. In many cases, however, it will be desirable to provide external heat to the pretreating operation. This is particularly the case when forced circulation of the electrolyte is not provided, reliance being placed solely on the natural currents induced by the electrolysis operation. When desired, heat may be supplied to the pretreating step by immersing submerged combustion burners in the material in the pretreating zone. Such submerged combustion burners are merely conduits for the passage of a burning gaseous fuel and air mixture through the system.

As previously indicated, external means for circulation of the electrolyte may be utilized to augment the natural hydraulic forces generated in the electrolysis zone. Such external means may be, for example, a jet of inert gas flowing in the space below the weir 11 towards the pretreating zone 12. Alternatively, a power driven propeller may be similarly located to induce further flow of the electrolyte to the pretreating chamber.

In addition to the specific description and example above, it is to be understood that the process is capable of numerous additional variations and alternative embodiments, subject only to limitation inherent in the claim below.

I claim:

Apparatus for the electrolysis of fused alkali chloride and the manufacture of an alloy of lead and alkali metal, and for the formation of feed materials therefor, comprising a horizontally disposed elongated cell vessel of refractory, nonconductive material, said vessel including a cover and defining a space for holding electrolyte and alloy and including a feed pretreating zone, an electrolysis zone and an alloy collection zone, the cover having parallel, vertical downwardly extending first and second weirs projecting into the vessel space and below a level corresponding to the level of fused electrolyte during operation, thus establishing said feed preforming zone, said electrolysis zone and said alloy collection zone, the feed pretreating and alloy collection zones being relatively small in proportion to the electrolysis zone, and the alloy collection zone having a bottom below the bottom of the electrolysis zone, the cover further having a feed opening to the pretreating zone, a gaseous halogen discharge opening from the electrolysis zone and anodes projecting through the cover and into the electrolysis space to a level normally within the fused electrolyte, an electrically conductive plate being further provided on the bottom of the vessel, said plate extending horizontally and continuously through the pretreating zone and the electrolysis zone, and including an upwardly projecting weir immediately below the above mentioned second weir and continuing to the bottom of the collection zone, the pretreating zone further having a horizontal partition wall dividing said zone into two spaces, the wall being in a plane normally beneath the surface of fused electrolyte, and extending horizontally from a line below the first weir to a line near the opposite end of the pretreating zone, thus providing a communicating opening from the top space of the pretreating zone to the bottom space thereof, the vessel further having electrical connections through the bottom boundary thereof to the portion of the electrically conductive bottom within the electrolysis zone, and an alloy discharge opening from the alloy collection zone.

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