

[54] **PROCESS FOR THE ELECTROLYTIC REFINING OF POTASSIUM**

[75] Inventors: **Karl Ziegler**, Kaiser-Wilhelm-Platz 1; **Herbert Lehmkuhl**, both of Mulheim/Ruhr, Germany

[73] Assignee: **said Ziegler, by said Lehmkuhl**

[22] Filed: **Jan. 14, 1971**

[21] Appl. No.: **106,593**

[30] **Foreign Application Priority Data**

Jan. 4, 1970 Germany..... P 20 01 409.9

[52] **U.S. Cl.**..... **204/60, 204/59, 204/68**

[51] **Int. Cl.**..... **C22d 1/06, C22d 3/06**

[58] **Field of Search**..... **204/590 M, 68, 59 QM, 204/59 R, 60**

[56] **References Cited**

**UNITED STATES PATENTS**

3,028,322 4/1962 Kobetz et al..... 204/68 X

3,028,323 4/1962 Kobetz et al..... 204/68 X  
3,234,114 2/1966 Ziegler et al..... 204/68

**FOREIGN PATENTS OR APPLICATIONS**

955,252 4/1964 Great Britain ..... 204/59 R

*Primary Examiner*—F. C. Edmundson

*Attorney*—Burgess, Dinklage & Sprung

[57] **ABSTRACT**

A process for refining potassium electrolytically using an organo-aluminium potassium complex compound as electrolyte in which the electrolyte used contains potassium-aluminium tetra-alkyl compounds and the electrolysis is effected at a temperature of not above 70°C. In particular the electrolysis is carried out at a temperature within the range of 64° - 70°C and the melting point of the electrolyte is lowered to this range or below it by the addition of a potassium-aluminum-monoalkoxyalkyl compound or an inert solvent or diluent.

**2 Claims, No Drawings**

## PROCESS FOR THE ELECTROLYTIC REFINING OF POTASSIUM

This invention relates to a process for the electrolytic refining of potassium.

A large number of proposals have been made in the literature for separating sodium cathodically by the procedure of electrolysis, using anode material which contains sodium. It is a common characteristic of all these processes that they work with complex organometallic compounds, more especially organic aluminium complex compounds, in molten form or dissolved in neutral solvents, as electrolytes. A principal use which has been proposed is the recovery of sodium metal from sodium amalgam, the sodium amalgam being obtained in known manner from the electrolysis of aqueous sodium chloride solutions.

For more detailed information, reference is made to the German Pat. Nos. 1,114,330, 1,146,258, 1,168,651, and 1,144,490, which are all concerned with the separation of sodium. There is no reference in these patents to separating out alkali metals other than sodium, and in particular there is also no reference to potassium metal, although potassium amalgam is just as easily accessible from the electrolysis of aqueous potassium chloride solutions as sodium amalgam. There is a good reason for this limitation. The separation of potassium metal from molten or dissolved organopotassium complex compounds, more especially of aluminium, does in fact present such serious difficulties that experimental arrangements and processes which can be utilised for sodium cannot be readily transferred to potassium compounds and potassium metal.

The electrolytes most suitable for the separation of sodium consist either totally or to a high percentage of sodium-aluminium tetraethyl. The capacity for smoothly separating out the sodium metal, and in fact in molten form, from such electrolytes is possible because the electrolyte is completely stable at the electrolysis temperatures (100° - 140°C) with respect to molten sodium-aluminium tetraethyl. Under similar conditions, however, molten potassium is active with respect to potassium-aluminium tetraethyl and the electrolyte slowly becomes decomposed, finely divided aluminium separating out. Consequently the separation of the potassium in a coherent, liquid form in appreciable amounts is made impossible. An electrolytic arrangement which has constantly to supply potassium at the cathode without any disturbance and over a relatively long time period, it is a requirement that the metal is separate out in a layer which coheres satisfactorily, from which layer it is possible at a suitable position either to skim off the liquid potassium or to remove it by way of an overflow.

In a related sphere of the electrolysis of organometallic compounds, namely, with the production of metal alkyls of the type of lead tetraethyl or mercury diethyl, it is true that some positive experience exists concerning the cathodic deposition of potassium metal from complex organo-metallic electrolytes (see German Pat. No. 1,127,900). The electrolysis cells to be employed in these cases are however unsuitable for refining potassium or for forming potassium from potassium amalgam as anode. They either necessitate working under vacuum or the use of a diaphragm, and it was found in connection with testing such an arrangement in practice that also in these cells, where the electrolyte con-

tains only potassium as cation, an effective continuous operation with deposition of potassium in a form suitable for continuous separation causes serious difficulties, even if it is not completely impossible. This has also already been referred to in German Pat. No. 1,127,900, column 3, lines 15-25, where it reads (in translation)

“It (the sodium compound) offers the great advantage that the electrolysis can be so easily organised that metallic sodium in a coherent liquid form separates out on the cathode. The corresponding potassium compounds cause difficulties in the separation, but conduct the current even better than the sodium compounds. Consequently, the best possible electrolytes consist of potassium-aluminium tetraalkyls and sodium alkoxy- or -aroxy aluminium trialkyls.”

It has now been found that a good electrolytic deposition of potassium metal from a molten electrolyte containing only potassium as cation is in fact possible if the temperature is limited to an extraordinarily narrow range, and in fact it is possible successfully to deposit potassium without any difficulty at temperatures up to about 70°C. Disturbances occur at a few degrees above this temperature and these prevent a reasonable deposition of the potassium in a coherent molten layer. Particularly suitable is the temperature range from the melting point of potassium (63.5°C, i.e. practically 64°C) up to 70°C. On account of this very strict limitation of temperature, pure potassium-aluminium tetraethyl is unsuitable as electrolyte for the deposition of potassium, since it melts at 74°C. Consequently, it is necessary to work with potassium-aluminium tetraethyl, of which the melting point has been depressed by a suitable addition to the said temperature range or even better to temperatures which are just below said range, for example, to about 60°C.

Suitable additives of this nature are, for example, potassium-monoalkoxy-triethyl-aluminium compounds of the general formula  $K[ROAl(C_2H_5)_3]$ , in which the radical R preferably represents a hydrocarbon radical with at least three carbon atoms, for example, three to 10 carbon atoms. It is true that they lower the conductivity of the potassium-aluminium tetraethyl, but not so strongly that the electrolysis would be impossible. Another possibility as regards adjusting the melting point of the electrolyte to a suitable degree is the concurrent use of limited quantities of inert solvents or diluents for the organic potassium complex compound used as electrolyte. Particularly suitable for this purpose can be ethers of sufficiently high-boiling point as well as inert hydrocarbons, for example, of the toluene type.

The main compound of the electrolyte is potassium-aluminum tetraalkyl, and alkyl radicals with up to 2 carbon atoms are preferred. Potassium-aluminium tetraethyl is especially suitable.

Technologically, the electrolytic deposition of potassium offers a distinct advantage as compared with the electrolytic deposition of sodium. With the electrolytic deposition of sodium from the analogous sodium-containing complex compounds (or even their mixtures with complex potassium compounds, from which, up to a relatively high potassium content, only sodium is deposited), the densities of the molten sodium and of the molten electrolyte are normally so very close to one another that the problem of a clean, spontaneous layer formation arises, for the solution of which problem certain measures have proved to be advantageous (Ger-

man Pat. No. 1,168,651). By contrast, the molten potassium in the molten state at 63°-70°C is of substantially lower specific gravity than the molten electrolyte and consequently is certain to rise to the top in the electrolysis cell. The deposition of the potassium from potassium amalgam can consequently be operated in a particularly simple manner in accordance with the known principle of the so-called three-layer electrolysis. In this case, the starting material containing potassium, for example, potassium amalgam, as the lowermost layer, is covered with the molten electrolyte. The potassium product purified by the procedure of electrolysis separates out at the top as a third layer on the electrolyte. Where it is a case of desiring to refine electrolytically a crude potassium and not perhaps of desiring only to recover the potassium from a low-percentage amalgam, the crude potassium can be alloyed with a small quantity of mercury, in which case an amalgam is obtained which is of decidedly greater specific gravity than the electrolyte, and then the electrolysis is once again operated in the usual way by the principle of the three-layer process.

The following Example illustrates the invention:

#### EXAMPLE

Disposed on the bottom of a cylindrical electrolysis vessel are 3240 g of 0.516 percent potassium amalgam as anode, while arranged above the anode at a spacing of about 0.7 cm is an upwardly open, cylindrical basket made of a copper lattice with 25 meshes per square centimetre, which is provided with a cadmium coating in a thickness of about 10 - 100  $\mu$  for the better adhesion of the alkali metal. The basket is immersed to about two-thirds to three-fourths into the electrolyte

melt. The potassium which separates is of lower specific gravity than the electrolyte and ascends in the basket to the surface of the liquid and can be withdrawn from this surface at intervals.

5 Conditions:

Electrolyte: — 27.3 g(150 m.mol)—potassium tetraethyl-aluminium

17.0 g( 75 m.mol)—potassium triethyl-aluminium butoxide

10 Temp: — 67-69°C

Voltage: — 4 volts

Current strength: — 0.2 ampere

Anode surface: — 12.6 cm<sup>2</sup>

15 Cathode surface, calculated only for underside of basket: — 6.25 cm<sup>2</sup>

2.68 amp.-hours supply 3.9 g of potassium of melting point 63.0°C; the melting point is about 0.5°C higher than that of a comparison sample of commercial potassium.

20 What is claimed is:

1. A process for cathodic deposition of pure potassium which comprises electrolyzing between an anode which is a potassium amalgam and a cathode for deposit of pure potassium at a temperature of about 64°-70°C. an electrolyte consisting essentially of potassium aluminium tetraethyl and enough K [ROAl (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] wherein wherein R is an alkyl radical of three to 10 carbon atoms to lower the melting point of said tetraethyl compound to said temperature range, for deposition of the pure potassium at the cathode.

2. Process according to claim 1, the cathode being cadmium coated copper.

\* \* \* \* \*

35

40

45

50

55

60

65

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,775,270

Dated November 27, 1973

Inventor(s) Karl Ziegler and Herbert Lehmkuhl

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the prologue, [30], Foreign application priority date, change "Jan. 4, 1970" to --Jan. 14, 1970--.

Col. 4, line 27, (claim 1, line 7), cancel one "wherein".

Signed and sealed this 11th day of June 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents