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Klotz

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[54] **PURIFICATION OF MERCURY**

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[52] **U.S. Cl.** ..... **75/101 R;** 75/121; 204/64 R; 204/99; 204/124

[51] **Int. Cl.** **C22b 43/00**

[58] **Field of Search** ..... 75/121, 101 R; 204/64 R, 204/124, 125, 99

[56] **References Cited**

UNITED STATES PATENTS

2,032,602	3/1936	Stearns	75/121 X
2,846,305	8/1958	Ashley et al.	75/121
3,437,476	4/1969	Dotson et al.	75/103
3,639,118	2/1972	O'Grady	75/121

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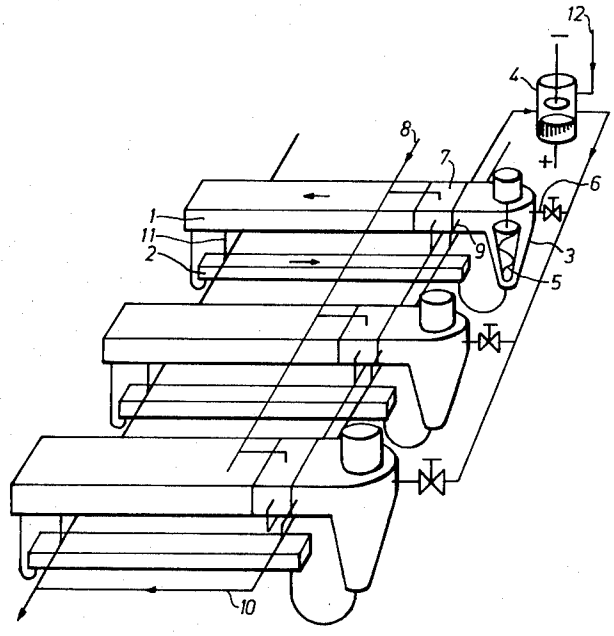
[57] **ABSTRACT**

In the electrolysis of an alkali metal chloride in a cell containing mercury there is produced an alkali metal amalgam which is withdrawn and decomposed to regenerate mercury containing impurities introduced from the alkali metal chloride. The impure mercury is mixed turbulently with an aqueous solution of sulfuric acid having mercury (I) sulfate dissolved or suspended therein whereupon the impurities are extracted into the solution and the purified mercury is recycled.

6 Claims, 3 Drawing Figures



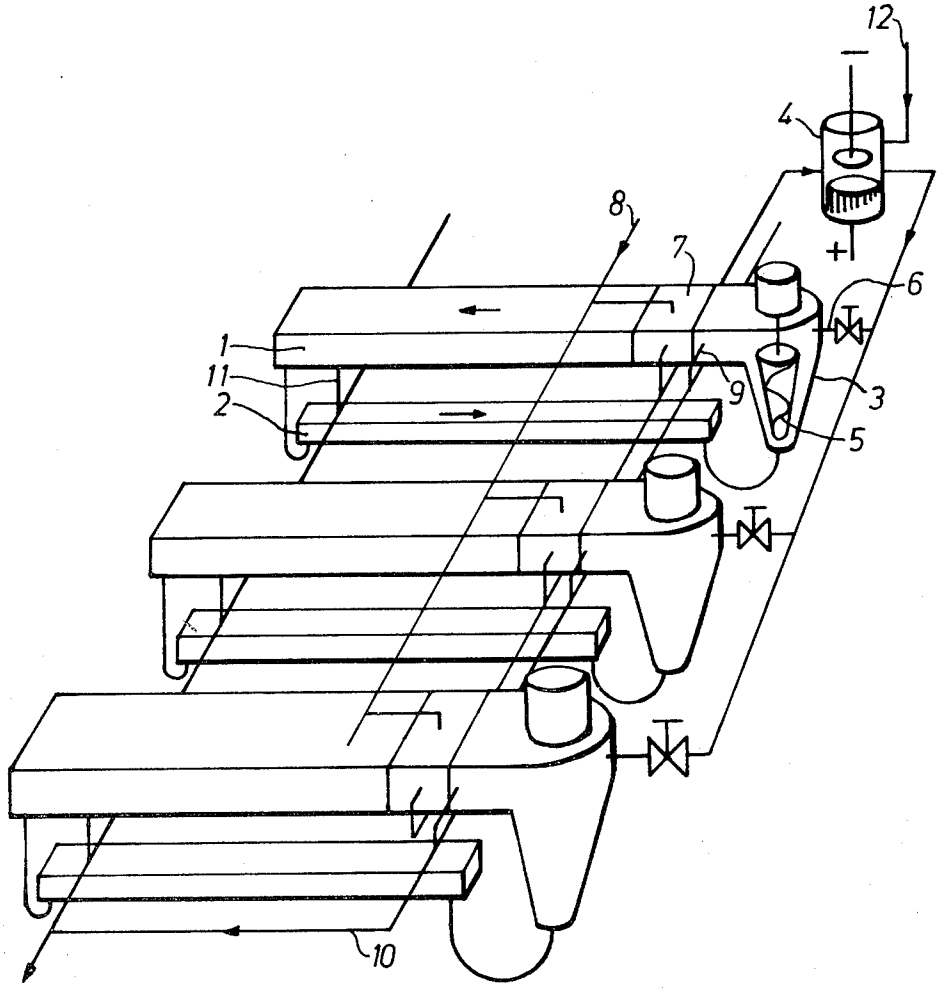


FIG. 1

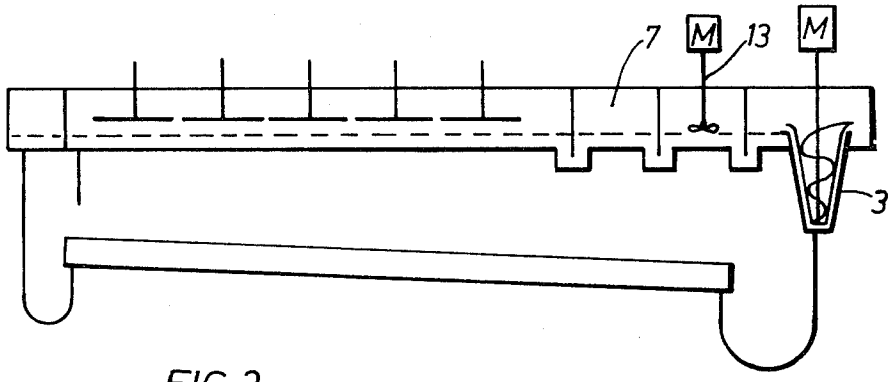


FIG. 2

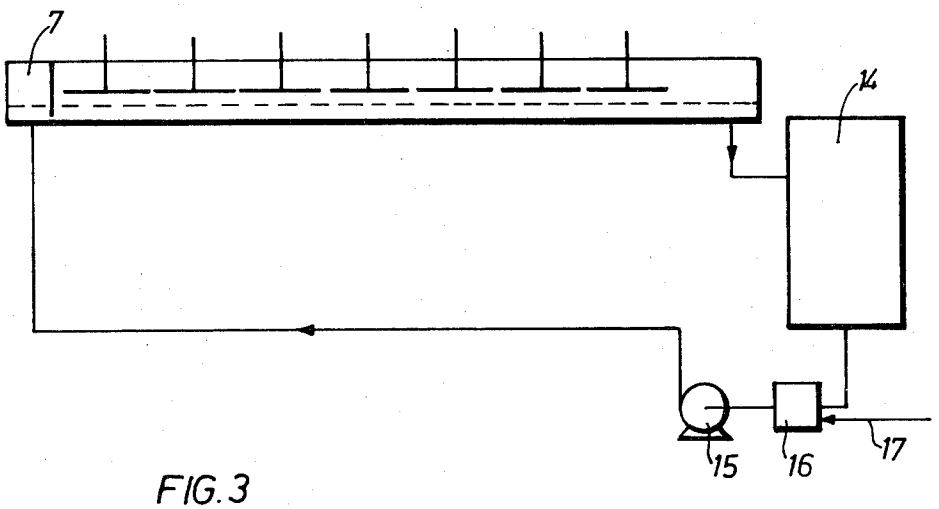


FIG. 3

PURIFICATION OF MERCURY

The present invention relates to the purification of mercury.

A number of chemical elements, especially metals, are soluble in mercury to a certain extent. In practical application, therefore, mercury generally absorbs metals as its principal impurity. For a number of applications involving mercury, for example switches, discharge lamps, diffusion pumps and valves, but especially for the electrolysis of alkali metal chlorides by the amalgam process, the mercury has to be present in a highly pure form. If the electrolysis of alkali metal chlorides is carried out using mercury which, in addition to alkali metals, contains other metals dissolved or dispersed in it, electrolysis is seriously affected insofar as the resulting chlorine has an increased hydrogen content, and the bottom of the cell, the amalgam decomposer vessel, the pipes and the pumps are contaminated. In addition, contamination of the cell base can lead to short circuits between anode and cathode unless the spacing between the electrodes is increased, which in turn has an adverse effect upon the economy of the process. Furthermore, the absorption of impurities by the mercury results in an accumulation of impurities (so-called amalgam butter formation), because, despite careful preparation, the starting materials (for example alkali chloride sols) continuously entrain traces of metal ions, or the material with which the mercury comes into contact and the anodes give off traces of metals or alloys. The metals iron, chromium and vanadium frequently occur as impurities in mercury with detrimental effects.

German Offenlegungsschrift No. 2,020,480 describes a process for purifying the mercury accumulating after the decomposition of sodium amalgam by means of solutions containing chlorine or iron(III)-chloride. By virtue of this process, it is possible to remove the iron in particular, although the iron content cannot be reduced to less than 0.01 percent by weight without the danger of the mercury itself being dissolved in appreciable quantities. This value is not sufficient to avoid detrimental contamination of the cell base in the presence of strong magnetic fields, which corresponds to high specific loads of the electrolysis cells. In order to avoid these disadvantages, it is necessary to reduce the foreign metal content to values far below those that can be obtained with the process according to German Offenlegungsschrift No. 2,020,480.

It is accordingly an object of the invention to provide a simple process for purifying mercury to a very high degree.

These and other objects and advantages are realized in accordance with the present invention pursuant to which contaminated, impure mercury is treated with an aqueous solution of sulfuric acid having mercury (I) sulfate dissolved or suspended therein and the purified mercury is separated from the solution into which the impurities have been extracted.

The process according to the invention is eminently suitable for rapidly purifying mercury, either continuously or in batches, by freeing it from metals, metallic phases, alloys and metal oxides down to an impurity content of less than about 10^{-5} percent by weight, providing the chemical elements in question are less noble than the mercury, i.e. lower down in the electromotive series.

The undesirable metal impurities dissolved and/or dispersed in the mercury are dissolved out of the mercury in the form of metal sulfates under the oxidizing effect of the acid solution and/or suspension containing mercury (I) sulfate, the Hg (I) of the mercury (I) sulfate being reduced to metallic mercury. Accordingly, the reaction which takes place during the process according to the invention is in principle a "cementation reaction," in other words the base impurities in the mercury cause the more noble mercury in the mercury (I) sulfate solution to be precipitated, and are themselves dissolved so that they can readily be separated from the liquid mercury phase. Accordingly, the mercury (I) sulfate solution and/or suspension used for purification will always be referred to hereinafter as the "cementing solution." According to the invention, the cementation reaction takes place with intensive admixture of the two liquid phases, the mercury phase and the cementing solution. Admixture can be carried out turbulently, for example by means of a high speed stirrer, a reciprocating pump, a vibrating mill or by atomizing the mercury by conventional methods for atomizing metal melts. It is also possible to apply an electrical rotary field, under the effect of which the mercury rotates and enables a phase exchange with the underlying cementing solution to occur. The process according to the invention can be carried out at temperatures of about 10° to 120°C, although it is preferably carried out at temperatures of about 20° to 100°C.

The cementing solution contains mercury (I) sulfate in disolved form, although it can contain more mercury (I) sulfate in solid form beyond the solubility of the mercury (I) sulfate. The cementing solution can also contain a mixture of mercury and mercury (II) sulfate, in which case mercury (I) sulfate is formed in situ in accordance with the equation $Hg(II) + Hg(O) \rightarrow Hg(I)$. However, the cementing solution advantageously contains mercury (I) sulfate from the outset. By virtue of the low solubility of mercury (I) sulfate in the aqueous medium, a cementing solution of this kind is easily prepared by suspending mercury (I) sulfate in sulfuric acid or by passing sulfuric acid over mercury (I) sulfate. The sulfuric acid should be from 0.05 to 5 molar, preferably from 0.1 to 1 molar. The mercury (I) sulfate can be prepared separately by conventional methods. However, the continuous production of a mercury (I) sulfate solution, bypassing the solid salt stage, is of greater advantage. Continuous production can be carried out, for example, by directly reacting sulfuric acid with mercury at temperatures above 80°C (Gmelin, "Hg," 34 B, 1005), or by electrolysis of a dilute sulfuric acid solution with a mercury anode (G. A. Hulett, Z. phys. Chem., 49, 483 (1904)).

As already mentioned, the process of cementation with sulfuric acid and mercury (I) sulfate according to the invention is particularly suitable for the batch purification and continuous purification of mercury. Purification can be carried out, for example, in an ordinary vessel equipped with a stirring mechanism, and the resulting mercury is washed with dilute sulfuric acid and water. The cementation reaction is carried out by providing the mercury (I) sulfate in slightly more than stoichiometric amount in relation to the impurities. The adjustment can readily be regulated by monitoring the content of mercury (I) sulfate in the already spent cementing solution which is separated.

In a preferred embodiment, the process according to the invention is used in the electrolysis of alkali metal chlorides by the amalgam process for purifying the mercury formed during decomposition of the amalgam before it is returned to the electrolysis cell. This preferred embodiment is described by way of example in the accompanying drawings, wherein:

FIG. 1 is a schematic perspective view of a battery of electrolysis cells;

FIG. 2 is a schematic lateral elevation of one of the cells and its structure for recycling spent mercury; and

FIG. 3 is a schematic lateral elevation of one cell and an alternate structure for recycling spent mercury.

Referring now more particularly to the drawings, FIG. 1 shows an embodiment for the electrolysis of alkali metal chlorides comprising a cell **1**, an amalgam decomposer **2**, a so-called Aussiger-cup (Winnacker-Kuchler, Chemische Technologie (1969), Vol. 1, page 255) in the form of a mercury pump **3** and an apparatus **4** for producing mercury (I) sulfate, comprising a small electrolysis cell for producing the cementing solution and various pipes. The Aussiger-cup and all components which come into contact with the cementing solution have to be made of or coated with a material that is resistant to the cementing solution. Materials suitable for this purpose include, for example, ceramic material such as, for example, sintered corundum, enamel, plastics such as, for example, polypropylene, and rubber. The mercury flowing out of the amalgam decomposer **2** into the bottom of the Aussiger-cup **3** is turbulently admixed by a cup-shaped rotor **5** with the cementing solution flowing in at **6** and, at the same time, is purified. The mercury flowing out again from the top of the Aussiger-cup is washed in a chamber **7**, separated from the cell **1** and Aussiger-cup **3** by submerged seals, with dilute sulfuric acid introduced through pipe **8.** The dilute sulfuric acid collected can be returned to the apparatus **4.** The spent cementing solution flowing out of the Aussiger-cup **3** at **9** can be delivered through a collecting pipe **10** to the anolyte which flows out of cell **1** at **11.** The salts, for example iron sulfate, present in the spent cementing solution can be precipitated in a conventional sol-preparation stage (not shown) after resaturation of the anolyte. Any undesired residue of mercury salts still present in the anolyte can be removed by cementation with iron scraps (not shown) before entering the anolyte. Additional dilute sulfuric acid may optionally be introduced into the electrolysis cell **4** at **12.**

In another embodiment shown in FIG. **2,** cementation is not carried out in an Aussiger-cup, but instead in a stirrer vessel **13** which is situated between the Aussiger-cup **3** and the cell inlet. A washing chamber **7** is here also provided.

It is of course also possible by the process according to the invention to purify only a portion of the mercury following decomposition of the amalgam. This embodiment is advantageous in cases where the mercury reentering the cell does not spread completely, which can occur in the case of wide cells, for example.

The process according to the invention can also be used in electrolysis installations which employ a vertical decomposer instead of a horizontal amalgam decomposer, and feed systems other than the so-called Aussiger-cups, for example in the form of pumps such as reciprocating pumps, immersion pumps, bucket-wheel pumps, electromagnetic pumps or pulsating pumps. FIG. 3 illustrates an embodiment with a pump. From a vertical decomposer **14,** the contaminated mercury flows back into the cell **1** through a pump **15.** The cementing solution can be introduced into the feeder (pump) at **17** either directly or by way of a mixing zone **16.** The mercury is washed in the washing chamber **7** before entering the cell.

In the embodiments shown in FIG. **2** and **3,** preparation of the cementing solution, the associated pipe system and introduction of the spent cementing solution into the impoverished sols, correspond to the embodiment shown in FIG. **1.** Other processes can also be used for separating the impurities from excess mercury (I) sulfate in the aqueous phase, for example cathodic deposition of the more noble mercury or, as already mentioned, cementation with iron scrap.

The process according to the invention is illustrated by the following Examples:

EXAMPLE 1

A dispersion of iron in mercury with an iron content of 2.10^{-1} percent by weight was prepared by reducing iron (II) chloride with sodium amalgam, and was stored for four days at 25°C. 2.7 kg of the dispersion were reacted at 30°C with a cementing solution of 10 g of mercury (I) sulphate, 20 g of sulphuric acid and 200 g of water in a quadrangular polyethylene bottle provided with a high speed stirrer (4,700 r.p.m.). After a reaction time of only 2 minutes, the iron content had been reduced to 5×10^{-6} percent by weight of iron.

EXAMPLE 2

Purification by cementation was carried out in an 80 kA cell for the electrolysis of alkali metal chlorides by the amalgam process in accordance with FIG. **1.** In the apparatus **4,** 1 molar sulphuric acid was continuously reacted on a mercury anode at 0.12 A and 0.6 V to form mercury (I) sulphate. The sulphuric acid cementing solution saturated with 0.5 g of mercury (I) sulphate was passed through the mercury feeder (Aussiger-cup 3) at a rate of 40 litres per day. In this way, it was possible to keep the electrolysis cell, the amalgam decomposer and the Aussiger-cup free from deposits so that the cell did not have to be taken out of operation for several months.

It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. In the purification of mercury by contacting it with an aqueous medium to extract the impurities into the aqueous medium the improvement which comprises employing as said aqueous medium a solution of sulfuric acid having mercury (I) sulfate dissolved or suspended therein.

2. The process of claim **1** wherein the temperature is about 10° to 120°C.

3. The process of claim **1** wherein the sulfuric acid solution is about 0.05 to 5 molar.

4. The process of claim **1** wherein the mercury is turbulently mixed with the sulfuric acid solution.

5. The process of claim **4** wherein the temperature is about 20° to 100°C and the sulfuric acid solution is about 0.1 to 1 molar.

6. The process of claim **5** wherein the impure mercury is obtained by decomposition of an amalgam formed during electrolysis of an alkali metal chloride in a cell containing mercury, and the purified mercury is thereafter returned to said cell.

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