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ELECTROLYZING PROCESS WITH THE USE OF A MERCURY CATHODE

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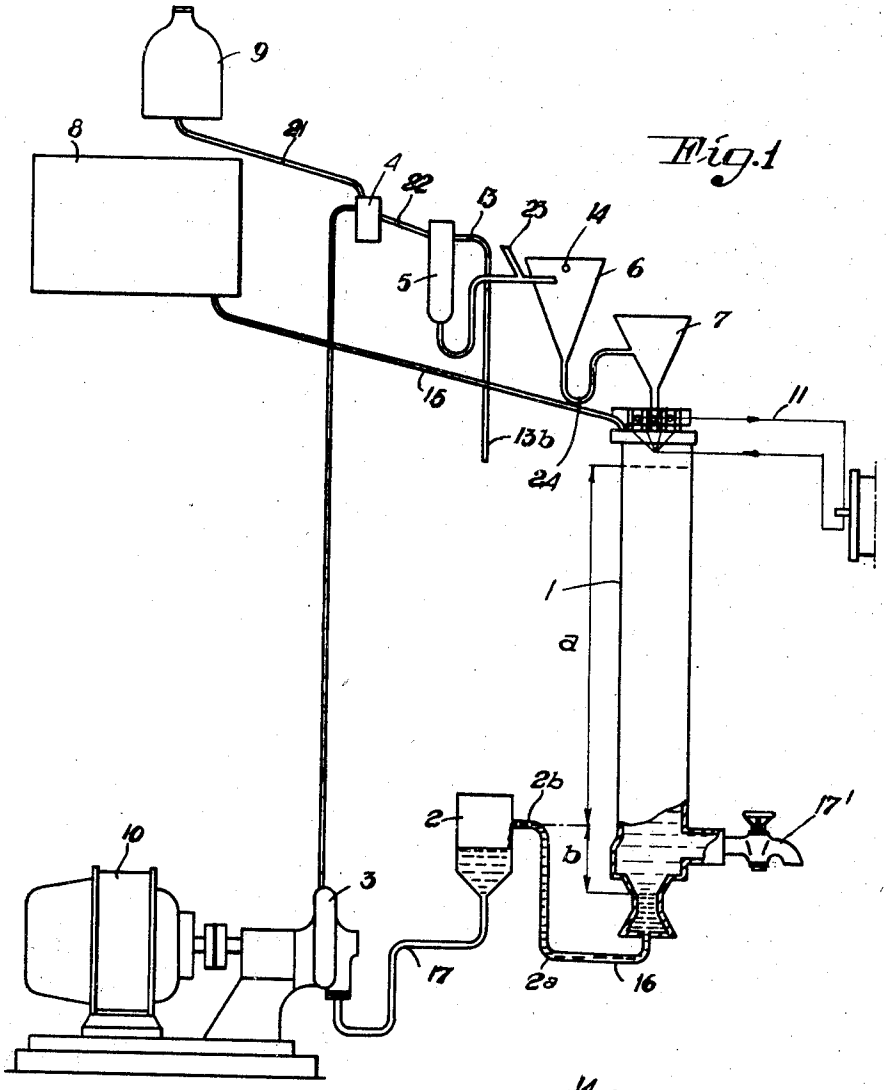


Fig. 1

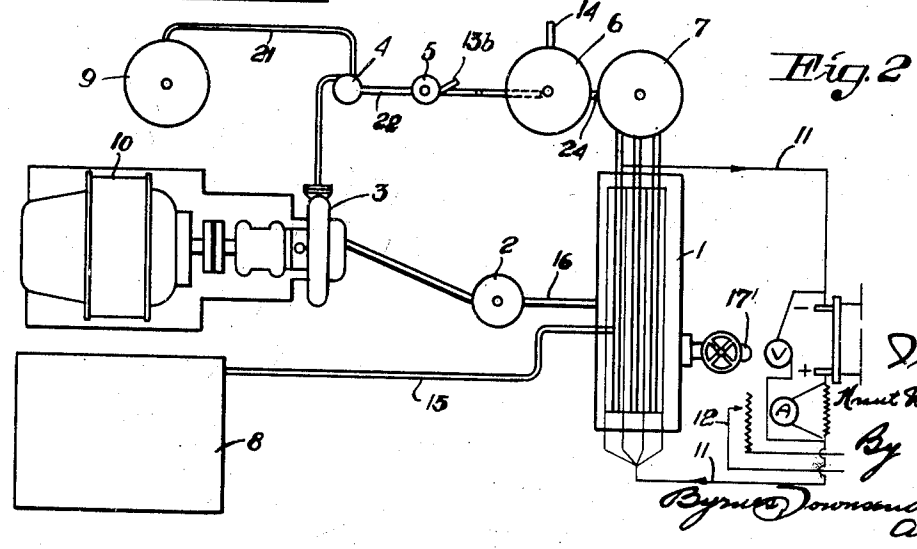


Fig. 2

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ELECTROLYZING PROCESS WITH THE USE OF A MERCURY CATHODE

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The present invention relates to improvements in the art of electrodepositing metals of less positive character than alkali metals and alkaline earth metals, especially one or more of the metals of the eighth group of the periodic system, such as iron, from solutions containing salts of one or more of said metals while using a cathode consisting of mercury flowing for instance in a vertical or inclined direction.

One feature of the invention consists in using as bearer or support for the flowing mercury a previously amalgamated metallic object so as to obtain a better electric contact with the mercury as well as a good spreading of the mercury over the surface of the bearer even if the mercury layer is thin.

In the electrolytic production of alkali and chlorine according to the mercury process the use of vertical or inclined cathodes has been proposed. In such cases the mercury has been caused to flow along metallic objects, such as sheets or wire gauze of copper or iron in order thus to realize contact for the electric current. The mercury then spreads as a homogeneous layer over the surface of the metallic bearer even if said bearer, when taken into use, is coated by oxides, as is the case with most metals on account of the action of the air. The reason why the mercury in this instance behaves quite contrarily to what is usually the case is that the alkali metal deposited on the mercury from the alkali metal chloride solution reduces the oxide coatings on the surface of the bearer on account of its highly positive character so that the surface is wetted by the mercury. An oxidized metal surface is not wetted by mercury. It is known for instance that if a piece of rusty iron is brought into contact with sodium amalgam under water or an aqueous solution the rust will soon be reduced and the piece of iron will become amalgamated, i. e. wetted by the mercury. In the appertaining literature it is also pointed out that mercury which contains alkali metal spreads over the metallic support as a very thin layer without any special measures (see for instance the German Patents Nos. 145,749 and 213,808).

It is quite different in the electrodeposition on mercury of metals having a less positive character, from solutions containing salts of such metals. The metals deposited on mercury in this case are not able to reduce oxide coatings if such are present on the surface of the support. Thus it is obvious that iron, for instance, cannot reduce the oxide coatings on iron or nickel objects. If there is used in this case an oxide-coated metallic support for mercury it will thus be impossible to obtain a cohering mercury layer which covers completely the surface of the support. Because all other metals have a lower overvoltage for hydrogen than has mercury this means that the electric current will deposit more hydrogen and less of the desired metal or metals than would be the case if the surface of the carrier were completely covered by the mercury. In other words: the current efficiency is diminished.

This is especially detrimental in the deposition of one or more of the metals of the eighth group of the periodic system from solutions containing salts of one or more of said metals by electrolysis with the use of flowing mercury as cathode, as described in the U. S. Patent No. 1,900,996 (application Ser. No. 385,466).

According to one feature of the present invention the mercury is caused to wet the surface of the metallic support completely so that a cohering mercury film is obtained by previously amalgamating the surface of the metallic objects, such as plates or sheets, which are to be used as bearers or supports for the flowing mercury acting as cathode, said amalgamation being effected in any known manner, as by rubbing with acid and mercury, by the electrodeposition of mercury on the support etc. In use the whole surface of the metallic carrier will then be wetted and completely flooded by mercury, whereby the drop in current efficiency referred to is avoided.

Obviously the support should have small solubility in mercury, since it will otherwise be destroyed too rapidly. Thus for instance a metal of the eighth group of the periodic system or a metal related to iron (as chromium or manganese) may be used. Likewise an alloy may obviously be used instead of metal.

The invention also comprises certain improvements in the removal by electrolysis of one or more of the metals of the eighth group of the periodic system from solutions containing salts of said metals, as well as apparatus for this purpose, all as hereinafter described and claimed in the appended claims.

A suitable embodiment of an apparatus for carrying out the invention will be described in the following with reference to the attached drawing in which Fig. 1 shows a side elevation and Fig. 2 a plan of an installation for effecting an electrolyzing process according to the invention.

Referring to Figs. 1 and 2 the electrolysis is carried out in the cell 1 which comprises a number of cathodes consisting of mercury flowing over

suitable bearers or supports for instance of the kind above referred to, as well as a corresponding number of anodes. The cathodes and anodes are connected to the current conductors 11 which are, in their turn, connected to a suitable current generator. V and A designate a voltmeter and an amperemeter respectively. 12 is an adjustable resistance for regulating the current. The solution to be electrolyzed is conveyed, preferably in a heated state, from the container 8 through the pipe 15 to the electrolytic cell 1. The liquid introduced through the pipe 15 is subjected to electrolysis in the electrolytic cell, the deposited metals being taken up and carried away in amalgamated state by the flowing cathode mercury. The lower portion of the electrolytic cell is connected with one end of a U-tube 16, the other end of which opens out into a vessel 2. The contaminated cathode mercury flows off through this U-tube. The level on which one shank of the tube 16 is joined to the vessel 2 is taken so that the column of mercury of the height b in the tube 16 is sufficient, according to the law of communicating vessels, to counterbalance the column of electrolyte of the height $a+b$ in the cell 1. Hence no electrolyte will flow off together with mercury through the tube 16, and the whole quantity of electrolyte may be drawn off through the cock 17^1 after the electrolysis has been finished. The idea is thus that the electrolytic cell communicates with a mercury trap 2^a with overflow 2^b, in which trap there is a mercury column of such a height that the hydrostatic pressure prevailing in the electrolytic cell is counterbalanced by said mercury column so as to permit the continuous flow-off of mercury out of the cell without accompanying electrolyte.

From the vessel 2 the mercury flows through a pipe 17 to a centrifugal pump 3 driven by an electromotor 10, which pump raises the mercury to the purifying vessel 4. The mercury is continuously pumped up into the purifying vessel 4. Purifying liquid is introduced—preferably also continuously—into this vessel through a pipe 21 from a container 9. This liquid contains in solution or suspension an agent which is capable of removing metal taken up by the cathode mercury. Thus for instance, a solution of ferric sulphate may be used. During the purification the kinetic energy of the mercury admitted into the vessel 4 is utilized to effect a sufficient mixing of mercury and the liquid containing the purifying agent. Trials have shown that the mixing brought about in this way is very effective. The effect may be increased by making the purifying vessel 4 with a circular cross-section, the mercury being introduced in a tangential direction as shown in Fig. 2.

From the purifying vessel 4 the mixture of mercury and purifying agent flows to one widened shank of a U-tube 5. This shank is provided with an overflow 13 where the liquid containing consumed purifying agent flows off and is conveyed through the conduit 13^b to a container (not shown) or the like where it may be regenerated if desired, and from which it may be returned to the vessel 4. Through the other shank of the U-tube mercury is discharged to a washing vessel 6. The last-mentioned shank opens out into the washing vessel 6 on such a level that the mercury column in this shank counterbalances the liquid column in the other widened shank according to the law of communicating vessels so that the mercury passing to the vessel 6 will not be accompanied by any appreciable quantity of purifying liquid. In front of the inlet of the washing vessel 6 wash water is introduced by a branch pipe 23 and is mixed with mercury so as to remove the last traces of purifying liquid. The wash water and the mercury are separated in the vessel 6 due to their different specific gravities. The mercury sinks to the bottom and passes on through the U-shaped conduit 24 to the collector vessel 7 from which it is introduced into the electrolytic cell. The wash water flows off through the overflow 14. Also here the law of communicating vessels is applied, the U-shaped conduit 24 acting as a mercury trap so that no wash water goes with the mercury into the collector vessel 7.

As set forth hereinbefore the mercury circulates and is purified continuously during the process. It is obvious, however, that the purification may be effected intermittently instead of continuously.

It has been established by experience that the purification of the mercury must be effected under certain conditions in order to obtain a good result. Thus the mercury used for the electrolyzing operation should be purified from metal or metals taken up in it in such a way that the mercury itself is not attacked during the purification. To this end it is possible either to use a substance, which is indifferent to mercury, e. g. mercurous salts, preferably in solution, or the purifying process may be effected so as to remove only part of the total quantity of contaminating metal or metals present in the mercury. For reasons which will be explained in the following such a partial removal involves advantages also if a substance indifferent to mercury, e. g. a mercurous salt solution, is used as a purifying agent. Accordingly the purifying agent in both cases is preferably used in quantities less than equivalent to the quantity of metal which is incorporated in the mercury. Preferably the conditions during the purification of the mercury are regulated so that only such quantity or approximately such quantity of metal is removed from the mercury as was taken up by said mercury during the electrolysis. In the electrolysis care should preferably be taken that the percentage of deposited metal or metals in the cathode mercury is kept constant at a value not higher than 0.5%, preferably lower than 0.3%.

The reasons why an attack on the mercury during the purification should be avoided are the following. An attack on the mercury means firstly that mercury is converted from the metallic state into a compound. If this compound is not recovered loss of mercury occurs. If the compound is recovered (e. g. by decantation or filtration, if insoluble; by precipitation followed by decantation or filtration if said compound is soluble) loss of mercury may be avoided but on the other hand more or less expensive processes for recovering the mercury will be necessitated.

Attack by the purifying agent on the mercury, however, often results in a considerably more serious drawback. If the mercury is attacked so that a slightly soluble or an insoluble compound (oxide or slightly soluble salts) is formed it easily happens that the mercury body disintegrates into small drops, the surface of which is covered by the formed compound. These drops recombine extremely slowly. It is obvious that mercury in such a form is unsuitable or unuseful as cathode material.

One method of effecting the purification so as to avoid attacks on the mercury consists, as pre-

viously mentioned, in using as a purifying agent a substance which is indifferent to mercury, such as mercurous salts, preferably in solution. If, on the other hand, a purifying agent is used, which is capable also of attacking mercury, this attack is avoided by carrying out the purification so that only part of the metal or metals taken up in the mercury during the electrolysis is removed. This can be explained by the following illustrative example.

The normal potential of iron is −0.43 volt, and the normal potential of mercury is about +0.8 volt. Iron is thus less noble than mercury in a degree which, expressed in the difference between the normal potentials, amounts to approximately 1.2 volt. This means that, other conditions being equal, as for instance the kind, concentration and temperature of the solution used, iron is attacked (for instance is dissolved) much more readily than mercury. Accordingly if a mixture of iron and mercury is treated with a substance capable of attacking both these metals the first one of them to be attacked (dissolved out) is iron. Only when the iron has been practically completely consumed, the mercury is attacked. Consequently, if the quantity of the attacking substance is regulated with respect to the iron-mercury mixture so that the attacking substance is consumed before all the iron in the mercury has reacted with the substance, there will be no attack on the mercury. It is preferable, also when using a purifying agent which is indifferent to mercury, to carry out the purifying process in such a way that only part of the quantity of metal or metals taken up in the mercury is removed, since the purifying agent in this way may be more completely utilized.

In certain cases, as for instance that type of elctrolytic process which is described in the U. S. Patent No. 1,900,996 (application Ser. No. 385,466) it is preferable for reasons which will be given in the following that during the purification of the mercury the conditions are so regulated that only such quantity or approximately such quantity of metal is removed from the mercury as was taken up by said mercury during the electrolysis. Preferably the percentage of deposited metal in the mercury used as cathode is kept constant and at a value not exceeding 0.5%, preferably lower than 0.3%. If the removal of the metals of the eighth group from mercury is effected continuously in such a way that the mercury flows through the purifying vessel at the same rate as through the electrolytic cell, and if purifying agent is supplied to the purifying vessel at a certain rate x, care should obviously be taken that the rate x will not become too low. This is so for the reason that if the rate x becomes too low the amount of deposited metal or metals in the mercury will increase, and by and by it will attain such a value that the circulation of the cathode mercury is rendered impossible or difficult due to the fact that the mercury has become too viscous. On the other hand the rate x must not be too great, since in such a case the percentage of the metal or metals in question in said mercury will fall, until finally the mercury is beginning to be attacked (if there is used a purifying agent which is capable of attacking mercury). The rate x should obviously be regulated so that the percentage in the mercury of incorporated metal is kept at a value approximately right between the point at which the inconvenience relating to the circulation begins to appear, and that point where the attack on the mercury of the purifying agent starts. The margin of safety is then equal in both directions. A percentage of about 0.1 to 0.2% of metal in the mercury has been found suitable. If the percentage of metal in the mercury exceeds 0.5% serious inconveniences are met with, the mercury becoming so viscous that it can be caused to flow only with the greatest difficulty.

One method of removing one or more of the metals, iron, cobalt and nickel from such contaminated cathode mercury as is obtained in the electrolytic removal of said metals from solutions containing salts thereof consists in reacting an oxidizing agent with the mercury containing the metal or metals. To dissolve for instance iron out of mercury by means of a non-oxidizing acid only is not possible, as this would mean that iron were dissolved with development of hydrogen for instance according to the equation:

$$Fe+H_2SO_4=Fe\ SO_4+H_2.$$

In order to deposit hydrogen on mercury from a 1-normal acid solution a voltage of about 0.8 volt is required, whereas the normal potential of iron is only −0.43 volt. Already at a concentration of ferrous ions as low as 10^{-12}-normal the iron accordingly loses its power to deposit hydrogen on mercury from a 1-normal acid solution, and it is consequently practically impossible to dissolve iron out of mercury by means of for instance sulphuric acid only, in accordance with the equation set forth above.

If, however, a suitable oxidizing agent is present, this acts as a depolarizer for the hydrogen and the dissolving out of the metals taken up in the mercury becomes possible. Iron may for instance by dissolved according to the equation:

$$Fe+H_2SO_4+H_2O_2=Fe\ SO_4+2H_2O.$$

What has been stated above with respect to iron applies also to cobalt and nickel.

The purifying agent should preferably be of such a nature that it can be readily regenerated, i. e. if it is an oxidizing agent it should have the property of being readily re-oxidized. For such reasons one or more of the following substances is/are preferred: ferric salts, e. g. ferric sulphate, hypochlorites, nitric acid or nitrates, preferably in aqueous solutions. Of course also when using oxidizers as purifying agent it is to be observed that only part of the total quantity of metal in the mercury should be removed before the mercury is returned to the electrolytic cell, because otherwise the oxidizing agent will attack the mercury. Hence it is preferable to keep the amount of the oxidizing agent below that which is equivalent to the quantity of metal taken up in the mercury. According to one embodiment of the invention the conditions during the purification of the mercury by means of oxidizing agents are regulated so as to remove only such quantity or approximately such quantity of metal from the mercury as was taken up by said mercury during the electrolysis. When an aqueous solution of oxidizing agent is used, the solution should be kept acid in order to aid the reaction between the oxidizing agent and the metal present in the mercury. For economical reasons the consumed oxidizing agent should be re-oxidized and re-utilized. Also where the purification is effected by means of oxidizing agents the percentage of deposited metal in the mercury used as cathode may be kept at a constant or approximately constant value, not exceeding 0.5% but preferably being lower than 0.3%.

What I claim is:—

1. Method for the electrodeposition of metals which are less electropositive than the alkali and alkaline earth metals which comprises subjecting solutions containings salts of such metals to electrolysis with a metallic cathode support which has been amalgamated prior to the electrolysis, and flowing mercury over said cathode support during the electrolysis.

2. Method for the electrodeposition of metals of the iron group which comprises subjecting solutions containing salts of such metals to electrolysis with a cathode support consisting of a metal selected from the iron group, said support having been amalgamated prior to the electrolysis, and flowing mercury over said cathode support during the electrolysis.

3. Method as defined in claim 1, characterized in that the metallic cathode support consists of chromium.

4. Method as defined in claim 1, characterized in that the metallic cathode support consists of manganese.

5. Method as defined in claim 1, characterized in that the metallic cathode support consists of an alloy of at least two metals of the group comprising iron, cobalt, nickel, chromium and manganese.

6. In a method for the removal by electrodeposition of metals of the eighth group of the periodic system from solutions containing salts of said metals which comprises subjecting said solutions to electrolysis in contact with a mercury cathode, removing the contaminated mercury from the cell, subjecting it to a purification treatment in a compartment which is separated from that compartment where the electrolysis is carried out, introducing contaminated cathode mercury from the cell into said purifying compartment and returning purified mercury from the said compartment to said cell, the purification treatment being effected by means of a liquid containing a purifying agent, the improvement consisting in utilizing the kinetic energy of the mercury flowing from the cell into the purifying compartment for effecting the necessary intermixing of mercury and the purifying liquid.

7. Method as defined in claim 6, wherein the purified mercury is washed substantially free from accompanying purifying liquid prior to entering the cell.

8. Apparatus for the electrodeposition of metals less electropositive than the alkali and alkaline earth metals from solutions containing salts of such metals, which comprises an electrolytic cell having an amalgamated cathode support adapted for the flowing of mercury thereover, a purifying chamber for said mercury, a conduit for conveying mercury from the cell to the purifying chamber, a conduit for conveying the purified mercury from the purifying chamber to the cell, and means for circulating the mercury through said cell, chamber and conduits, characterized in that the purifying chamber is provided with an inlet for liquid containing a purifying agent, and an inlet for contaminated cathode mercury, the said inlets being so disposed relatively to each other and to the purifying chamber that the kinetic energy of the in-flowing mercury is utilized for effecting the necessary intermixing of mercury and the purifying liquid.

9. Apparatus as defined in claim 8, characterized by a substantially cylindrical purifying chamber having a mercury inlet disposed tangentially relatively to the cylindrical wall of said chamber, and an inlet for purifying liquid.

10. Apparatus as defined in claim 8, characterized by a mercury trap with an overflow, said trap communicating with the cell, in which trap there is a mercury column of such a height that the hydrostatic pressure prevailing in the electrolytic cell is counterbalanced by said mercury column so as to permit the continuous flow-off of mercury from the cell without substantial quantities of accompanying electrolyte.

11. Apparatus as defined in claim 8, characterized in that the purifying chamber communicates with a separating compartment in which mercury and purifying liquid are separated from each other.

12. Apparatus as defined in claim 8, comprising a separating compartment in which mercury and purifying liquid are separated from each other, characterized in that the said separating compartment is connected to a washing vessel in which mercury flowing over from the said separating compartment is washed prior to its being returned to the cell.

13. Apparatus as defined in claim 8, comprising a separating compartment in which mercury and purifying liquid are separated from each other, characterized in that the separating compartment is provided with an overflow for the purifying liquid as well as with a mercury trap through which mercury is discharged.

14. Apparatus as defined in claim 8, comprising a vessel for washing purified cathode mercury substantially free of purifying agent, characterized by a collecting vessel communicating with said washing vessel and adapted to receive mercury from the washing vessel as well as to discharge mercury into the cell.

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