The process of the present invention provides certain improvements in the practice hereinafore regarded as standard for recovering precious metals contained in anode slimes from electrolytic copper refineries; and more particularly, the present process provides certain improvements in the electrolytic parting of silver from gold, it dealing, more particularly, with modifications of the generally accepted practice having for their broad purpose the effecting of improved economies in operation thereof, particularly with reference to the preparation of electrolytic solutions, and to the handling of the gold slimes resulting from the electrolytic decomposition of the doré anodes produced from the treatment of the aforesaid anode slimes.

The doré anodes are produced from the residues left from the leaching of the anode slimes resulting from electrolytic copper refining, such residues being importantly high in precious metals which are subject to recovery by a reverberatory refining with soda ash and nitre, and casting the resulting doré metals into anodes. These anodes are electrolyzed in suitable cells, for example cells of the well-known Moebius type, utilizing a silver nitrate electrolyte produced by solution of a portion of the doré anodes in nitric acid. During the course of this electrolysis, silver is deposited on the cathodes as fine silver, and the gold from the anodes forms slimes which are collected in suitable bags enclosing the anodes, and which, after a suitable treatment, are cast into anodes and electrolytically refined in Wohlwill cells in a gold chloride-hydrochloric acid electrolyte for the deposition of substantially pure gold on the cathodes of the cells.

During electrolysis of the doré anodes, there must be replenishment of the electrolyte in the cells from time to time, as required by the depletion of electrolyte through evaporation and deposition of the sliver content thereof; this replenishment being accomplished by the addition of further quantities of silver nitrate solution as make-up electrolyte for the cells.

Also, slimes which are collected during the decomposition of the anodes are subject to treatment for separation therefrom of entrained impurities, mostly silver, before the slimes are melted out and cast as Wohlwill anodes which are refined, subsequently, to substantially pure gold in Wohlwill cells.

The present invention provides improvements in the carrying out of the electrolysis under closely controlled conditions which are found to enhance the purity of the recovered silver, with consequent diminution of accompanying losses of values, particularly precious metals other than the gold and silver present in the doré anodes.

It may be pointed out in this connection that copper tank house slimes, from which the doré anodes are produced, may contain important amounts of precious metals other than gold and silver; and especially palladium, which enter the doré anodes; and in the electrolytic refining of these anodes important losses of palladium have been encountered quite regularly in the operation of the standard procedure because of the inclusion of such palladium in the cathodic silver deposits.

The present process includes, accordingly, an improved operating procedure whereby such palladium losses are reduced to a very substantial extent, and frequently substantially entirely eliminated.

In accordance with the present process, doré anodes which may have been produced from refined leached anode slimes from electrolytic copper refining operations, are electrolyzed in Moebius cells using as electrolyte, a solution of neutral silver nitrate, which solution may be produced by dissolving suitable quantities of the doré metal in nitric acid.

As a result of the electrolysis, sliver from the anodes is deposited as fine silver crystals, which in practice are scraped from the cathodes as deposited, so that these silver crystals settle to the bottom of the cells, where they collect.

The gold and other precious metals present in the anodes are collected as slimes in bags which enclose the anodes, and as the anodes become consumed, the resulting scrap is melted and recast, and electrolyzed again as anodes.

The fine silver crystals which are collected at the bottom of the cells are washed in hot water, preferably in filter bottom trucks, the bulk of the resulting wash water which contains silver nitrate electrolyte from the silver crystals being returned to the storage tank for addition to the electrolytic cells as required. Excess quantities of wash water are sent to a cementation tank, where the silver present in the wash water is precipitated by the addition of a suitable cementation metal such as zinc.

The liquid from the cementation operation is separated from the metallic precipitate and the solution is discarded, the precipitated metal being cupelled to silver.

The fine silver crystals recovered from the electrolytic cells are melted and cast into bars, there being reserved, however, a suitable, but relatively small quantity of such crystals for use in preparing further quantities of silver nitrate electrolyte which is to be substantially neutral with respect to free nitric acid.

This neutral silver nitrate solution is returned to the storage tank and mixed with the wash water from the washing operation on the silver crystals, the resulting solution being returned to the electrolytic cells as make-up solution as is required in accordance with depletion of the electrolyte in the electrolysis.

In operating the electrolysis in accordance
with the usual practice, it has been observed that if the doré anodes contain palladium, the fine silver may contain important amounts of palladium which is deposited along with the silver.

One aspect of the present invention is to provide an improved procedure for electrolysis of the doré anodes which will eliminate excessive losses of palladium in the fine silver.

It has been found that the higher the pH value of the electrolyte (that is, the lower the free nitric acid concentration) the lower becomes the palladium content of the fine silver deposited, values of less than 0.001 part palladium per thousand of silver being obtainable, if the pH of the electrolyte is maintained at a value greater than 3.0, but less than what would cause precipitation of copper and silver salts. In practice, a range of pH 2.8 to 3.8 is utilized. It has been observed also that during normal operation of the cells the pH tends to reach an equilibrium depending upon the anode current density. During the interval in which pH is decreasing, the cathode current efficiency is greater than the anode current efficiency, so that silver nitrate must be added to maintain the silver ion concentration of the electrolyte.

The effect of the pH value of the electrolyte on the palladium content of the fine silver is shown illustratively by the following figures:

<table>
<thead>
<tr>
<th>pH</th>
<th>Palladium in fine silver in parts per thousand</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>0.016</td>
</tr>
<tr>
<td>2.9</td>
<td>0.030</td>
</tr>
<tr>
<td>3.0</td>
<td>0.010</td>
</tr>
<tr>
<td>3.1</td>
<td>0.001</td>
</tr>
<tr>
<td>3.2</td>
<td>0.004</td>
</tr>
<tr>
<td>3.3</td>
<td>0.004</td>
</tr>
<tr>
<td>3.4</td>
<td>0.007</td>
</tr>
</tbody>
</table>

It will be seen from the above that there is a definite decrease in the palladium content to a pH value of 3.0 and while further slight decreases are noted, with increasing values of pH these decreases are very slight and may arise through the limits of analytical accuracies as much as from an actual decrease in palladium content in these extremely small amounts. Additionally, it has been noted that increases in the pH value substantially above 3.0 results in an accompanying precipitation of basic salts of copper, which occurs with a pH of about 4.2, and of basic salts of silver, which occurs with a pH of 5. In the electrolyte, so that a pH of approximately 3.0 may be taken safely as the critical limit of practical operativeness.

It will be understood, of course, that the process of the present invention is applicable to palladium-containing doré anodes from any source, such as for example, from lead refining operations, as well as from copper tank-house refining processes.

During the course of the investigations, incident to the present invention, it has been found that the requisite pH value may be maintained by controlling the anode current density so as not to exceed a definite maximum, and that with any given current density the pH of the electrolyte comes to an equilibrium. It has been found that, starting with an electrolyte of pH=3, an increase of current density of 40 amps./sq. ft., or more, the pH value goes down; whereas with a current density of less than 40 amps./sq. ft., the pH value increases. For practicable commercial operation, a current density range of from substantially 30 to 40 amps./sq. ft. is found to be the best operating range for maintaining a pH of requisite range of 2.8 to 3.8. In practice, it has been found in practice that the current density should not be increased above 45 amps./sq. ft.

It will be understood, of course, that the current density in itself does not affect directly the palladium content of the silver, the current density effect on such content being exerted only through its effect on the pH of the electrolyte.

What is claimed is:

1. Process for electrolytic parting of silver from doré anodes which comprises preparing electrolyte from silver-bearing products of electrolysis of the anodes by dissolving silver from the said products in controlled amounts of nitric acid to avoid the presence of substantial amounts of free nitric acid in the electrolyte, and electrodepositing the silver from the said electrolyte while maintaining the pH value of the electrolyte at approximately 3.0, thereby avoiding important inclusions of palladium in the deposited silver.

2. Process for electrolytic parting of silver from doré anodes which comprises preparing electrolyte from silver-bearing products of electrolysis of the anodes by dissolving the said products in controlled amounts of nitric acid to avoid the presence of substantial amounts of free nitric acid in the electrolyte, and electrodepositing the silver from the said electrolyte while maintaining the pH value of the electrolyte at approximately 3.0, thereby avoiding important inclusions of palladium in the deposited silver.

3. Process for electrolytic parting of silver from doré anodes which comprises maintaining the silver nitrate electrolyte continuously at a pH value below 4.2 to avoid precipitation of basic compounds in the electrolyte during electrolysis and maintaining the pH value of the electrolyte between 2.8 and 3.8 to avoid the formation of large amounts of free acid in the electrolyte as well as precipitation of basic salts therein and thereby excluding important amounts of palladium from the deposited silver.

4. Process for electrolytic parting of silver from doré anodes which comprises maintaining the silver nitrate electrolyte while continuously maintaining the pH of the electrolyte between 2.8 and 3.8 to substantially eliminate inclusions of palladium in the deposited silver.

5. Process for electrolytic parting of silver from doré anodes which comprises maintaining the pH value of the electrolyte between 2.8 and 3.8 to substantially eliminate inclusions of palladium in the deposited silver.

6. Process for electrolytic parting of silver from doré anodes which comprises maintaining the pH value of the electrolyte between 2.8 and 3.8, to substantially eliminate inclusions of palladium in the deposited silver.

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