

# UNITED STATES PATENT OFFICE.

FREDERICK GUTZKOW, OF SAN FRANCISCO, CALIFORNIA.

## PROCESS OF REFINING COPPERY SILVER BULLION.

SPECIFICATION forming part of Letters Patent No. 572,342, dated December 1, 1896.

Application filed July 14, 1896. Serial No. 599,166. (No specimens.)

*To all whom it may concern:*

Be it known that I, FREDERICK GUTZKOW, a citizen of the United States, residing in the city and county of San Francisco, State of California, have invented certain new and useful Improvements in Processes of Refining Coppery Silver Bullion; and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

Heretofore the refining of coppery silver bullion, that is, its separation into metallic gold, silver, and copper, has baffled the art of the refiner. In the electrical process the rapid saturation of the bath with copper causes trouble. In the so-called "Oker" process by oxidation and treatment with dilute acid the large percentage of silver interferes. In the ordinary sulfuric-acid process the insolubility of the copper sulfate in the acid and the incrustations of the bullion make the parting slow and incomplete. It is therefore at present the general practice in this country and abroad to remove the copper from such bullion by cupellation or by its conversion with sulfur into a matte.

The object of my invention is to adapt the sulfuric-acid process to the treatment of such bullion by making it possible to employ a large excess of acid for dissolving. In the ordinary sulfuric-acid process such excess of acid would be lost or can only be recovered at great cost. In my improved process, however, it is at once made available for the dissolving of another lot of bullion.

To carry my invention into effect, I subject the coppery bullion, in the order to be described, to four operations, a combination of all four being necessary.

In the following description, but merely as an illustration, I shall refer to the treatment of bullion consisting, essentially, half of copper and half of silver, with small quantities of gold, lead, or other metals.

First operation: Into a flat-bottomed cast-iron vessel which can be heated I place two and one-half ( $2\frac{1}{2}$ ) parts of concentrated sulfuric acid for one (1) part of bullion, which acid represents the stoichiometrically necessary amount for converting the copper and silver into sulfates, together with some allow-

ance for losses. A second and equal weight of the same acid is diluted with water to about sixty ( $60^\circ$ ) degrees Baumé and is stored in another vessel. The bullion, in the shape of bars, grains, or retorted amalgam, is placed into the cast-iron vessel containing the strong acid, heat is applied, and while the action of the acid on the bullion is progressing the weaker acid is allowed to flow in a small stream into the said vessel or is added in portions until it has thus been entirely spent. Copper and silver readily dissolve; but the acid becoming more concentrated by evaporation the copper sulfate gradually and finally completely separates as a powder, because, although soluble in a sufficient amount of diluted acid, it is entirely insoluble in concentrated sulfuric acid. The silver, however, remains in solution. The said high concentration of the acid ought to be delayed until most of the metal has been dissolved, in order to prevent the bullion from getting buried in the separating copper sulfate. Therefore the diluted acid is added progressively, as stated above, or in portions whenever in the judgment of the operator the acid becomes too highly concentrated; that is, when copper sulfate separates before it is desirable that it should do so.

Second operation: The clear solution of silver is removed by siphon or otherwise into another vessel, where, while still hot, it is diluted with so much water as to bring the now again fully concentrated acid back to sixty ( $60^\circ$ ) degrees Baumé. On cooling crystals of silver sulfate will separate, leaving as "mother liquor" essentially the same volume of acid of the same strength of about sixty ( $60^\circ$ ) degrees Baumé, which had been prepared and utilized in the first operation. It will serve now for dissolving another batch of bullion.

Third operation: To the residue in the cast-iron vessel, which consists principally of copper sulfate, there is now to be added the same amount of concentrated sulfuric acid originally employed, that is, two and one-half ( $2\frac{1}{2}$ ) parts of acid to one (1) of bullion. By heating and stirring the copper sulfate is freed from the silver sulfate, which in solution or otherwise still adheres to it, such sulfate dissolving in the comparatively large



amount of fresh acid. The residue thus purified is ladled out, leaving behind in the cast-iron vessel an amount of strong acid which is essentially the same as originally employed in the first operation, which will serve now in its stead for dissolving an equal amount of the same bullion as has been previously treated.

Fourth operation: The residue removed in the third operation is placed into a lead-lined vessel and is treated with so much water and steam as to produce a concentrated solution of copper sulfate, which, after treatment with metallic copper for desilverization, is run off into another vessel for crystallization into blue-stone.

Thus at the end of the four operations described above there is on hand the same amount of strong and weak acid as at the beginning of the first operation. While in the example illustrated the two and one-half ( $2\frac{1}{2}$ ) parts of strong acid represent the actual consumption, stoichiometrically or otherwise, which only slightly varies according to the nature of the bullion treated, it is evident that the volume of diluted acid of about sixty ( $60^\circ$ ) degrees Baumé may be materially increased or diminished, as circumstances may prescribe, the mother liquor returning for reutilization the amount of diluted acid which had been previously utilized.

The crystals of silver sulfate are mixed with charcoal and melted in a crucible into metallic silver or are otherwise brought to the metallic state. The crystals of copper sulfate or blue-stone are also mixed with coal and melted into copper or are otherwise utilized.

The residue left in the lead-lined tank referred to above is washed and melted into a bar. It contains all the gold and a few per cent. of the silver which the bullion treated did contain, and may be parted for gold and silver by the usual sulfuric-acid process, by which I understand here, as also where it has been mentioned previously, the process practiced, for instance, at the United States mints and assay offices.

Having fully described my invention, I do not claim the separation of crystals of silver sulfate, which forms the subject of United States Patent No. 401,828, granted to me April 23, 1889; but

What I claim, and desire to secure by Letters Patent, is—

The process of refining coppery silver bullion, which consists of the following successive operations, to wit: heating and dissolving the bullion in strong sulfuric acid, and during this operation progressively adding diluted sulfuric acid, separating the resulting copper sulfate by boiling to high concentration, separating the silver solution from the precipitated copper sulfate, diluting it with water and cooling, thus precipitating the silver as silver sulfate and leaving diluted acid, washing the precipitated copper sulfate with strong sulfuric acid to remove any adhering silver sulfate and reutilizing the diluted and strong acid thus obtained for dissolving fresh bullion, substantially as set forth.

FREDERICK GUTZKOW.

Witnesses:

BELLE A. CURTIS,  
EDW. WOLLAFRATH.