

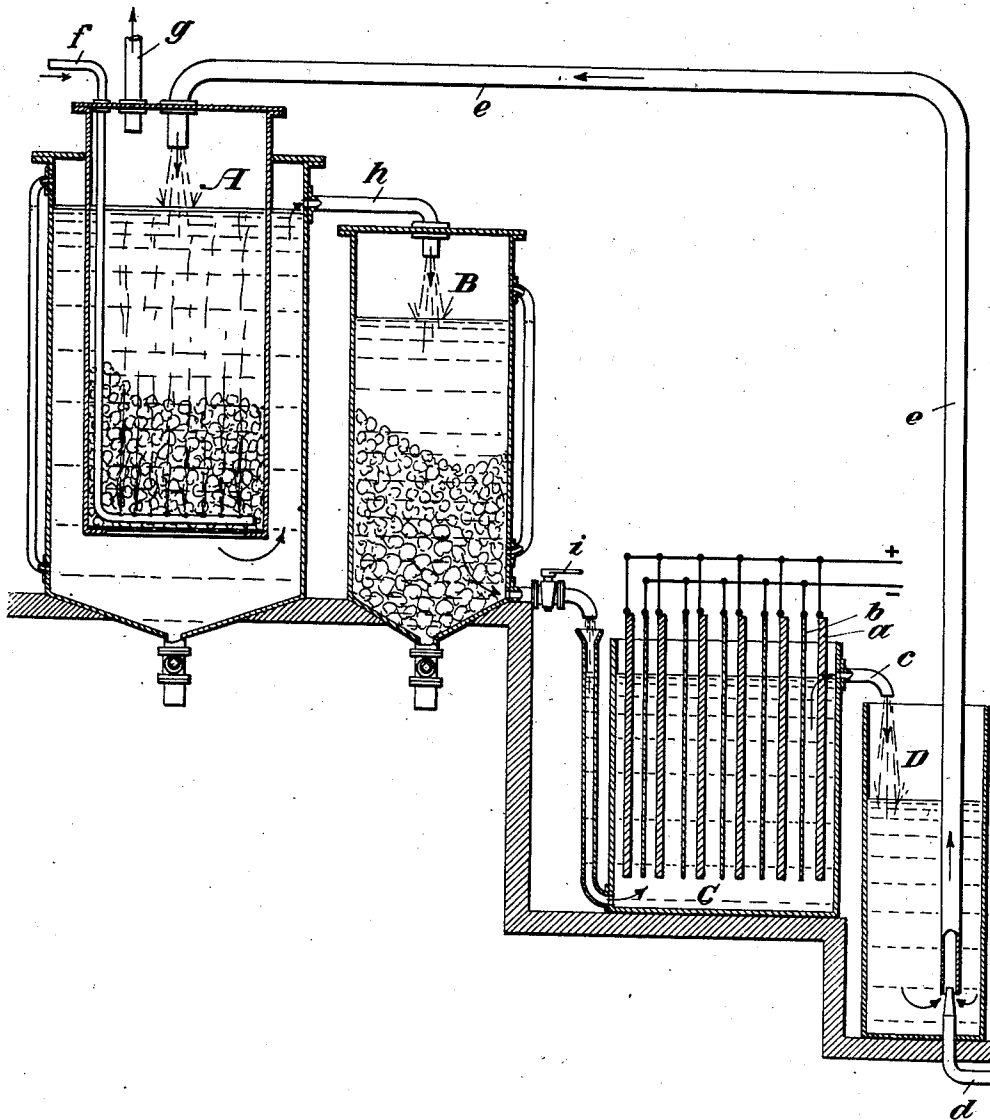
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PROCESS OF ELECTROLYTICALLY REFINING COPPER OR COPPER ALLOYS

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UNITED STATES PATENT OFFICE

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PROCESS OF ELECTROLYTICALLY REFINING COPPER OR COPPER ALLOYS

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Our invention relates to a new process of electrolytically refining copper or copper alloys and to an improved apparatus for this process.

In the electrolytic refining of impure copper part of the impurities goes into the sludge and part dissolves in the electrolyte and gradually becomes more and more concentrated therein. For each quantity of impurities that dissolves in the electrolyte the electrolyte becomes poorer in the working to the extent of the chemically equivalent quantity of copper. This phenomenon occurs to a relatively unimportant extent in the case of the usual commercial copper of the copper refineries which work with a pre-refined material of 98% purity. If, however, one commences to refine alloys which are poor in copper and contain rather large quantities of impurities, one soon arrives at conditions in which the whole refining process together with the subsidiary operations connected therewith of working up the liquor become troublesome and inconvenient. The point will soon be reached at which the electrolyte has been rendered poorer in copper to such an extent that the copper separates at the cathode only in a powdered or spongy condition. In order to keep the copper concentration in the electrolyte constant to some extent it has been necessary to add copper sulphate continually to the electrolyte. Such a mode of operation is economical only in processes in which the copper sulphate is obtained as a by-product. These conditions also obtain in the case of copper alloys which contain rather large quantities of other soluble metals, such as nickel, cobalt, etc. If copper bronzes, i. e., alloys containing rather large amounts of tin—are treated whilst employing the usual copper-containing electrolytes, the tin in the form of stannic acid goes into the anode sludge, so that the above mentioned impoverishment as to copper itself does not take place. The stannic acid separating out gives rise, however, to other disturbing factors. It is known that the larger part of such stannic acid separates out very readily in colloidal form. There have been employed for precipitating the stannic acid various processes

which are based on heating and then suddenly cooling the liquor outside the baths, or on the addition of certain substances to the liquor etc., all being processes which complicate the operation.

Attempts have for a long time been made to increase the copper content of the liquor or to keep it constant in some other way. As such an attempt may be mentioned the use of electrolytes containing cuprous chloride. It should however, be noted that in the case of the known experiments it is a question of doubling the yield per ampere-hour, and thus reducing the size of the plant, by using a monovalent copper.

Now the object of the present invention is likewise to use a cuprous chloride solution as electrolyte, but to keep its copper content constant by special means. If a cuprous chloride solution be used as electrolyte, the liquor flowing from the baths can, according to the invention, be oxidized to cupric chloride by the addition of oxidizing means and this cupric chloride can be reduced to cuprous chloride by taking up suitable quantities of copper whereby the copper content is restored to the original percentage.

This process is especially suitable for refining alloys of copper which contain rather large quantities of nickel, cobalt, tin etc., or admixtures which are likewise soluble in the cuprous chloride electrolyte.

As oxidizing means for the oxidation of the cuprous chloride to cupric chloride there is preferably employed a gaseous agent such as, for example, air or chlorine. For the reduction of the resulting cupric chloride solution it is most advantageous to use, instead of pure metallic copper, black copper which it is intended to refine or the copper alloy itself which it is intended to refine.

It is evident that the electrolyte will, in the course of working, become richer in the soluble admixtures to the copper, such as zinc in the form of zinc chloride, nickel in the form of nickel chloride, etc., and consequently from time to time a purification of the electrolyte by removing these compounds must be undertaken. This purification may be effected by one of the commonly known

chemical processes. However, an electro-chemical process can also be employed for this purpose. In the process, after removing the last remnant of copper from the electrolyte the remaining components—for example nickel, tin, or zinc—are separated cathodically in accordance with their separation potentials. The chlorine produced at the anode at the same time can be again used as oxidizing means as above described.

It has been found to be advantageous for carrying out the aforesaid process to add from time to time to the electrolyte during the oxidation stage a small quantity of hydrochloric acid—for example 10 to 20 grains per liter; it is likewise advantageous to add a colloid—for example 1 gram of gelatine per liter of electrolyte—to the electrolyte for the purpose of obtaining a good cathodic deposit of copper.

The following is an example of a mode of carrying out the invention. Let it be assumed that an alloy of copper, nickel, and zinc, containing about 70% of copper, 20% of nickel, and 10% of zinc, is to be refined according to the new process. As electrolyzer there is employed one of the known usual arrangements in which anodes and cathodes are opposite to each other—preferably, without the interposition of a diaphragm. As the cathode, a plate of electrolytic copper can be employed whilst suitable pieces of the alloys to be refined can serve as the anode. The refining can be carried out, for example, with the usual current strength—i. e., 100 amperes per square metre—and one of the usual voltages—i. e., about 0.3 volt in the case of a distance of about 5 cms. between the electrodes. The temperature is advantageously kept at 45°–50° C. The refining is carried out as follows:—The electrolyte, containing copper as cuprous chloride besides a little free hydrochloric acid, for example, 10 to 20 grams per liter, and a little common salt, for example, 150 grams per liter, flows in the usual manner into the bath and, after flowing through the bath, leaves it in the manner that is usual in the case of refining baths. The electrolyte, now poorer in copper, is then first conducted either circulating continuously or in discontinuous manner into the oxidation vessel into which air or chlorine is blown and which in addition contains copper, advantageously the copper that is to be refined, in the form of granules, strips of plate, or in some other desired form, so that directly after the oxidation that takes place the reduction of the cupric chloride to cuprous chloride is undertaken by these pieces of metal. In order to obviate the presence of any unreduced copper chloride, the electrolyte is advantageously passed into a further vessel charged with copper in the above mentioned state (granules, etc.) before it flows into the bath. Instead of employing a single bath, naturally in larger plants baths arranged preferably in cascade would be used. From time to time the electrolyte, when containing large quantities of nickel chloride and zinc chloride, is freed from these by one of the usual chemical processes.

The accompanying drawing is a diagrammatic vertical section of an apparatus embodying the present invention and suitable for carrying out the improved process. This apparatus consists of four main parts, viz.: The combined oxidation and reduction vessel A, the reduction vessel B, the electrolyzer C and the storage tank D. The electrolyzer C is filled with the solution of the electrolyte, into which dip the anodes *a* made of carbon or other suitable insoluble material and the cathodes *b* made, for instance, of sheet copper. It will be understood that during the refining of crude copper or copper alloy, such material will form the anode; while for the extraction of the copper or other metals contained in the electrolyte, an insoluble anode must be used. The electrolyte solution may pass through an overflow *c* from the electrolyzer C into the storage tank D, from which it is propelled upwardly through a pipe *e* by means of a pumping device of any suitable character (not shown), which is connected with the pipe *d*. The pipe *e* discharges the liquid into the combined oxidation and reduction vessel A. The latter is filled with copper in the nature of grains. Into this vessel there is also introduced through the pipe *f* a stream of oxidizing gas, the unabsorbed or unused part of which escapes through the outlet *g*. The treated electrolyte solution passes through a pipe *h* into the reduction vessel B, likewise containing a filling of copper in the nature of grains. From the reduction vessel B the electrolyte solution is discharged into the electrolyzer C through an outlet controlled by a cock *i*. In operation, the cock *i* is opened just sufficiently to cause only such an amount of electrolyte solution to flow back into the bath as has been treated in the manner described above. The arrows indicate the path of electrolyte solution and of the oxidizing gas.

Copper-tin alloys can also be refined according to the above process since tin is likewise soluble in hydrochloric acid solution.

What we claim as our invention and desire to secure by Letters Patent is:—

1. The process of electrolytically refining copper or copper alloys which comprises using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, said copper or alloys being used as the anode, converting the cuprous chloride after completion of the electrolysis into cupric chloride solution, acting thereon with metallic copper for reducing the cupric chloride substantially completely to cuprous

chloride solution, and re-using the latter as electrolyte.

lyte, which is brought back to the electrolyzer, and adding a colloid to the electrolyte.

In testimony whereof we affix our signatures.

MARTIN HOSENFELD.
GÜNTHER HÄNSEL.

2. The process of electrolytically refining copper or copper alloys which consists in using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, said copper or alloys being used as the anode, exposing the cuprous chloride solution after completion of the electrolysis to the influence of a gaseous oxidizing agent and acting thereon with metallic copper for reducing the cupric chloride solution to cuprous chloride electrolyte.

3. The process of electrolytically refining copper or copper alloys which consists in using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, bringing at least a part of the electrolyte out of the electrolyzer, converting this part into cupric chloride solution by the action of a gaseous oxidizing agent and by means of metallic copper reducing the cupric chloride solution to cuprous chloride electrolyte, which is brought back to the electrolyzer.

4. The process of electrolytically refining copper or copper alloys which consists in using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, bringing at least a part of the electrolyte out of the electrolyzer, converting this part into cupric chloride solution by the action of a gaseous oxidizing agent and bringing solid parts of the copper or copper alloy to be refined into contact with the said cupric chloride solution for reducing it to cuprous chloride electrolyte, until the original copper content of the solution is restored, and then conducting such part of the electrolyte back to the electrolyzer.

5. The continuous process of electrolytically refining copper or copper alloys which consists in using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, converting the cuprous chloride, after completion of the electrolysis, into cupric chloride solution and reducing the so produced solution to cuprous chloride electrolyte, and after depositing all the copper from the electrolyte throwing out the dissolved other components cathodically in accordance with their separation potentials, and using the chlorine produced at the anode as oxidizing agent for other spent cuprous chloride electrolyte.

6. The process of electrolytically refining copper or copper alloys which consists in using an electrolyte containing cuprous chloride, passing an electric current through said electrolyte, bringing at least a part of the electrolyte out of the electrolyzer, converting this part into cupric chloride solution by the action of a gaseous oxidizing agent, adding a small quantity of hydrochloric acid and by means of metallic copper reducing the cupric chloride solution to cuprous chloride electro-

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