

ALIEN PROPERTY CUSTODIAN

METHOD FOR ELECTROLYTICALLY REFINING COPPER AND ITS ALLOYS

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The present invention relates to a method for electrolytically refining copper and its alloys as well as for electrolytically treating copper- and copper alloy-plated metals.

In refining impure copper the electrolysis is, as a rule, effected in a solution of sulfate of copper. This method presupposes the use of coarse copper in which the traces of impurities are slight. Considerable amounts of foreign metals which are not so noble as copper, such as, for instance, zinc or nickel, impair the efficiency of this method materially so that it was not advisable to treat copper alloys, such as bronze, brass, German silver, etc., according to this method. If, for instance, an alloy containing 85% Cu and 15% Zn is refined according to an electrolytic method the copper sulfate electrolyte is so considerably contaminated with zinc after a rather short time that the deposit of solid copper on the cathode is materially impaired; furthermore, the bath voltage increases considerably as a result of a decrease in the conductivity. A separation of the zinc from an electrolyte so contaminated in the manner that the zinc precipitates in any form as a chemical compound and that the sulfate of copper remains in the solution is not possible in a solution of copper sulfate. In this case the copper must first be completely precipitated, for instance, by electrolysis and then the zinc sulfate must be crystallized out of the solution by concentrating the latter by evaporation. A complete separation of the sulfate of zinc from the sulphuric acid to be produced is only possible by concentrating the acid to a very considerable extent.

A further very great drawback of the above-mentioned method is the fact that the electrolyte becomes rapidly poor in copper if copper alloys are employed. In the treatment of a copper-zinc alloy as, for instance, above described only 85 parts go anodically into solution, whereas 100 parts are, however, deposited on the cathode. The result is that the electrolyte becomes poor in copper and that copper must be continuously added as copper sulfate or in any other form.

It has already been proposed to effect the electrolysis in the electrolyte containing cuprous chloride. When using such solutions containing chlorine ions the regeneration of the copper content of the solution may then be effected in a very simple manner if care is taken to oxidize a portion of the cuprous chloride after leaving the electrolysis to copper chloride, which, for instance, may be accomplished by the supply of air or chlorine. This solution of copper chloride is then brought in a suitable manner into contact with

copper metal or also with the alloy itself to be treated, for instance, in the form of a granulated metal. The regeneration of the copper content, thus effected, is performed according to the equation:



In the case of an electrolysis in a solution containing cuprous chloride the treatment of the solution rich in foreign metals presents, however, also the same difficulties as encountered in the copper sulfate solution.

It could be ascertained that the treatment of copper containing foreign metals by electrolysis is readily possible and that in this case all disadvantages of the electrolysis presented in sour solutions are eliminated if the electrolytic refining of copper and its alloys as well as the electrolytic treatment of copper- and copper alloy-plated metals is effected in an ammonium solution containing copper in which the copper is dissolved both in a bivalent and univalent form.

The effect of the method according to the invention as to preventing an impoverishment of the copper content in the electrolyte is explained by the fact, that during the electrolysis of a copper alloy containing, for instance, 85% copper and 15% zinc, not 85 parts of copper but 100 parts of copper go anodically into solution and this is accomplished by the additional chemical dissolution of the anode alloy in the ammoniacal solution. The reaction occurs according to the equation:



Consequently, considerably greater amounts of copper or of the alloy to be treated go anodically into solution than would correspond to the electrochemical equivalent. In this manner alloys containing rather great amounts of foreign metals, such as, for instance, German silver having 70% Cu, 20% Ni, 10% Zn as well as brass having 63% Cu and 37% Zn may be treated.

In treating such alloys it is essential according to the invention that the electrolyte has a sufficiently high percentage of free ammonia in order to attain always a rapid dissolution of the copper as an amine compound. A content of more than 10 to 15 g/l proved favorable. An electrolyte containing 20 to 50 g free ammonia per liter was employed to advantage. The higher the content of NH₃, the more rapid and easier is effected the reaction according to the above equation. Since it is, however, important to maintain the copper content as far as possible as great as at the beginning of the electrolysis it is advisable to choose

the above-indicated NH_3 percentages. In this case the losses of ammonia by volatilization are also kept at a low value. Besides copper also all other metals go into solution which are soluble in ammonia, such as, for instance, nickel, zinc, cobalt.

In keeping constant the copper content in the electrolyte it is important that the electrolyte is always properly stirred, for instance, by an agitator or also by causing a very strong circulation of the electrolyte when the same is circulated through the baths. This intense stirring of the electrolyte is necessary in order to always maintain as high as possible a percentage of free ammonia in the immediate neighborhood of the anodes. Otherwise, the purely chemical and also the electrochemical dissolution is impaired by the NH_3 impoverishment.

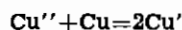
The above-mentioned percentage of free NH_3 as well as the stirring of the electrolyte are very important for the treatment of copper- or copper alloy-plated metals. It has been found that copper and its alloys may be the more completely separated from the basic metal the higher the percentage of free ammonia in the neighborhood of the alloy to be treated. The separation of the coating metal is effected the easier, the higher the content of the accompanying metals in the plated copper alloys. Thus, for instance, tombac or brass separates much easier than pure copper.

In refining copper and its alloys as well as in treating copper- or copper alloy-plated metals it is, however, not only essential that the desired reaction occurs at the anode, i. e., the metals go into solution or other metals remain undissolved but that at the cathode a highly pure copper deposit of such nature be produced as to meet the requirements and to ensure the efficiency of the method. Copper separated in spongy form requires the additional work of the reducing refusion in the flame furnace, since the copper when removed from the electrolyte bath easily converts into oxide.

According to the invention it has also been possible to separate copper at the cathode in a solid and compact form. Accordingly, a solid and compact deposit of copper will be only produced at the cathode from an ammoniacal solution of carbonate of ammonium containing copper if the copper is contained in the solution both in the bivalent and in the univalent form. It has been found that a solid copper deposit occurred if instead of cupric salt a cuprous compound, for instance, cuprous oxide was employed in the electrolyte. It was also found that for the production of solid and compact deposits it is not necessary to employ a pure cuprous salt solution but that it suffices if the electrolyte contains besides cupric salt a univalent copper salt. Thus, for instance, by the use of an ammoniacal cupric salt solution as an electrolyte, provided that during the electrolysis the electrolyte has been thoroughly stirred, copper was first deposited in a spongy to fine grained form in the case of a cathodic current density of 100 amp/m². Only when the electrolysis has been continued for some time, i. e., when cuprous copper has been produced from the cupric copper by a thorough stirring of the electrolyte the cathode deposit became more and more solid. The brown to dark red color of the deposit changed into bright red. The copper became solid and compact and could no longer be stripped.

The percentage of cuprous ions necessary for the electrolysis is maintained constant in the

bath in a rather simple manner by stirring very thoroughly the electrolyte. According to the already above-mentioned reaction equation



a sufficient amount of cuprous ions will then be always available. When circulating in operation the electrolyte, for instance, through the baths it has proved sufficient if the liquid in the electrolyte tank is renewed every hour. The speed of circulation is considerably higher than in the case of the usual cycles in which the liquid is renewed every 2½ to 3 hours. In order to prevent oxidizing influences or to maintain as high a cuprous ion concentration as possible in the bath liquid and to prevent losses of ammonia the bath is preferably poured on with oil which should not form an emulsion therewith, notwithstanding the intense agitation of the electrolyte. For instance, the pouring on of the bath with paraffin oil to a height of 1 to 2 cm proves sufficient. This covering of the bath has, however, still another important advantage in that the volatilization of ammonia is thereby prevented to a rather great extent. The losses of ammonia occurring as a result of the volatilization are so low as to be negligible and depend only upon the quantities of electrolyte which adhere to the electrodes to be removed from the bath. By suitable measures it is, however, possible to regain to a great extent these quantities of electrolyte.

For the deposit of good copper coatings it is advantageous according to the invention that the cathodic current density does not exceed 250 amp/m², otherwise the copper deposits are of a grained to spongy nature. The current densities may be chosen the higher, the higher the percentage of univalent copper in the electrolyte.

For the deposit of the copper it is advisable to choose cathodes of iron-, aluminum-sheet or of any other metal which is insoluble in the electrolyte to be used or is only soluble to a slight extent. Such sheets have the great advantage that the copper may be removed in a simple manner in thin sheets or also in plates if the cathode edges are insulated, for instance, by wooden ledges, rubber tube or the like.

Ammoniacal copper solutions which produced by dissolution of copper carbonate or copper sulfate with the aid of an exactly necessary amount of ammoniacal liquor or a slight excess thereof, for instance, with a copper content of 7 to 10 g/l normally produce a bath voltage of 3.5 to 5.0 volts. To increase the efficiency of the method according to the invention as low a bath voltage as possible is essential. Thus by adding suitable carbonates it is possible to reduce the bath voltage considerably, which is very important for treating plated metals. A solution which, for instance, contains

Cu	-----	g/l
(NH ₄) ₂ CO ₃	-----	20
Na ₂ CO ₃	-----	100
Free NH ₃	-----	30

in the case of a distance between the cathodes of 40 cm presents a voltage of about the order of 1 volt and less. This measure proves then to be very advantageous if the relatively wide anode cages must be employed for treating plated metals, sheet strips etc.

It has been found that the electrolytic refining of copper and its alloys as well as the electrolytic treatment of copper- and copper alloy-plated

metals may be effected with a considerably higher current utilization at the cathode if the electrolysis in a solution of ammonia containing copper and ammonium carbonate and in which the copper is contained both in bivalent and univalent form has an alkali carbonate content of more than 100 g/l electrolyte.

The effect of the higher percentage of alkali carbonate may be so explained that the purely chemical redissolution of the copper already deposited on the cathode is prevented owing to the presence of alkali carbonate in the ammoniacal electrolyte, this being the more the case the higher the alkali carbonate content. The separation of the copper from plated iron is, however, effected normally the more rapid, the lesser alkali carbonate is contained in the electrolyte. In order to effect a proper electrolysis it is, however, very essential that the electrolyte continuously retain the same composition. This condition is, however, only to be fulfilled if it is feasible to render as equal as possible both the cathodic and anodic current utilization. Thus, for instance, a continuous increase of the copper content in the electrolyte occurs by an increased anodic copper dissolution in the case of an electrolysis with an anodic current utilization of 200% and a cathodic current utilization of only 35%. Such conditions as to the current utilization are present, for instance, in an electrolyte having a low percentage of alkali carbonate (about 50 g/l). By the increasing copper content considerable amounts of free ammonia and ammonium carbonate are also chemically combined in the electrolyte owing to the formation of complex copper amine salts. It follows that in the long run the electrolyte attains the maximum percentage of copper, thereby preventing completely an anodic dissolution of copper.

To remove these difficulties it is in the long run essential that the cathodic current utilization be kept as high as possible in order to approach as far as possible the anodic current utilization.

A series of tests, carried out for improving the cathodic current utilization in an electrolyte containing 20 g/l copper, 50 g/l ammonium carbonate and 30 g/l ammonia, gave the following percentage cathodic current utilization by increasing the content of carbonate of sodium:

Addition of Na_2CO_3	Cathodic current utilization in percent
0	0
50	36.8
100	45.0
150	80.2
200	80.2

The method according to the invention may be adapted to the various requirements. Thus, for instance, when employing an electrolyte containing 200 g/l carbonate of alkali iron parts will be practically completely decoppered in the case of an anodic current utilization of about 120%. If the electrolysis is effected for a somewhat longer time in the manner just described, in which case a complete separation of copper occurs the current utilizations may be so adjusted that they are practically of the same value. Thus, for instance, with an electrolyte containing 20 g/l copper, 100 g/l carbonate of ammonium, 200 g/l carbonate of sodium and 15 g/l ammonia a cathodic current utilization of 83.11%

and an anodic current utilization of 87.6% might be obtained.

It has further been found that by the addition of other metal carbonates, metal oxides or metal hydroxides soluble in the electrolyte a considerable increase in the cathodic current utilization may be attained during the electrolysis. The above-mentioned or similar compounds must be present in a form which brings about an increased tendency of free ammonia and ammonium carbonate to the formation of corresponding amine salts. Thus, for instance, the cathodic current utilization in an electrolyte containing 20 g/l copper, 100 g/l carbonate of ammonium, 100 g/l carbonate of sodium and 30 g/l ammonia might be increased by adding zinc oxide from 35.3% to 66.2%. In this case the solution contained 15 g/l zinc.

It must be noted, when adding other metal compounds besides the carbonate of alkali that in the case of a very high percentage of carbonate of alkali, such as, for instance, 200 g/l electrolyte, a further increase of the cathodic current utilization no longer occurs.

Furthermore, it has been found that the temperature of the electrolyte exerts a very considerable influence on the electrolysis. Thus it has been found that temperatures between 25 and 40° centigrade present particular advantages as to the compact deposit of copper or the production of smooth coatings. In the case of lower temperatures of the electrolyte, for instance, of about 20° centigrade, hitherto employed as a rule, it is true that solid coatings are produced which, however, present depending upon the agitation of the electrolyte more or less great excrescences (warts, long threads etc.) which fall off very easily from the cathodes and are besides a continuous danger as to the formation of short circuits.

Two electrolytic tests, in which according to the invention an alkali carbonate content of more than 100 g per liter was employed and the electrolyte temperature amounted to about 35° centigrade, gave the following current utilizations:

	Test 1	Test 2
Cathodic current utilization	Per cent 97.6	Per cent 97.8
Anodic current utilization	99.1	100

The electrolyte employed in this case had the following composition:

Copper as sulfate of copper	20 g/l
Carbonate of ammonium	75
Carbonate of sodium	200
Ammonia	30

The cathodic current density amounted to about 150 amp/m².

In the treatment of plated iron or aluminum plates the electrolysis may be exactly controlled by reference to the bath voltage; whereas at the beginning the voltage amounts to about 0.6 to 0.8 volt and during the electrolysis increases to about 1 volt, the voltage increases at the end of the electrolysis, i. e., when the coating metal is practically separated and attains values from 1.5 to 2 volts and more. If after the increase in voltage occurring at the end of the electrolysis constant voltage values are again measured, this is a sign that the coating metal, such as, for instance, cop-

per or tombac, is completely separated from the basic metal.

To produce the electrolyte suitable for the electrolysis in a simple and economic form, it has proved very suitable that a solution be employed which contains in a dissolved state the copper as cupric salt, for instance, as carbonate of copper or sulfate of copper. This solution is then intimately agitated in the electrolyte container itself or in a particular container in which copper or its alloys or also metals plated therewith are contained in a sufficient quantity so that according to the above-mentioned equation the bivalent copper is converted to the greatest extent into the univalent form. If the desired percentage of cuprous copper is attained, for instance, 10 g/l, the electrolysis is initiated, whereupon the copper separates in a solid and compact form presenting a bright red color.

Example 1

An alloy containing 63% Cu and 37% Zn is subjected at a cathodic current density of 100 amp/m² to the electrolysis in a solution which contains per liter

Cu	g/l	20
(NH ₄) ₂ CO ₃		100
Na ₂ CO ₃		100
Free NH ₃		30

The alloy to be treated which, for instance, is used in the form of strips of sheet metal is inserted into the bath in a suitable manner with the aid of iron anode cages. The electrolyte is thoroughly agitated by circulation, the speed of circulation being maintained in such a manner that the bath liquid is renewed in the electrolyte cell every hour. The bath voltage mounts from 0.7 to 0.9 volts. The copper is deposited in a solid and compact form onto the sheet iron cathodes to be employed. In the case of a relatively long duration of the electrolysis when the copper sheet has attained, for instance, a thickness of about 2 to 3 mm, the copper sheet is removed from the iron base. The copper produced shows a high purity as is the case with electrolytic copper. The electrolytic conductivity of the copper produced was the same as that of the electrolytic copper produced in a known manner during the electrolysis from a solution of sulfate of copper.

Example 2

Copper-plated steel iron cuttings are placed in a basket surrounded with wire gauze and then subjected to the electrolysis in the same manner as in Example 1. By maintaining the cathodic current density of $D_K=100$ amp/m² solid and compact copper is deposited onto the cathode plate. The bath voltage amounts at the beginning of the electrolysis from 0.7 to 0.9 volts. Only towards the end of the electrolysis if practically all copper has been deposited the voltage increases to a slight extent. At voltages from 1.5 to 2 volts the separation of the copper from the iron is terminated, thus leaving at the anode an iron free of copper.

Example 3

Cuttings of copper-plated aluminum sheet which is employed, for instance, in the form of strips are placed in a suitable manner in an anode cage and are subjected to the electrolysis as in instances 1 and 2. The copper separates

from the aluminum and is deposited onto the cathode in a solid form. At the beginning of the electrolysis the voltage amounts to 0.6 volt. When the voltage attains a value from 1.9 to 2.0 volts the electrolysis is interrupted, since the copper has then been completely separated from the aluminum, thus leaving at the anode the aluminum sheet free from copper. The copper was deposited as in the instances 1 and 2 on iron cathodes and separated from the sheet when it attained a sufficient thickness after removing the edge insulation. Instead of iron also aluminum cathodes are employed in this case in which the removal of copper from the cathode was effected in the same manner as in the case of iron cathode plates.

In treating copper alloys, particularly plated metals, in ammoniacal lyes the solutions become gradually rich in metals besides copper contained in the alloys, for instance, zinc and nickel. If the solutions are rich in these foreign metals beyond a certain degree the copper electrolysis is impaired. While pure ammoniacal copper solutions or such poor in foreign metals produce under circumstances solid deposits the latter become under the same circumstances but with higher percentages of foreign metal more granular and brittle until finally they are converted in the case of very great amounts of impurities into a useless spongy form. To ensure a good deposit of copper it is therefore necessary to maintain the solution as pure as possible; the electrolyte must be freed of the foreign metals at given intervals in order that its percentage of impurities does not exceed the permissible maximum value.

According to the invention it is possible to precipitate in a very simple manner the foreign metals from the ammoniacal copper solution or to purify the solution to such an extent that it causes no difficulties when used again for the electrolysis. Various tests have shown that by concentrating the contaminated ammoniacal copper solution by evaporation a precipitation of foreign metals in the form of hydroxides occurs, whereas the copper remains surprisingly in solution. With an ammoniacal solution containing 20 g/l copper and 30 g/l zinc a zinc hydroxide precipitation sufficient for the operation might be attained if the solution had been concentrated by evaporation to 50% of the original quantity. Under these circumstances 65.5% of the zinc contained in the solution could be precipitated, whereas at the same time only 1.1% of the copper contained in the solution before the concentration by evaporation was converted into hydrate deposit. The relationship between the precipitation of zinc and the degree of concentration by evaporation will be apparent from the following table:

Degree of concentration by evaporation in per cent	Decrease of the metal content in per cent referred to the metal quantity before the concentration by evaporation		Metal contents of the dried residue in per cent	
	Copper	Zinc	Copper	Zinc
20	0	12	0	41.1
50	1.1	65.5	0.2	37.8
60	17.7	81	4.1	34.5

As will be seen from the above table it is possible by properly selecting the degree of con-

centration by evaporation to precipitate to a rather great extent the zinc concentrated in the solution, while the percentage of copper remains practically constant. The ammonia volatilized during the evaporation is then regained in a particular condensation system. A complete separation of the zinc, as is required, for instance, in analytic work is not required in this connection, since it is only essential when using the electro-

lyte in circulation to precipitate such a great amount of foreign metal that the copper electrolysis may function without any disturbances. According to the same method also other metals besides zinc such as, for instance, nickel and cobalt which are soluble in an ammoniacal solution may be separated from the copper.

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