J. COULSON.

ELECTROLYTIC PICKLING PROCESS.

APPLICATION FILED NOV. 3, 1917.

1,347,897. Patented July 27, 1920.

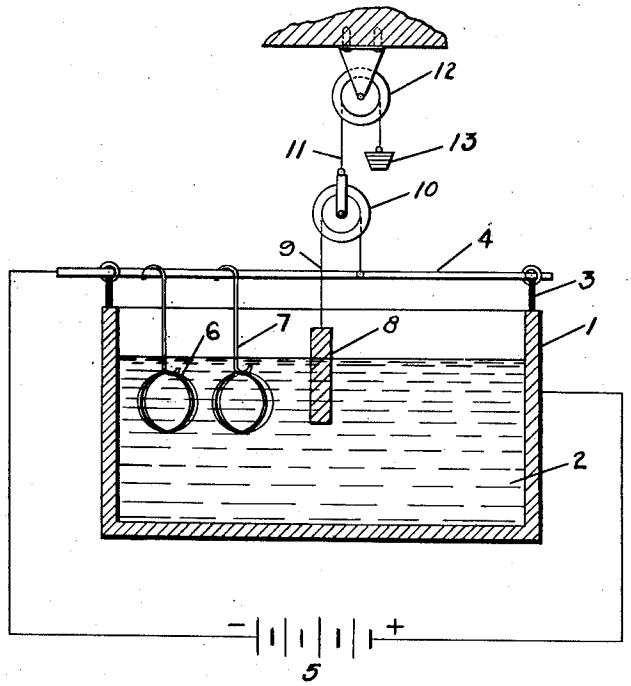



Fig. 1.

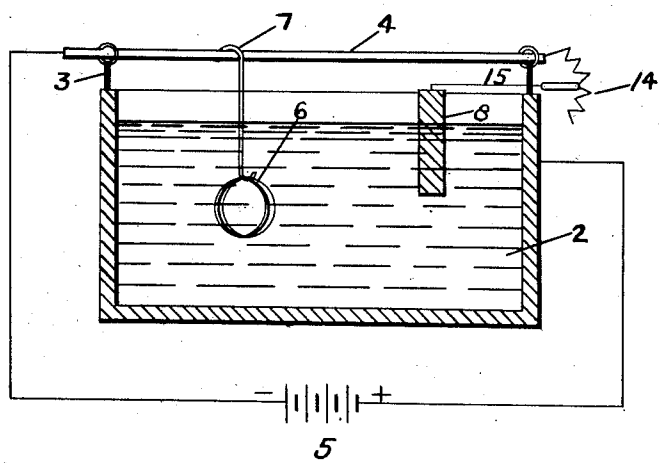



Fig. 2.

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## ELECTROLYTIC PICKLING PROCESS.

1,347,897. Specification of Letters Patent. Patented July 27, 1920.

Application filed November 3, 1917. Serial No. 200,043.

*To all whom it may concern:*

Be it known that I, JOHN COULSON, a subject of the King of Great Britain, and a resident of Wilkinsburg, in the county of Allegheny and State of Pennsylvania, have invented a new and useful Improvement in Electrolytic Pickling Processes, of which the following is a specification.

My invention relates to a process of electrolytically pickling copper, and it has for one of its objects to provide a method of removing the surface scale and other impurities from copper articles and structures.

Another object of my invention is to provide a process of pickling copper that shall be cheap and rapid in operation.

A further object of my invention is to provide a method for the recovery of copper which may be set free in the disassociation of surface scale.

A further object of my invention is to provide a method for keeping in solution, impurities which may be present in the electrolytic bath, and which would otherwise be deposited upon the copper body undergoing treatment.

A further object of my invention is to provide a method whereby leaks in the containing tank, or accidents to the electrolyte, will not cause considerable loss of copper.

A still further object of my invention is to provide a continuous process of pickling in which the containing tanks may be kept in continuous operation and the electrolyte may remain in perfect operating condition throughout the process.

It is well known that copper loses much of its ductility when it is cold rolled, drawn or subjected cold to mechanical work. It is, therefore, often necessary to work it while hot, and, in this state, it oxidizes very readily. In many cases, the oxid scale thus formed must be removed, and the most common method of removal of this scale is to pickle the copper in an aqueous solution of sulfuric acid. Such a pickling bath, however, attacks not only the oxid but also the metal, which is brought into the solution as copper sulfate. If the copper, in solution, which amounts to many thousands of pounds per week, where pickling is necessary on a large scale, is to be recovered, a deposition process must be resorted to, but great quantities of the copper sulfate are lost by leaks in the tanks and by accidents during operation.

According to my invention, the copper body to be pickled is made the cathode in an electrolyte of dilute sulfuric acid, a lead containing tank serving as the anode. The arrangement of the apparatus is such as to permit the articles being treated to be attached to the negative pole of the source of electric current before entering the electrolyte in order to prevent, from the outset, electrolytic action of the current upon the metallic copper. The copper oxid is, however, reduced to metallic copper by nascent hydrogen evolved from the electrolyte at the cathode. This process reduces the oxid very rapidly.

In order to recover, from the electrolyte, the copper which is present in the form of copper sulfate, I provide a third or auxiliary electrode which may also be electrically connected to the negative terminal of the source of electrical energy. Copper from the electrolyte is deposited upon this auxiliary electrode and is thus recovered.

In the drawing, Figure 1 is a cross sectional view of an electrolytic pickling cell constructed according to my invention, and Fig. 2 is a cross sectional view of a modified form of pickling cell.

In Fig. 1 of the drawing, is shown a tank 1, preferably of lead, containing an electrolyte 2, preferably a dilute solution of sulfuric acid. Upon the walls of the tank are placed insulating standards 3 which support a cathode bar 4 connected to negative terminal of battery 5, the positive terminal of which is connected to the walls of lead tank 1 which serves as the anode. Articles 6 of copper, illustrated as bands or rings, which are to be treated, are suspended from cathode bar 4 by means of electrically conducting hooks 7. An auxiliary electrode 8, which may also be of copper, is electrically connected to bar 4 by a flexible conducting lead 9 which passes over a pulley 10 supported by an insulating cable 11 which passes over a fixed supporting pulley 12 and has an adjustable weight pan 13 attached to its free end to counterbalance pulley 10 and its suspended load.

In the modified form of cell illustrated in Fig. 2, the adjustable support of electrode 8, shown in Fig. 1, is replaced by a

variable-resistance connection which serves to permit control of the rate of deposition of copper upon electrode 8. Electrode 8 is connected, by conductor 15 and variable resistance 14, to bar 4.

In operation, the copper oxid of the surface scale on the objects being treated is rapidly reduced to metallic copper, the oxid entirely disappearing in from 30 to 40 seconds. The metallic copper, which drops from the bands 6, as the oxid is disassociated, reacts with the acid electrolyte to form copper sulfate. The copper sulfate acts to hold in solution in the electrolyte various impurities, such as antimony, which are invariably present in commercial sulfuric acid. With continued use of the electrolyte, it becomes richer in copper sulfate than is desirable but the excess may be reduced by depositing copper upon the auxiliary electrode 8, which is adjustably supported, as previously described. The rate of deposition may, by adjustment of the position of the electrode 8, or by adjustment of the series resistance member 14, be made the same as the average rate at which copper goes into solution from bands 6. The operating voltage is generally not more than 5 or 6 volts and such adjustment may be easily and safely made without interfering with the pickling operation.

In pickling copper, there is generally a portion of the metallic copper, resulting from reduction of the surface oxid, which adheres loosely, in the form of dust-like particles, to the objects being pickled, and such particles may be washed off very readily and recovered in settling tanks after the copper objects are removed from the picking tank.

While I have illustrated a conventional form which the apparatus for carrying out my invention may take, it is to be understood that various modifications may be made in this apparatus and in the operation of the process as described without departing from the spirit of the invention, which is to be limited only by the scope of the appended claims.

I claim as my invention:

1. The process of electrolytically pickling copper objects which comprises subjecting said objects, as cathodes, to the action of an electric current, to dis-associate the surface oxid upon said objects, and simultaneously recovering the copper which is set free on account of insufficient cohesion.

2. The process of electrolytically treating copper objects which consists in subjecting said objects, as cathodes, in an acid bath, to the action of an electric current, recovering free copper from said bath, and regulating the rate of recovery of said copper to maintain the electrolyte at substantially the same efficiency.

3. A pickling system comprising a container anode, a copper cathode having an oxid coating which is to be removed, and an auxiliary electrode.

4. The method of pickling copper objects, to remove the scale therefrom and to recover the copper, that comprises electrolytically removing the scale as metallic copper by treating the objects as cathodes in an acid electrolyte which converts the metallic copper removed to a copper salt and electrolytically depositing the copper from the salt upon a supplemental cathode disposed in the electrolyte to thereby recover the copper and maintain the electrolyte in good operating condition.

5. The method of pickling copper articles, to remove the scale therefrom without loss of the acid pickling solution employed or of the copper in the solution, that comprises passing an electric current from an anode through the pickling solution as an electrolyte to the copper objects and to a copper-receiving electrode, as a cathode.

6. A pickling system for continuous operation comprising a container anode and a copper cathode, having an oxid coating, in contact with an electrolyte, means for supplying an electric current to the electrodes to remove the oxid from the cathode, and means for constantly maintaining the electrolyte at substantially its maximum efficiency during the operation.

In testimony whereof, I have hereunto subscribed my name this 22nd day of Oct. 1917.

JOHN COULSON.