M. PERREUR-LLOYD.

ELECTROLYTIC PROCESS OF PRODUCING COPPER.

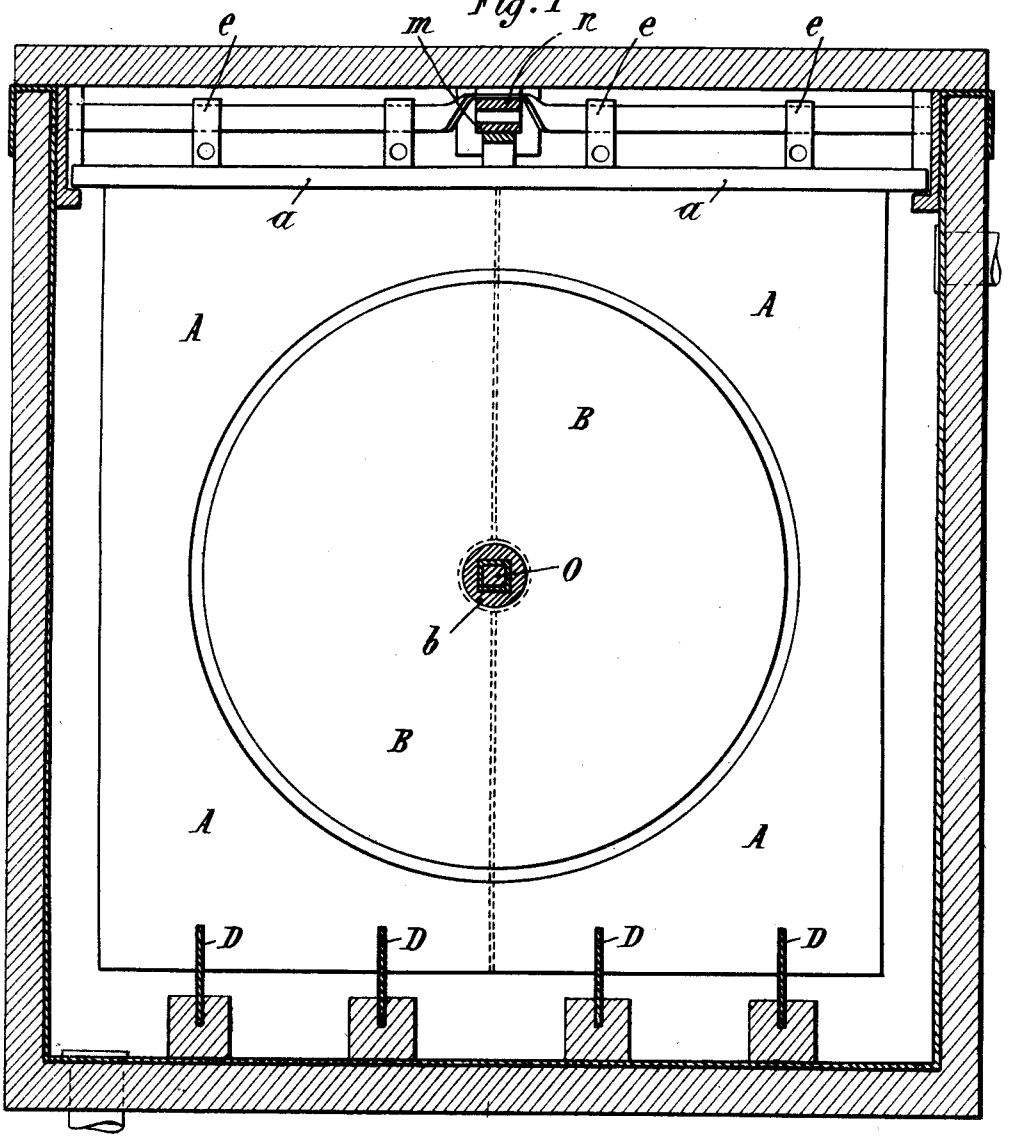
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1,133,059.

Patented Mar. 23, 1915.

2 SHEETS—SHEET 1.

Fig. 1



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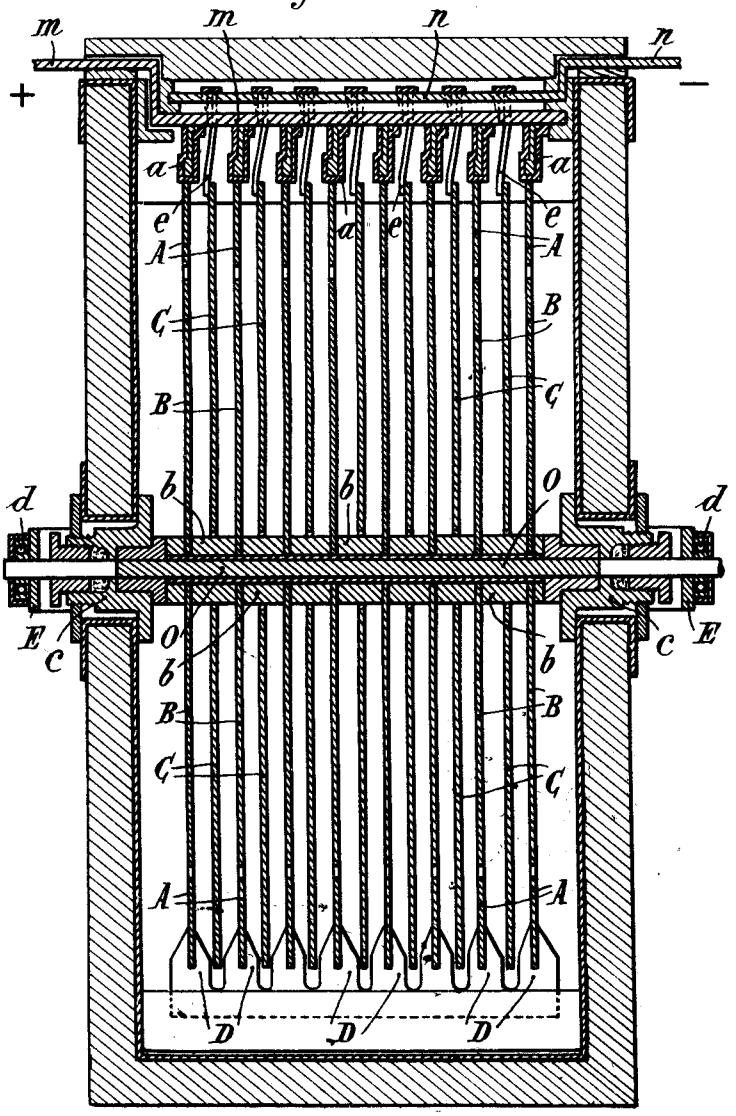
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2 SHEETS—SHEET 2.

Fig. 2



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ELECTROLYTIC PROCESS OF PRODUCING COPPER.

1,133,059. Specification of Letters Patent. Patented Mar. 23, 1915.

Application filed March 28, 1912. Serial No. 686,826.

To all whom it may concern:

Be it known that I, MARCEL PERREUR-LLOYD, a citizen of the Republic of France, residing in Boulogne-sur-Seine, Seine, France, have invented certain new and useful Improvements in Electrolytic Processes of Producing Copper, of which the following is a specification.

This invention relates to a process for the production of copper by electrolysis by means of solutions obtained by the lixiviation of copper ores, these solutions being always impure and being especially charged with iron in the state of ferric salts.

The improved process is applicable to all solutions of sulfates, chlorids and other salts of copper, but reference will be made more particularly in the following description to sulfate solutions by way of example.

When an impure solution of a copper salt is subjected to the action of an electric current, its strength decreases rapidly at the surface which is in contact with the cathode, so that it is necessary to increase the voltage in order to continue the decomposition of the solution. For instance an electromotive force of 1.26 volts is sufficient to decompose a solution of copper sulfate, but when the copper content decreases the voltage rapidly rises to 1.5 volts with a resulting decomposition of the water of the solution. The yield of the process then decreases considerably, and furthermore the increasing oxygen arising from the decomposition of the water, rapidly destroys the anodes.

It has been proposed to employ sulfur dioxid in solution in the electrolyte as a depolarizing agent which combines at the anode with the radical SO_4 resulting from the decomposition of the copper sulfate, thus facilitating the decomposition of the solution, with a low voltage, such as .6 or .7 of a volt instead of 1.26 volts which is necessary, as stated above, when there is no sulfur dioxid in solution.

The presence of sulfur dioxid in the solution has the additional advantage of preventing the harmful action of the ferric salts contained in the impure solution on the copper which is deposited on the cathode, it being well known that the ferric salts dissolve a part of the copper during its formation, so that the yield of the process is very small. This disadvantage does not exist if the electrolyte contains sulfur dioxid in solution, since the latter reduces the ferric salts into ferrous salts, which have no action upon copper. These advantages, due to the presence of the sulfur dioxid, are not sufficient to make the process practicable, because the solution of the copper salt becomes gradually weaker at the parts which are in contact with the cathode, so that a continually increasing voltage will be necessary, which rapidly becomes high enough to cause the decomposition of the water. The oxygen as thus produced, is liberated at the anode and forms with the dissolved sulfur dioxid, sulfuric acid, while the hydrogen resulting from the decomposition of the water is liberated at the cathode, forming with the sulfurous acid, *i. e.* sulfur dioxid in solution, hypo-sulfurous acid.

$$H_2SO_3+2H=S(OH)_2+H_2O.$$

The hypo-sulfurous acid is itself decomposed by the hydrogen produced by the decomposition of the water, and forms sulfureted hydrogen in contact with the cathode, on which it precipitates black copper sulfid. The products of the electrolysis which are formed at the cathode then become gradually impure and impregnated with copper sulfid.

It will be understood from the preceding explanations that if the sulfur dioxid is used as a reducing means for the ferric salts which are detrimental in their dissolving action on the copper, so as to enable the voltage to be reduced due to the depolarizing action, the use of sulfur dioxid at the same time necessitates an increase in the voltage due to the solution becoming gradually exhausted at the surface which is in contact with the cathode this increased voltage causing the water to be decomposed, which gives rise to the production of black copper sulfid. This disadvantage is due to the action of the sulfur dioxid under the conditions in which it has been used up to the present.

The process forming the object of this invention, in which sulfur dioxid in solution in the electrolyte is employed, contemplates in combination with the action of the sulfur dioxid, the constant agitation of the electrolyte. This agitation has a double result: Firstly, the surface of the electrolyte which is in contact with the cathode, being constantly renewed, the solution is only exhausted very slowly, which permits of the voltage being maintained at a very low

value, and this is an absolutely necessary condition, as has been explained above in order that there shall be no decomposition of the water and formation of black copper sulfid. Secondly, the agitation of the electrolyte renews continuously the layer of sulfur dioxid which is in contact with the anodes; the depolarization by the sulfur dioxid is therefore insured, which again permits of the voltage being decreased, while at the same time the depolarization thus produced keeps the anodes in perfect condition whether they are composed of lead or of carbon.

The improved process for the production of copper by electrolysis, which permits of the treatment of impure solutions, such as are produced by the lixiviation of ores, is thus characterized by the combination of the action of the sulfur dioxid in solution in the electrolyte (which reduces the ferric salts and prevents them attacking the copper deposited, at the same time insuring the depolarization and the diminution of the voltage) and the agitation of the electrolyte which effects the constant renewal of the electrolyte in contact with the cathode, obviates its impoverishment, and consequently the increase in the voltage, so that the latter is always maintained sufficiently low to prevent decomposition of the water and formation of black copper sulfid. This process therefore enables the advantages which may be secured by the use of sulfur dioxid in solution in the electrolyte to be obtained without its disadvantages. The combination of the action of the sulfur dioxid and the agitation gives a result which it is impossible to obtain by agitation alone, as has previously also been proposed, but without the use of the sulfur dioxid, so that the harmful effect of the ferric salts was not avoided.

With sufficient agitation of the electrolyte, keeping the sulfur dioxid in solution, it is possible to employ a current of 100 amperes or more per square meter of cathode area and to extract copper from the most impure solutions up to 0.1% while obtaining good deposits of pure and coherent copper. It should be noticed that this electrolytic process insures the production on the spot of all the acid necessary for the lixiviation of the ores. In fact, if we take for example the treatment of a solution of copper sulfate, the electrolytic decomposition results in depositing at the cathode a molecule of copper while the radical SO_4 is liberated at the anode, where it combines with the sulfurous acid in solution in the electrolyte as has been explained above, and thus forms two molecules of sulfuric acid. This depolarization is also facilitated by the salts of iron which are present in the solution under treatment; the ferrous salts being transformed at the anode into ferric salts by the radical SO_4, these ferric salts being in turn brought back to the condition of ferrous salts by the sulfurous acid with a liberation of two molecules of sulfuric acid. It is known that the sulfurous acid used for the treatment may advantageously be obtained from the roasting of the ores used.

The agitation of the electrolyte may be produced in different ways; by the movement of the electrodes or by the movement of the electrolyte. It is difficult to produce the latter easily and without inconvenience otherwise than by a blast of air which would have the effect of expelling all the sulfurous acid contained in the bath; and it is preferable to impart a movement to the electrolyte by means of the electrodes themselves. As, however, the weight of the electrodes is considerable, it is preferable only to put either the anodes or the cathodes in motion. The cathodes could be rendered rotatable by forming them of cylinders or disks secured to a shaft, but such an arrangement is costly and their effective surface is very small compared with the space occupied. The simplest and most advantageous arrangement consists in using stationary cathodes arranged on each side of the anodes, the latter, which are of lead or carbon, being constructed in two parts, one of which is stationary and the other movable.

In order that the nature of the invention may be clearly understood a preferred form of construction will now be described by way of example in reference to the drawing.

Figure 1 is a transversal section and Fig. 2 is a longitudinal section.

The electrolytic apparatus comprises a tank of wood or other suitable material in which are supported a number of rectangular or square electrodes, the anodes A B and cathodes C being arranged alternately. Each of the anodes comprises a rotating center portion in the form of a disk B, the remainder A of the anode being stationary and being suspended from a suitable supporting bar *a* secured to the top of the tank, the supporting bars *a* being also connected to the positive terminal *m* of the apparatus. The stationary portions of the anodes are held in position at their base by means of strips of ebonite or other suitable material D within slots in which the lower edges of the anodes rest. The disks B constituting the movable portions of the anodes are mounted on a horizontal shaft O carried by ball bearings *d d* fixed upon stirrups E, the shaft passing through suitable stuffing boxes *e* so as to prevent leakage of the electrolyte.

The disks are preferably secured to the shaft by means of washers or sleeves of hardened lead *b* mounted upon the shaft and

attached to the disk. The cathodes are similarly supported in the ebonite strips D at the base of the tank and are suspended at their upper edges by means of hooks *e* secured to a horizontal bar *n* forming the negative terminal of the apparatus. The cathodes, which may be of copper or any other suitable metal, can be arranged in very close proximity to the movable anodes so as to obtain a maximum effective surface for a predetermined bulk. The movement of the rotating disks is transmitted to the electrolyte so that its whole mass is properly agitated and circulated between the electrodes. The tank is preferably provided with a cover in order to avoid loss of sulfurous acid by evaporation. The anodes are, preferably composed of lead but if it is desired to economize electromotive force, carbon anodes similarly arranged may be employed.

It is found in practice that with the improved apparatus the amount of electric energy required per kilogram of copper deposited may be reduced to less than 1 kilowatt hour. In the operation of the apparatus the rapid movement of a portion of the anodes and the agitation of the electrolyte resulting therefrom are favorable to the depolarization and consequently the production of sulfuric acid which is ultimately utilized for the solution of the copper contained in the ores and also to replace that which is lost by neutralization during the lixiviation of the carbonates or of certain oxids contained in the ores.

The production by electrical means and on the spot of the sulfuric acid is of the greatest importance since it permits of employing a liquid process and electrolyzes the copper ore at the mine itself, thus obviating transport of the acid. The latter is evidently produced at a very low cost since it is manufactured in the electrolytic apparatus itself by means of the sulfurous acid necessary for depolarization, this sulfurous acid itself being obtained by the roasting of the ores when they are of the sulfid variety or from the roasting of the pyrites when the ores to be treated are oxids or carbonates of copper.

The apparatus herein set forth is claimed in my divisional application, Serial No. 723,495, filed Oct. 2, 1912.

Claims:

1. A process for the production of a metal by the electrolysis of impure solutions of salts of the metal, wherein sulfur dioxid is added to the electrolyte to be decomposed, and an active vertical circulation is produced in the electrolyte whereby the density of the bath is rendered uniform and the film of electrolyte in contact with the anodes of the apparatus is continually renewed.

2. A process for the production of a metal by electrolysis of an electrolyte yielding the metal, comprising adding sulfur dioxid to the electrolyte to be decomposed, and actively vertically circulating the electrolyte containing the dissolved sulfur dioxid in such manner that fresh portions of the electrolyte are brought into contact with the electrodes of the apparatus, and the density of the bath is rendered uniform.

3. A process for the production of a metal by electrolysis of an electrolyte yielding the metal, comprising adding sulfur dioxid to the electrolyte to be decomposed, and actively vertically circulating the electrolyte containing the dissolved sulfur dioxid by movement of an electrode of the apparatus, in such manner that fresh portions of the electrolyte are brought into contact with the electrodes of the apparatus and the density of the bath is rendered uniform.

4. A process for the production of a metal by electrolysis of an electrolyte yielding the metal, comprising adding sulfur dioxid to the electrolyte to be decomposed, and actively vertically circulating the electrolyte containing the dissolved sulfur dioxid by movement of the anode in such manner that fresh portions of the electrolyte are brought into contact with the electrodes of the apparatus, and the density of the bath is rendered uniform.

5. A process for the production of a metal by electrolysis, of an electrolyte yielding the metal, comprising adding sulfur dioxid to the electrolyte to be decomposed, and rotating an electrode on a horizontal axis parallel to adjacent electrodes, to produce an active vertical circulation of the electrolyte and to render the density of the electrolyte uniform.

In witness whereof, I have hereunto signed my name in the presence of two subscribing witnesses.

MARCEL PERREUR-LLOYD.

Witnesses:

LUCIEN MEMMINGER,

RENÉ BARDY.