M. PERREUR-LLOYD.

APPARATUS FOR PRODUCTION OF COPPER BY ELECTROLYSIS.

APPLICATION FILED MAR. 19, 1913.

1,233,906. Patented July 17, 1917.

Fig. 1

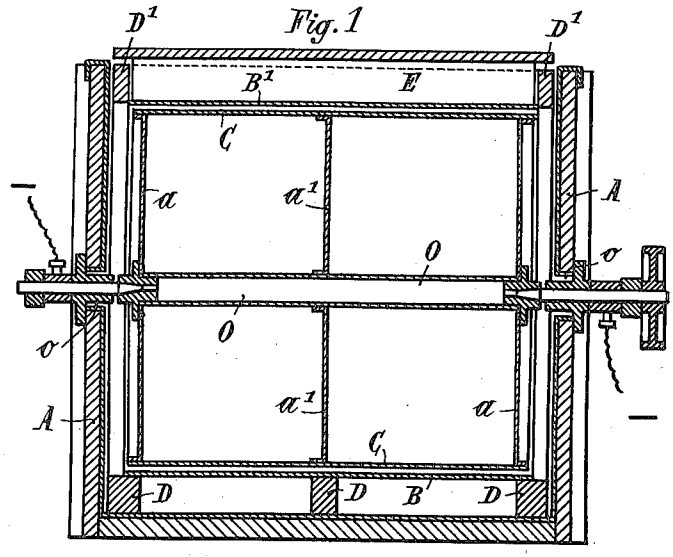
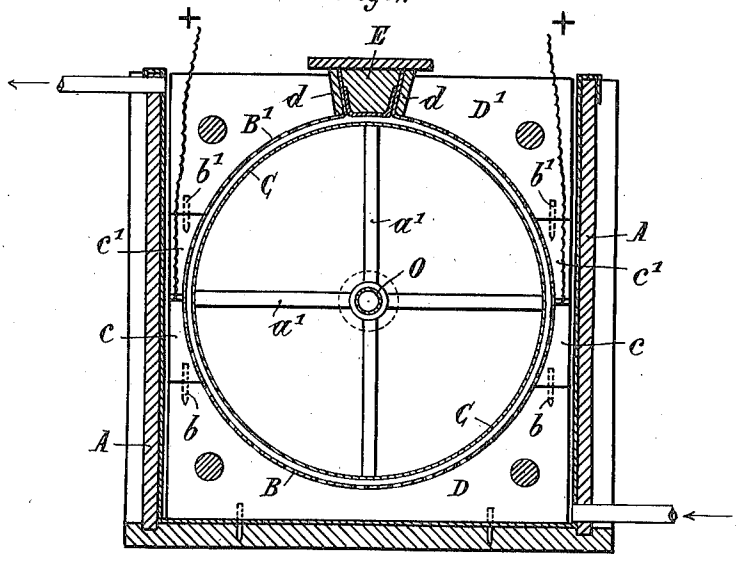


Fig. 2



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APPARATUS FOR PRODUCTION OF COPPER BY ELECTROLYSIS.

1,233,906. Specification of Letters Patent. Patented July 17, 1917.

Application filed March 19, 1913. Serial No. 755,428.

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 Apparatus for Production of Copper by Electrolysis, of which the following is a specification.

The treatment of copper ores by electrolysis as at present practised consists in lixiviating the ores (previously roasted if required) with sulfated or chlorinated solutions more or less rich in acid, and in subjecting these solutions to the action of an electric current.

It has already been proposed to employ insoluble anodes of lead or carbon in combination with fixed or rotary cathodes; also the action of the ferrous and ferric salts which are always present in the solutions obtained from the lixiviation of the ores has been recognized. It has likewise been proposed to employ sulfurous acid to facilitate the electrolysis by depolarizing the anode. These various means that have been tried have had for object to obtain good deposits of copper while expending as little current as possible and avoiding wearing away of the anodes. It has also been proposed to employ anodes of copper matte in combination with rotary cathodes and the sending of sulfurous acid into the baths.

Notwithstanding all these researches and attempts, the electrolysis of impure solutions of copper derived from the lixiviation of ores has not given entirely satisfactory results.

The most encouraging results up to the present have been obtained by employing rotary cathodes, lead anodes and solutions charged with sulfurous acid, but irregularities always occur in the electrolysis. At the end of a certain time the electrolytic deposit becomes dusty and even quite black and absolutely useless, or again, the output of the apparatus which appeared to be normal during the first days of working, diminishes gradually to almost nothing.

These irregularities in the products on the one hand and the output on the other are avoided in the process forming the subject of this invention.

As regards the irregularity of the products obtained, it is to be remarked that when a copper solution containing sulfurous acid is subjected to electrolysis in an electrolyzing apparatus with a lead or carbon anode and a cathode stationary or in motion the deposit remains good and compact for a suitably determined intensity if there is absolute parallelism between the anode and the cathode and if all points of the cathode are equally distant from the corresponding points of the anode. It is also necessary that the anodes and the cathodes shall preserve this parallel form and shall not be deteriorated or attacked. If, for example, one employs anodes of perforated lead and cylindrical cathodes of copper, the anodes must envelop the cathodes entirely and all points of the anodes must be equally distant from the corresponding points of the cathodes.

Moreover the composition of the electrolyte must be the same throughout and the agitation of the electrolyte must be sufficient to attain this result. In point of fact, when an impure copper solution charged with sulfurous acid is subjected to electrolysis, regard must be had to the liability of this sulfurous acid to be decomposed electrolytically, the consequence of which is to produce black sulfid of copper upon the cathode.

Now this decomposition occurs as soon as the voltage at any point of the electrolyzer rises in such manner as to cause decomposition of the water. This rise in voltage may occur (1) in consequence of the impoverishment of the bath at any part of the electrolyzer, (2) in consequence of the production of local couples.

As soon as this decomposition happens the following reactions occur:—

The sulfurous acid combines at the anode with the oxygen to form sulfuric acid, and the hydrogen goes to the cathode and forms hydrosulfurous acid with the sulfurous acid:—

$$SO_3H_2+H_2=S(OH)_2+H_2O.$$

Now this hydrosulfurous acid is itself decomposed by the nascent hydrogen produced by the decomposition of the water, and it forms sulfureted hydrogen in contact with the cathode, upon which it precipitates black sulfid of copper.

These reactions although known had not

hitherto been taken into consideration and their intervention has up to the present prevented the production of regular electrolytic deposits. As soon as they occur at any point the deposit becomes black there and the spot gradually spreads until it covers the whole surface of the cathode.

The only way of preventing this formation of copper sulfid is to obviate the decomposition of the water. Now for this purpose it is necessary, as above mentioned, (1) that the electrodes shall be absolutely parallel and indeformable, (2) that the electrolyte shall be homogeneous in composition throughout. In point of fact, if there is any point in the electrolysis at which the electrodes are closer together than at others as the resistance is less at this point the deposit will be more abundant there and the solution will be depleted or impoverished more rapidly at this point. As the solution becomes poorer, the voltage rises the deposit becomes less compact, then spongy and from this time the water begins to decompose and the deposit of black copper sulfid is at once seen to appear.

Moreover, as the resistance is less at this point than at others, parasitic or local couples are formed between these points of lower resistance and those of greater resistance, the copper dissolves at the points of greater resistance and deposits at the points of lower resistance, as is well known; as any formation of local couples is accompanied by decomposition of water, formation of sulfid at once occurs. To avoid this effect it is therefore indispensable that the electrodes shall be absolutely parallel to each other and indeformable. Want of homogeneity in the electrolytic bath produces the same detrimental effects, for the same reasons.

The above explains why the employment of anodes of matte (processes of Marchese and Siemens and Halsue) which dissolves in the bath and consequently vary materially in form, gives rise to considerable polarization and at the same time the deposits are defective and charged with sulfid of copper.

As soon as a cathode is covered partially or entirely with sulfid of copper, the electrolytic treatment is altogether disturbed and at last the output falls to nothing.

The present invention remedies this drawback by means of electrolyzing apparatus constructed in such manner that the electrodes have an absolutely fixed and parallel form and that the electrolyte therein is kept homogeneous in composition at all parts by a brisk agitation.

I have indicated as the second cause of the insuccess of the electrolysis, the diminution of the output which manifests itself in the known processes after a few days'-working and in such a way that at last the output becomes *nil*. The chief reason of this diminution of output lies in the intervention of the salts of iron contained in the electrolytic bath.

The electrolytic action, in the case of the electrolysis of pure solutions of sulfate of copper impregnated with acid, is as follows:

In consequence of the decomposition of the sulfate of copper, the copper is deposited on the cathode acid SO_4 encountering sulfurous acid at the anode forms therewith two molecules of sulfuric acid. With such solutions and under certain conditions of working, the depolarization is complete and the output is properly maintained.

But it is not the same with impure copper solutions containing salts of iron. It is well known, in fact, that if a solution of salts of iron is subjected to electrolysis (Tommasi "Traite d'électrochimie") the action of the hydrogen will partially reduce the ferric salts at the cathode, and the oxygen will partially oxidize the ferrous salts at the anode. It is impossible to oxidize one of these salts completely or to reduce the other completely.

There is produced a state of balance, which is attained when about 60 per cent. of the salts of iron contained are brought to the state of ferric salts and 40 per cent. to the state of ferrous salts.

If we consider what happens in the electrolysis of a solution of sulfate of copper mixed with sulfate of iron, obtained from the lixiviation of the ores, the decomposition of the sulfate of copper will give rise to the deposition of one molecule of copper, and the radical SO_4 in contact with the anode and the ferrous salts will convert the latter into ferric salts. This conversion of ferric salts will continue until all the iron salts contained in the solutions are transformed into ferric salts to the amount of 60 per cent., and this notwithstanding the presence of sulfurous acid, the action of which is but little appreciable under these conditions and does not prevent the before mentioned state of balance from being set up.

Now such a solution of ferric salts chemically dissolves the copper deposited at the cathode. This dissolving action is stronger as the proportion of ferric salts increases, and this is the reason why in an apparatus where solutions of copper sulfate charged with sulfate of iron are electrolyzed, the copper deposited electrolytically gradually dissolves chemically; and as this redissolution is proportional to the quantity of ferric salts contained in the bath, and as this quantity itself increases with the time, until the state of balance before mentioned is established, the output of the apparatus gradually diminishes and may fall to nothing after a time if the quantity of copper chemically dissolved becomes equal to or greater than that deposited electrolytically.

It has been attempted to remedy this ac-

tion of the ferric salts by employing diaphragms, but up to the present without success, and moreover the diaphragms do not prevent the diffusion while at the same time they complicate the apparatus.

The best thing is to recognize the redissolution by the ferric salts, but to effect such an increase in the rapidity of the deposit on the cathodes that the quantity of copper dissolved by the ferric salts shall be negligible relatively to the quantity of copper deposited electrolytically.

In the majority of processes hitherto proposed for the electrolysis of impure solutions the current density per square meter of cathode has not exceeded 50 amperes. In carrying out the process of the present invention the apparatus is adapted or constructed to bear currents of 400 to 500 amperes and more per square meter. Under these conditions and assuming as an example that 50 grams of copper are redissolved per hour for each square meter of cathode, the first style of working would give an output *nil*, while the second according to the new process gives an output of 90 per cent.

This last series of observations may be summed up by saying that in the electrolysis of the impure copper solutions, the iron salts contained therein are gradually converted into ferric salts until a state of equilibrium is established, that this state is reached when 60 per cent. of the iron salts are brought into the condition of ferric salts, that these salts redissolve the copper deposited at the cathode, but that in order to obtain a proper output it was necessary to find a means of considerably augmenting the quantity of copper deposited electrolytically for a given surface of cathode in a given time.

The accompanying drawings show by way of example an electrolyzer constructed for carrying out the process of the invention:

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

The apparatus is composed of a wooden vessel A lined with lead, for containing the solution of sulfate of copper and formed with openings *o* in its ends to give passage to the shaft O carrying the cylindrical cathode C, this shaft passing out through sleeves or liners of packing fitted in the openings. The cathode C is constituted by a drum formed of a plate of copper held at the ends by a crown supported by conducting arms *a* and intermediately by other arms *a'*. This cathode is so constructed and mounted as to be indeformable so as always to remain at all parts at an equal distance from the anode. The anode consists of a perforated lead cylinder formed of two semi-cylindrical portions B B'. One of these half cylinders B is held by circular wooden supporting frames D D and on which frames *c* rest and are attached by wooden pegs *b*. The other semi-cylindrical portion B' is held by the frames *c'* and D' likewise connected by wooden pegs *b'*.

At the top an opening is formed by two slightly inclined boards *d d* which connect the upper frames D'. The cylindrical surface B' of perforated lead is cut away and its edges are fixed on the oblique boards *d*. There is thus a wide upper opening in the fixed anode, which allows of inspecting the copper deposit on the cathode, and of cutting the covering of deposited copper after the operation and removing the sheet of copper obtained, without shifting the anode, this being indispensable to avoid rendering the mounting of the anode defective.

This upper opening of the anode is closed by a plug of wood or other material E faced with a sheet of lead the lower surface of which forms a continuation of the surface of the cylindrical anode.

In this electrolyzer the electrodes are of absolutely fixed shape and are parallel to each other. The electrolyte is kept homogeneous in composition throughout its mass in consequence of the brisk agitation produced by the rotation of the cathode. Moreover this rapid movement of the cathode constantly renews the layers of electrolyte in contact with the cathode and therefore permits of depositing the copper electrolytically with very strong currents, 400 to 500 amperes and more per square meter. Under these circumstances the redissolving action of the ferric salts has little effect upon the output, and the electrodes being perfectly parallel, the deposit remains sound, without production of sulfid of copper if care is taken to maintain the bath at a strength above 3 to 4 grams per liter of copper.

It should further be remarked that if the electrodes were not disposed in an absolutely parallel and regular way it would not be possible to employ such great current strengths. In fact with such strengths of current and to obtain compact copper, the electrodes have to be equidistant everywhere. For if the resistance is less at any point of the cathode than at another point, the current strength preponderates at the point of less resistance. It may therefore happen the agitation of the electrolyte sufficient to permit of a good deposit with the current strength which is appropriate at the point of greater resistance, is not sufficient for the current strength at the point of less resistance. Consequently the copper may be deposited compact at the point of great resistance and in a dusty or powdery condition at the points of less resistance,

and this would disturb the entire electrolytical operation. There must therefore be perfect parallelism between the anodes and the cathodes to permit of employing without inconvenience very strong currents.

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

An electrolytic apparatus, comprising a rotary cylindrical electrode mounted to turn on a horizontal axis, and an insoluble electrode completely circumferentially surrounding said first electrode and strictly parallel thereto, said surrounding electrode having a removable section through which the rotary electrode may be inspected and metal deposited thereon removed.

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

MARCEL PERREUR-LLOYD.

Witnesses:
RENI BARDY,
LUCIEN MEMMINGER.