

UNITED STATES PATENT OFFICE.

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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF COPPER.

No. 830,639.

Specification of Letters Patent.

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To all whom it may concern:

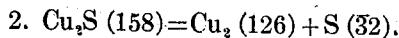
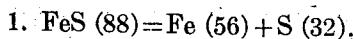
Be it known that we, JOHANNES ALBERT WILHELM BORCHERS, doctor of philosophy, professor of metallurgy, residing at 15 Ludwigswalle, Aachen, PAUL RUDOLF FRANKE, metallurgical engineer, residing at 44 Zeisingstrasse, Eisleben, and FRANZ EMIL GÜNTHER, metallurgical engineer, residing at 62 Templergraben, of Aachen, Kingdom of Prussia, Germany, have invented certain new and useful Improvements in Processes for the Electrolytic Production of Copper, of which the following is a specification.

The direct electrolytic treatment of copper matte is an old problem which, notwithstanding numerous experiments made both on a large and on a small scale and in many instances at considerable expenditure, has remained practically unsolved until the discovery of the principles constituting the basis of the present process.

The reasons for the want of success and the means whereby the difficulties may be overcome were not determined prior to experiments carried out by us.

In the experiments at Stolberg it was discovered that in the electrolysis in acid solutions of copper sulfate, of the kinds of copper matte formerly employed by the cooperation of ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, or of SO_4 ions from the sulfids forming the anode mass sulfur was deposited on the surface of the anode and the metals passed into the solution at first readily, but subsequently only with the consumption of considerable electromotive force the copper was transferred from said anode onto the cathode. Now we have discovered that the reasons for this are as follows: To overcome the affinity between Cu_2S and FeS and other sulfids requires of itself a larger expenditure of power than was allowed for in the calculations of previous experimenters. The amount per unit of volume and the mechanical nature of the sulfur that is separated out of FeS (which is the metallic sulfid occurring in greater part as a subsidiary constituent in copper matte) and that of the sulfur separated out of Cu_2S are

materially different, as a glance at the values of the molecular and atomic weights will show:



Thus for the same residual amount of sulfur there disappear in the process of solution fifty-six parts, by weight, of metal in the first case, and one hundred and twenty-six parts, by weight, of metal in the second case—that is to say, one atom of metal in the first case and two atoms of metal in the second case. The greater the percentage of contained FeS the greater the quantity and the denser the nature of the sulfur that remains behind per unit of volume on the anode.

The greater the amount of sulfur and the more densely it is deposited the more rapidly does the mechanical resistance against the access of the active constituents of the electrolyte to the anode mass which is still to be dissolved increase. The more slowly therefore the products of electrolysis formed on the still active surface of the anode are able to pass away so much easier substances which give rise to disturbing or costly electromotive counteractions are produced underneath the covering of sulfur which prevents the equalization of concentration. Naturally the amount and the chemical character of the foreign metals (which are still present in comparatively large quantities in matte poor in copper) play a certain part in the formation of such disturbing compounds (peroxid of lead, for example;) but these drawbacks are obviated without special measures in carrying out the ascertained preliminary conditions (which we shall now proceed to describe) for the electrolytic treatment of copper matte.

We have discovered that the difficulties which have hitherto hindered the electrolysis of copper matte are removed by smelting the matte to a degree of concentration of approximately eighty per cent. of copper by means of the well-known reverberatory or converter

furnaces, (preferably the latter,) casting the mass into plates or other suitable shapes and electrolyzing the latter as anodes in an electrolyte composed of acidulated aqueous solution of copper sulfate opposite to pure copper sheets as cathodes.

A concentration of seventy-eight per cent. of copper is sufficient in practice; but below this degree of concentration the difficulties which have been observed in the case of almost all earlier experiments with poorer matte increase in such a remarkable manner that a matte containing, say, seventy-two per cent. of copper may be said to be almost as unsuitable for electrolytic treatment as the matte containing fifteen to twenty per cent. of copper, which was formerly used at Stolberg.

It is not advisable to concentrate a matte to more than eighty per cent. of copper on account of the increasing separation of copper during the concentrating process. In such case the operation approaches the stages of the production of crude or black copper, whereas the object of the present invention is to electrolyze copper matte. Consequently the limits of direct electrolytic treatment of copper matte as determined by the present invention lie above seventy-two per cent of copper to, say, eighty per cent. of copper—that is to say, at seventy-eight per cent. when it is desired to restrict the separation of "bottom copper" as much as possible in the concentration by smelting.

As is well known, the concentration of copper matte can be carried beyond eighty per cent. of copper; but then separation of copper takes place in great quantities, so that in casting the concentrates into anodes there are obtained mixtures of copper sulfid and metallic separated copper and alloys of both, which naturally can also be electrolyzed. Metallic copper embedded in the matte does not hinder the electrolysis; but it is to be noted that a concentration beyond eighty per cent. of copper also increases the cost of production without obtaining any corresponding advantages.

If matte containing seventy-eight to eighty per cent. of copper be electrolyzed with a current density of about seventy-five amperes per square meter of the cathode or anode surface, the electrical pressure in the bath between the anode and the cathode will remain generally below 1.0 volt at ordinary temperature and with customary circulation of the electrolyte even after layers of sulfur of some thickness have been deposited.

Whether and how often the deposits of

sulfur must be scraped off from the anode during the electrolysis will depend chiefly on the local conditions, especially on the rate of wages and cost of power. No generally-applicable rules can be laid down on these points.

The sulfur crusts which are scraped off from the anodes or which remain as final residuals may be utilized by first lixiviating the sulfur by means of its known solvents, or by melting it out, (for instance, according to Schaffner, by means of water and steam pressure, described in Lunge, *Sodaindustrie*, 2d Edition, Vol. 2, pages 733 and 735,) or by working it up into known sulfur compounds (for instance, sulfuric acid) by means of known methods.

Any residue left after removal of the sulfur by carrying out any of these processes which may contain undecomposed sulfids and other compounds of the original constituents of the matte, and even metals, (for instance, copper and the precious metals,) is treated for the recovery of copper vitriol and the precious metals, as the case may be, like the anode mud of copper-refining works. Any nickel and other metals of the same group which may have been contained in the matte pass into the solution, but not on to the cathode. When a sufficient quantity of them has accumulated in the electrolyte, they are recovered in accordance with the known processes for treating the impure electrolytes of copper-refining works or for the separation of copper-nickel.

The technical and commercial advantages which are achieved by the hereinbefore-described manner of working are the following: The operation of smelting crude copper from concentrated copper matte (spurstein) is avoided—that is to say, electrolytic copper is obtained direct from rich "spurstein."

In the methods in use heretofore for smelting copper matte for the recovery of metallic copper in reverberatory furnaces or converters all the sulfur escaped into the air in the form of sulfurous acid. A condensation of this sulfurous acid into sulfuric acid was not possible, owing to the fact that said sulfurous acid was contained in the flue-gases of the furnace or converter in a too diluted state and was polluted through the presence of other volatile ingredients, (for instance, arsenic.)

With our process of electrolyzing the matte the entire sulfur remains in the baths as anode residuum, from which it can be recovered as solid sulfur by smelting or extraction in other ways.

The generation of gases which are difficult

to utilize and which have an injurious effect upon the vegetation in the neighborhood of metallurgical works is also avoided.

What we claim, and desire to secure by Letters Patent, is the following:

The process for the direct electrolytic production of pure copper from copper matte which consists in first bringing the copper matte to a richness of between seventy-two and eighty per cent. of copper, and then using said matte as an anode in an electrolyte composed of an acid solution of copper sulfate.

In testimony that we claim the foregoing as our invention we have signed our names, in presence of two witnesses, this 5th day of

September, 1905, respectively, 26th day of August, 1905, respectively, 30th day of August, 1905.

JOHANNES ALBERT WILHELM BORCHERS.

PAUL RUDOLF FRANKE.

FRANZ EMIL GÜNTHER.

Witnesses to signature of Borchers:

HERLA FROWERK,

FERDINAND LANGE.

Witnesses to signature of Franke:

MARIE SCHNEIDER,

EDUARD RICHTER.

Witnesses to signature of Günther:

BESSIE F. DUNLAP,

LOUIS VANDORY.