UNITED STATES PATENT OFFICE.

EUGÈNE HERMITE AND CHARLES FRIEND COOPER, OF PARIS, FRANCE.

PROCESS OF MANUFACTURING COPPER-SULFID RODS FOR THERMO-ELECTRIC COUPLES.

SPECIFICATION forming part of Letters Patent No. 685,472, dated October 29, 1901.

Original application filed February 23, 1901, Serial No. 48,462. Divided and this application filed August 20, 1901. Serial No. 72,707. (No specimens.)

To all whom it may concern:

Be it known that we, EUGÈNE HERMITE and CHARLES FRIEND COOPER, engineers, residing at 43 Rue de la Victoire, Paris, France, have invented a certain new and useful Process for the Manufacture of Copper-Sulfid Rods for Thermo-Electric Couples, of which the following is a specification.

These improvements were originally included in our application filed February 23, 1901, Serial No. 48,462, but have been made the subject of a fresh application, a division having been required by the examiner.

This invention relates to the manufacture of copper-sulfid bars of uniform electromotive force for thermo-electric couples by (*a*) casting copper sulfid, (*b*) sulfurizing the cast pieces by sulfur-vapor at red heat, and (*c*) driving off the excess of sulfur by heating in absence of air.

In 1827 Becquerel, père, showed that copper sulfid is strongly positive to ordinary copper, and he pointed out that thermo-electric couples of copper sulfid and copper yield electromotive forces greater than those yielded by any other bodies which he had tried, such as iron sulfid, manganese peroxid, &c. These researches were continued by Edmond Becquerel in 1865 and 1866. He showed that copper sulfid can be used in contact with copper or German silver for construction of thermo-electric couples, and he remarked that in order to obtain powerful effects the copper sulfid ought to be in a peculiar condition. According to him the best means of obtaining it is to heat thick sheets of copper in sulfur-vapor, then to melt the copper sulfid thus obtained, and to cast it in molds at a temperature as nearly as possible to its melting-point. We have proved by our researches that in this last point he was in error. He thus obtained bars of sufid having a fibrous fracture with bubbles disseminated through the mass. If the melting is repeated several times at a high temperature and if a homogeneous mass is cast, its thermo-electric power is nearly destroyed. In spite of all his precautions Becquerel did not always obtain bars giving the same electromotive force. Ruhmkorff stated that by adding to the copper sulfid a little antimony sulfid he obtained bars of a more regular thermo-electric power. Finally, Becquerel, continuing his researches, found that by reheating his cast bars of copper sulfid for several hours their thermo-electric power became more regular. Becquerel constructed a thermo-electric battery in the laboratory with bars of cast copper sulfid thus obtained, covered at their ends with coils of copper or German-silver wire. This battery gave an electromotive force relatively much higher than that given by any other thermo-electric couple studied; but the internal resistance of the battery was so great that it was inappropriate for any practical use, and this investigation remained in the condition of a laboratory research.

The difficulty is to obtain copper sulfid in a form virtually quite homogeneous and offering the least possible electric resistance and at the same time yielding a constant electromotive force variable for given temperatures.

We have succeeded in obtaining bars of copper sulfid melted at any temperature giving an electromotive force amounting to, quite regularly, from two-tenths to three-tenths of a volt by treating the melted sulfid in the following manner: The copper sulfid is melted without regard to the temperature, except that the mass must be thoroughly liquid. The sulfid is then cast in molds of sand to give it the form desired in the construction of the couples. The pieces thus obtained are placed in a crucible or furnace and heated to redness, whereupon they are submitted to the action of sulfur-vapor for about half an hour. The piece absorbs regularly the sulfur and increases in volume. If the crucible or furnace is opened, the piece will be seen surrounded by the blue flame of burning sulfur. Before the complete disappearance of this flame the piece is withdrawn from the furnace and allowed to cool. In this condition the copper sulfid thus treated gives only a very weak electromotive force and has a high resistance to the electric current. It is therefore put back into a well-closed furnace and heated to bright redness for several hours with exclusion of air, care being taken to place in the furnace some ingots or sheets of copper to absorb the sulfur-vapor evolved

from the piece. The latter is then allowed to cool slowly. Instead of absorbing the sulfur-vapor with copper the pieces of copper sulfid may be heated in an atmosphere of inert gas, the essential point of the treatment being that the piece shall be excluded from air at the moment of desulfurization. After this operation the resistance is found to have fallen considerably, and every piece gives a perfectly regular electromotive force of from two-tenths to three-tenths of a volt, according to the temperature at which it is heated.

We have found that by adding to copper sulfid at the moment of its fusion a small proportion of iron sulfid we obtained pieces which resist strongly the action of roasting, which is very important. A good proportion of sulfid of iron to use is from one to five per cent.; but we do not limit ourselves to this proportion.

Having thus described the nature of this invention and the best means we know of carrying the same into practical effect, we claim—

1. The herein-described process of manufacturing copper-sulfid rods for thermo-electric couples, consisting of heating copper sulfid until it becomes liquid, casting it in molds, heating and then submitting it to a sulfur-vapor in a closed vessel and afterward heating it in a closed vessel containing copper and then cooling, substantially as described.

2. The herein-described process of manufacturing copper-sulfid rods for thermo-electric batteries, consisting of heating copper sulfid until it becomes thoroughly liquid, casting it in molds, placing it in a crucible, heating and submitting it to sulfur-vapor, withdrawing the sulfid and cooling it, replacing it in the crucible and also placing copper therein for the purpose described, and again submitting it to heat, and finally cooling it.

3. The herein-described process of manufacturing copper-sulfid rods for thermo-electric couples, consisting of fusing copper sulfid with a small proportion of iron sulfid, casting it, and submitting the casting to sulfur-vapor, substantially as described.

In testimony whereof we have hereunto set our hands in presence of two subscribing witnesses.

EUGÈNE HERMITE.
CHARLES FRIEND COOPER.

Witnesses:
CHARLES DONY,
EDWARD P. MACLEAN.