

# UNITED STATES PATENT OFFICE.

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## IMPROVED PROCESS OF TREATING SULPHUROUS ORES OF COPPER.

Specification forming part of Letters Patent No. 59,693, dated November 13, 1866.

*To all whom it may concern:*

Be it known that we, JAMES D. WHELPLEY and JACOB J. STORER, of Boston, in the county of Suffolk and State of Massachusetts, have invented a new and useful Method of Treating the Sulphurous Ores of Copper and iron oxides obtained from them; and I do hereby declare that the following is a full, clear, and exact description of the construction and operation of the same.

Our method of working the sulphurous ores of copper is as follows:

1. *Pulverization.*—We pulverize the ore so finely that it will pass through a sieve of one hundred threads to the inch, or thereabout, by means of the machinery already patented by us.

2. *Aerial combustion and immediate lixiviation.*—We next burn the ore floated on an air-blast in a heated flue, and lixiviate it in hot acidulated water, as described in previous patents and applications.

3. *Burning without special fuel.*—After the flue has been heated in the earlier part of the burning we abandon the feeding of fuel to the water-furnace, and find that the radiation of heat from the walls of the flue is sufficient to inflame the sulphuret, and the generation of heat by the combustion of the sulphur is sufficient to maintain the heat of the flue. To this end we employ ores containing a large percentage of sulphur, or so mingled that a large proportion of sulphur is present.

4. *Treatment of the oxides.*—If the burning be slowly conducted the ore will be converted into soluble sulphate of copper and magnetic oxide of iron; but it may happen that, by rapid burning at a high degree of heat, the larger part of the copper will appear as difficultly-soluble oxide. When this is the case we take the pulp of the tank, consisting of magnetic oxide, gangue, and difficultly-soluble oxide of copper, all in a finely-divided state, and intimately mingle with it sulphate of iron, or wet it with sulphuric acid, and expose it at a low red heat upon the floor of a reverberatory furnace, frequently stirring the mass. The reaction is to change the magnetic oxide to colcothar and the oxide of copper to sulphate, which can at once be lixiviated, leaving the colcothar a soluble commodity. The heat is

to be slightly raised toward the last of the treatment.

Sulphuric acid may be replaced by hydrochloric, or the sulphate by a chloride (common salt, for instance, or chloride of iron or lime) in this manipulation. In either case we get a soluble salt of copper and insoluble colcothar.

The wetting of magnetic oxide with an acid to change it to colcothar and subsequent treatment, as described, are new in the arts, and we consider this use of sulphuric and hydrochloric acids as a means of hyperoxidation to be valuable, and to point out a way by which we can obtain in mineral paints still brighter tints than we have at present.

The proportion of acid or salt to be introduced will be indicated by the amount of oxide of copper present in the pulp, and the chemical equivalents of the salts desired to be formed with or from the oxide of copper must be supplied in the acid or salt introduced.

5. *Lixiviation and use of the centrifugal machine.*—We now lixiviate the pulp obtained from the fourth manipulation, either in the ordinary way, or we place it in a centrifugal machine, such as is used in sugar-houses, but lined with felt of a loose texture, and direct a stream of pure water or water acidulated with sulphuric or hydrochloric acid, according to the nature of the salt formed in the fourth manipulation, into the center of the machine while in motion, dissolve out the soluble salt and oxide of copper, and render the iron oxide nearly pure. This may be smelted for iron, as hematite or magnetic oxide is usually smelted, may be ground in oil for a cheap pigment, or may be reduced to revived or sponge iron for use in the further operations of the process, as described under manipulation sixth, or may be rendered malleable by manipulation seventh.

6. *Manufacture of revived iron and cementation.*—The magnetic oxide or the colcothar is now mingled with or placed adjacent to an equivalent amount of carbonaceous matter under a muffle or cover and heated to a red heat without access of air-current. A convenient way of doing this is to place two piles, one of iron oxide, the other of charcoal, on the floor of a muffle, adjacent to each other. Another



mode would be to fill a porous crucible with oxide, place it in a larger crucible, pack the interval with coal-dust, and then lute a cover over the whole. In the latter case the heat must be nearly white. After a short time the oxide is reduced by diffusion of gases, first, to a lower state of a oxidation, and, lastly, to metallic iron in spongy forms. This we call "revived iron." It is thrown into the disturber of the precipitating-tub, as described in a former application, and is in the best form for precipitating cement copper from the solution obtained in the second and fifth manipulations.

7. *Refining of sponge-iron after it has been revived.*—When the quantity of revived iron produced in the last manipulation is greater than needed in the precipitation of copper from its solution, we raise the sponge to a welding-heat without access of air, and, passing it through roughing rolls or squeezers, produce a fine quality of malleable iron. A suitable muffle for this purpose is the ordinary glass pot with flat bottom and domed top.

Variations in second, third, fourth, and fifth manipulations are as follows:

In case we have an ore carrying but little sulphur, like the lean Canadian ores, Phillipsite, or ores partly pyritous and partly oxidized, we shall be obliged to employ chlorine as a solvent, and this introduces some modifications in the burnings and subsequent treatment.

We prepare in the water-bottom of our furnace a bath of chloride of lime and hydrochloric acid, either by admitting into the tower through one of the inspection-holes a pipe communicating with a retort containing common salt and sulphuric acid, or by pouring hydrochloric acid into the water of the trough, and saturating with carbonate of lime until two-thirds of the hydrochloric acid is salified. In order to accomplish the absorption of the acid gas by the water, the water of the wetting-wheel must be derived from the water-bottom of the furnace, and during the burning of ores the wetting-wheel must work a chlorodized spray, partly derived from the water-bottom and partly from the settling-tubs of the chemical-wheel, as will be hereinafter described.

The general effect of the sulphurous acid evolved during the burning of the ores is to throw down insoluble sulphates of lime and substitute in solution chloride of copper in the water-bottom and tubs of the wetting-wheel. The freed chlorine not taken up by the oxide of copper will always be in the form of hydrochloric acid, and will pass to the chemical-wheel, where it is taken up by milk of lime, and the chloride of lime returned to the wetting-wheel.

The water-bottom, settling-tank, and tubs of the wetting-wheel will contain in the pulp sulphate of lime, undissolved oxide of copper, magnetic oxide of iron, some unburned sulphide, perhaps, and residuary earths. The

solution will hold chlorides of iron, copper, and lime, from which the copper can be precipitated, as we have already described in a former part of this paper.

We now spread the pulp on the floor of a reverberatory furnace, and apply a gentle heat, never rising above the low red. The effect is, first, the evaporation of the water; the residuary sulphides are next chlorodized, and next the oxides of copper are converted into chlorides, while the chlorides of iron are converted into oxides, and the escaping chlorine, if any, is transmitted to the water-furnace, to be again employed. The mass in the reverberatory furnace now consists of red and black oxide of iron, insoluble salt of lime, soluble chloride of copper, and residuary earths, the whole permeated by a fine sponge of soluble anhydrous chloride of lime. This we thoroughly pulverize and lixivate with water, or, if necessary to extract all the copper, with dilute hydrochloric acid, and treat the lixivate with milk of lime, which throws down hydrated oxide of copper, leaving chloride of lime in solution, to be used in the trough of the water-furnace or in lixiviating. If there be lime in the mineral it can be turned to account by employing the crushed ore to precipitate the solution of chloride. The carbonate of copper would be treated similarly to the hydrated oxide.

The hydrated oxide of copper is reduced and refined in the ordinary Welsh way. The final products of the working are metallic copper, oxides of iron, and sulphur salts of lime.

If carefully managed, but one burning in the reverberatory furnace will be required; but if a second is needed the pulp must be first wetted with some of the acid waters of lixiviation containing chloride of lime.

In the operations subsequent to the treatment in the water-furnace a muffle-furnace may be conveniently substituted for the reverberatory.

We claim as our invention, and desire to secure by Letters Patent—

1. The seven manipulations above set forth in their order and with the variations described, as a process for treating sulphurets of copper.

2. The first, second, third, and sixth manipulations and the variations described, as a process for treating sulphurous ores of copper.

3. The first six manipulations and the variations described, as a process for treating copper sulphurets.

4. The first, second, third, fifth, and sixth manipulations and the variations thereof caused by omitting the third and sixth and employing the method described after seventh, as a process for treating copper sulphurets.

5. The rearrangement of the equivalents of the ore by the heat generated by its own com-

bustion in presence of oxygen and without other fuel than that contained in itself, substantially as described.

6. The employment for the lixiviation of minerals of the centrifugal drying-machine, as described, and the arrangement of the felt lining upon its interior, substantially as described.

7. The revival of iron from iron oxides by

diffusion of gases between carbon and the oxides at a low degree of heat and without currents of air, substantially as described.

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Witnesses:

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