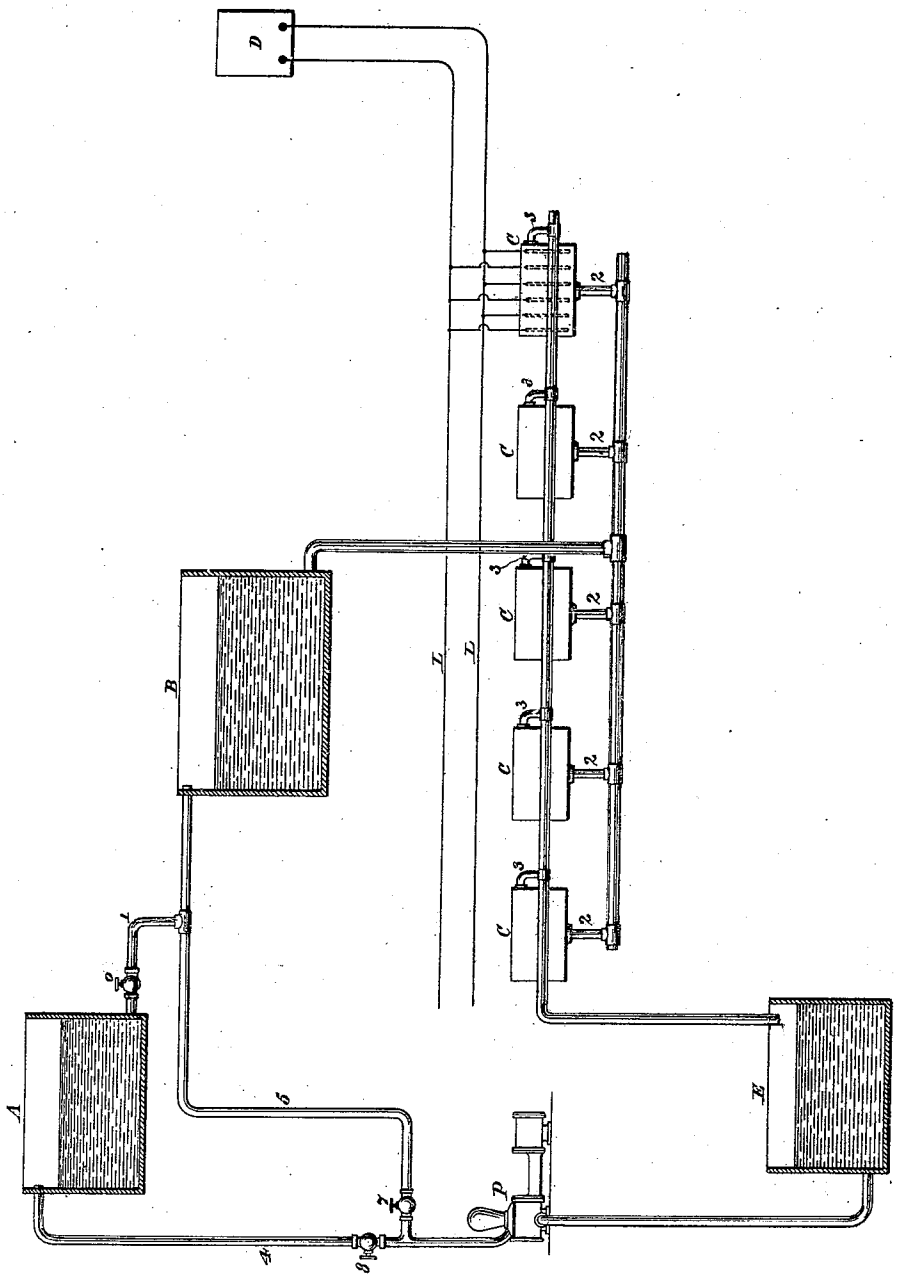
(No Model.)

# P. C. CHOATE.

## METHOD OF PRODUCING METALLIC ZINC.

No. 473,186. Patented Apr. 19, 1892.

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# UNITED STATES PATENT OFFICE.

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## METHOD OF PRODUCING METALLIC ZINC.

SPECIFICATION forming part of Letters Patent No. 473,186, dated April 19, 1892.

Application filed January 5, 1891. Serial No. 376,715. (Specimens.)

*To all whom it may concern:*

Be it known that I, PARKER C. CHOATE, a citizen of the United States, residing in Brooklyn, in the county of Kings and State of New York, have invented a new and useful Process for Producing Metallic Zinc, of which the following is a specification.

My invention relates to the production of metallic zinc from its ores by means of electrolysis; and the object of my improvement is to provide an economical method of producing commercially-pure metallic zinc.

While my method is applicable to the production of zinc as a metal from any of its ores, it is more especially valuable as applied to that class of ores known as "blendous" or "complex," which carry varying percentages of zinc, iron, sulphur, lead, gold, and silver, and also very often smaller percentages of other metals, and which on account of the difficulty of working them economically have heretofore been discarded at the mines in great quantities as waste products. In working such ores by the processes heretofore employed there has been a total loss of the zinc, except when utilized as a pigment, and at the same time its presence causes heavy losses of the other metals, such as gold, silver, &c. By my process, however, I am able to save the zinc as a metal and also to prevent loss of the other metals.

Heretofore the production of pure metallic zinc by electrolytic deposition has not been possible on a profitable commercial scale. The reason of this is that to insure purity of the product the zinc "electrolyte" or solution in the electrolytic baths upon which the electric current is to act to effect the deposition of the metal must itself be pure—that is to say, must be freed from the other metals and bodies which were present in the ore and which if carried with the zinc into the product would contaminate the latter—and although the desirability of this purity of solution may have been recognized by some metallurgists no adequate mode of attaining it has hitherto been proposed. The serious obstacle which has been encountered was that, as almost all these other metals and bodies are more readily acted upon by the electric current than zinc, they would enter into the deposited product in the bath with the zinc, and no satisfactory practical means has heretofore been found to eliminate them from the solution and thereby prevent this result. The only method proposed for the purpose has been to clear the solution by the use of successive precipitants; but these have failed to remove all the impurities, and, moreover, their employment is so inconvenient and costly as to render impracticable any process which depends upon them. Another difficulty heretofore encountered has been the inability, unless at prohibitory expense, of neutralizing the large volume of free acid liberated in the bath by the action of the current upon the electrolytic solution. Unless this free acid be annulled the working of the process will come to a standstill before any considerable amount of zinc will be deposited, because the acid will redissolve the zinc from the cathodes as fast as it collects there. By my improvement I overcome these difficulties, for it is a result of my process that the condition in which I take the zinc to subject it to the action of its solvent in order to produce the electrolytic solution enables me to obtain this solution in great purity, although I dispense entirely with the use of precipitants, while at the same time it provides an economical and efficient means of neutralizing the free acid liberated in the baths and regenerating the solution without impairing its purity.

The defects of prior processes have largely come from the fact that their electrolytic solutions were made direct from the ore, so that all the foreign matters present necessarily went into the solutions and then required to be removed. In my process, on the contrary, I at the outset take the zinc in a state in which all the soluble impurities can easily be eliminated before the solution is formed, while such insoluble impurities as go into the electrolytic baths will readily separate themselves out during the working of the charges, so that in this way I insure and constantly maintain a practically-pure solution for the action of the electric current.

From the point of view of my process all metals and other bodies which if they were to enter into the zinc product would contami-

nate it are treated as impurities. To the end, therefore, of securing the purity of solution referred to, my invention consists in producing commercially-pure metallic zinc by first converting the zinc in the ore into zinc oxide by volatilization in order that all the impurities in the ore which are volatilizable more quickly than or as quickly as the zinc may be driven off before or with the latter, to be eliminated from the "fume" afterward, leaving the non-volatilizable impurities behind in the furnace, then, whenever necessary, subjecting the collected fume to a moderate roast, so as to expel all its impure and soluble constituents, which are more readily volatilizable than the zinc—such as the oxides of antimony, arsenic, selenium, &c.—since its insoluble impurities will separate out in the subsequent treatment, then dissolving the oxide thus purified in dilute sulphuric acid, and finally treating this sulphate solution by electrolysis to produce the pure metallic deposit.

The accompanying drawing shows a sectional elevation of an apparatus containing the vessel in which the sulphate solution is formed and the baths for the electrolytic treatment of it, together with feed and overflow tanks, and also a pump and connecting pipes for keeping the solution in circulation.

Any usual or suitable mode may be adopted for obtaining the zinc oxide to be used in my process. As an example of one well-known method the ore may be first crushed, and then, when it contains an excess of sulphur, it may be roasted at a moderate temperature, not sufficiently high to volatilize the zinc, in order to drive off the excess of sulphur. The partially-desulphurized ore may then be mixed with carbonaceous fuel—such as coal-screenings—in a furnace in which air is admitted beneath its grate and may be roasted at a temperature high enough to volatilize the zinc until the zinc contained in the ore is driven off. The volatilized zinc and other volatilized bodies may then be caught and collected in a bag-room in the ordinary manner. The resulting product will be substantially pure oxide of zinc in the shape of a fine powder known as "fume," mixed with such lead as was contained in the ore and which is volatilized with the zinc. There may also frequently occur with the zinc and lead fume as condensed products other volatilizable oxides which may have been present in the ore in their metallic form, such as the oxides of antimony, arsenic, selenium, cadmium, bismuth, &c. These substances are all volatilizable at a lower temperature than zinc and lead. Hence when they occur in appreciable quantities I dispose of them by subjecting the fume to a moderate roast at a temperature of from 300° to 800° Fahrenheit in any well-known form of muffle-furnace, thereby driving them off, care being taken not to apply sufficient heat to revolatilize any of the lead or zinc contents. By means of this roast the fume is purified from its more volatile constituents, thereby easily eliminating all those impurities which are soluble and which would therefore otherwise enter into solution with the zinc and contaminate it. Other metals which may have been contained in the ore—such as iron, gold, silver, &c.—are not driven off with the zinc and lead, but remain in the furnace in the form of cinder or slag and may afterward be smelted out and recovered in the usual manner.

I do not confine myself to the above-described mode of producing or purifying the zinc oxide, as this may be done in any suitable way, it being only necessary to my invention that I should have for my subsequent operations an oxide of zinc which has been properly purified from its more volatile soluble constituents.

The next step in the process is the treating of the purified zinc oxide electrolytically in order to separate the metallic zinc. For this purpose the oxide is mixed with dilute sulphuric acid as a solvent in a treating-tank (shown in the drawing at A) in such proportions as to form a well-concentrated solution. The zinc oxide will be dissolved, while the other constituents—such as the lead sulphate, &c.—which constitute the only impurities now remaining, being insoluble, are not acted upon, and consequently separate out and settle to the bottom of the tank, leaving a clear solution, which contains out of all the elements originally present in the ore only the zinc, from which the others will now have been separated by the preceding steps of the process. It will thus be seen that I am able to obtain an electrolytic solution of a high degree of purity without the use of any precipitant and in a rapid and economical manner, thereby avoiding the great cost of handling bulky solutions, as well as of the precipitants themselves. The clear solution is next drawn off through a pipe (seen in the drawing at 1) into a feed-tank B, whence it is conveyed to the electrolytic baths *c c c* by pipes 2 2 2, opening into the bottoms of the baths. The baths are supplied with anodes of suitable material—such as lead or carbon—insoluble in the solution, and cathodes, which may be plates of zinc or copper. The anodes and cathodes are connected with mains L L, leading from a suitable source of electricity D, such as a dynamo of proper capacity. If desired, the solution may be heated in order to lower the resistance of the baths. On the application of the current the zinc in the solution will be deposited upon the cathode, while the freed acid will rise to the surface, whence it is drawn off through overflow-pipes 3 3 3 and carried to a tank E. The treating and feed tanks and the baths and the overflow-tanks should be set upon different levels, so as to produce a natural flow from the treating-tank and through the baths and thence to the overflow-tank. It will be found that the overflow from the baths will still contain a considerable proportion of zinc. By means of a pump P a por-

tion of this overflow is returned to the treating-tank A through the pipe 4 to be regenerated by the addition of fresh zinc oxide, and another portion is returned by pipe 5 to the feed-tank B to be again passed through the baths. In this manner I easily and effectually annul the free acid and regenerate and maintain the solution without impairing its purity, since I always have a sufficient supply of zinc oxide therefor, and thus enable the process to be carried on indefinitely, and at the same time I maintain a continual circulation through the baths and prevent the stratification of the acid, which would take place if the solution were not kept in motion.

There will practically be no loss of the acid, as it can be used again and again in carrying on the process. Water will have to be added to the solution in small quantities from time to time to supply the slight loss which will take place. The deposited zinc may be stripped off the plates and smelted, or where the zinc plates are used as cathodes the plates may be smelted whenever a sufficiently heavy deposit has been formed upon them. The residual metallic sulphates which settle to the bottom of the treating-tank may be smelted in the ordinary manner to recover the metals contained therein.

Any other convenient electrolytic apparatus may be employed, and I wish it to be understood that I do not limit myself in any portion of my process to any particular form of apparatus for putting it into practice.

The advantages of my invention will be readily apparent, since it affords an easy and economical method of producing metallic zinc from its ores, and by its use vast quantities of ore heretofore wasted and of no value can be reduced to their component metals and made valuable.

Having thus made known my improvement, what I claim, and desire to secure by Letters Patent, is—

1. The above-described process of producing metallic zinc from its ores, which consists in separating the zinc and the equally volatile and more volatile constituents from the less volatile constituents of the ore by the use of heat and a reducing agent, then volatilizing and oxidizing the reduced metal, thereby obtaining a condensed oxidized fume, subjecting this fume to a moderate heat in order to expel its soluble constituents more volatile than zinc, treating the remaining product with dilute sulphuric acid as a solvent, and finally subjecting the resulting solution to the action of an electric current to precipitate the zinc, as set forth.

2. The above-described process of producing metallic zinc from its ores, which consists in separating the zinc and the equally volatile from the less volatile constituents of the ore by the use of heat and a reducing agent, then volatilizing and oxidizing the reduced metal, thereby obtaining a condensed oxidized fume, treating this fume with dilute sulphuric acid as a solvent, and finally subjecting the resulting solution to the action of an electric current to precipitate the zinc, as set forth.

3. The above-described process of producing metallic zinc, which consists in forming an electrolytic solution by dissolving in dilute sulphuric acid oxide of zinc, however obtained, in the state of fume free from the lighter soluble impurities, such as the oxides of antimony, arsenic, selenium, &c., and then treating this solution by electrolysis, as set forth.

In testimony whereof I have hereunto subscribed my name this 20th day of December, A. D. 1890.

PARKER C. CHOATE.

Witnesses:
MELVIN BROWN,
ALBERT BURNSTINE.