H. H. WIKLE.

ELECTROLYTIC CELL AND METHOD OF OPERATING THE SAME.

APPLICATION FILED APR. 13, 1918, RENEWED APR. 4, 1921.

1,402,986. Patented Jan. 10, 1922.

2 SHEETS—SHEET 1.

Fig. 1

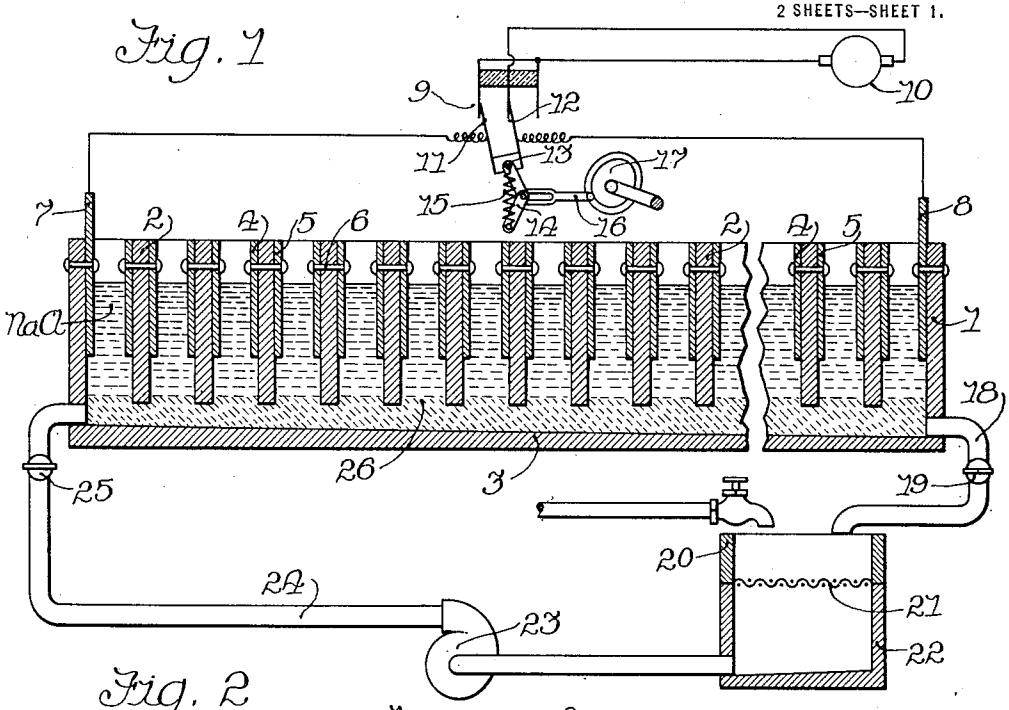
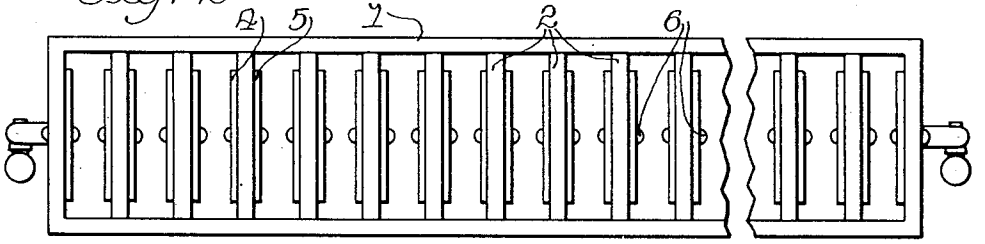


Fig. 2



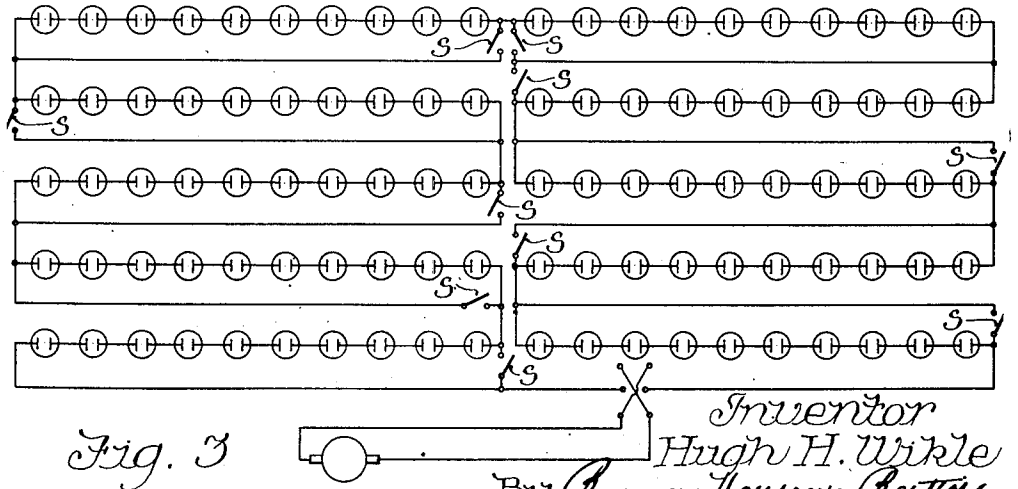


Fig. 3

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2 SHEETS—SHEET 2.

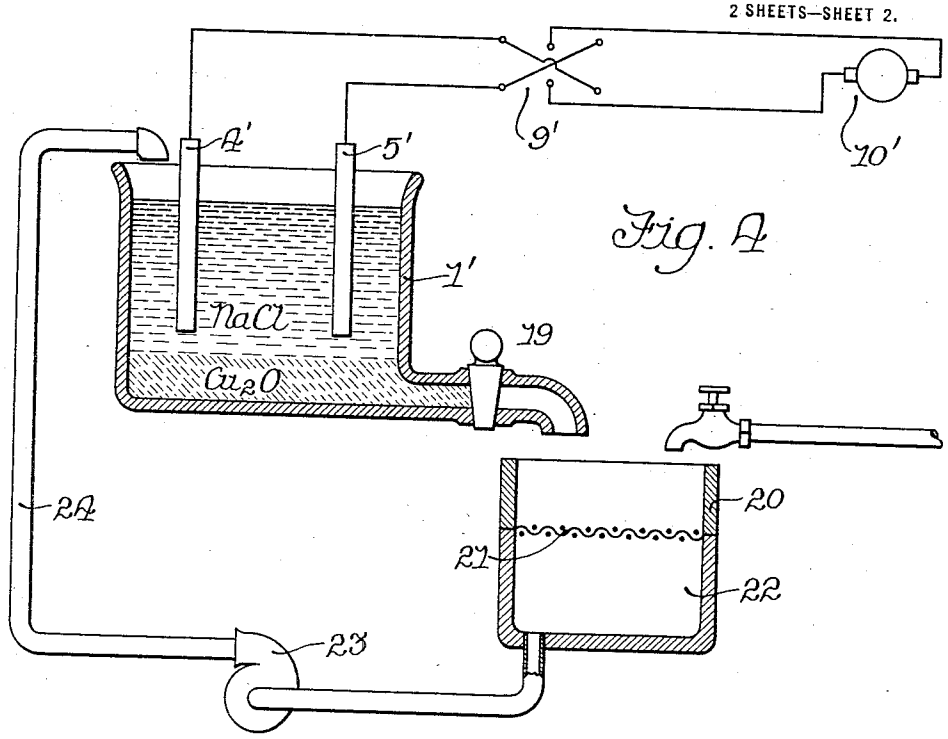


Fig. 4

Fig. 5

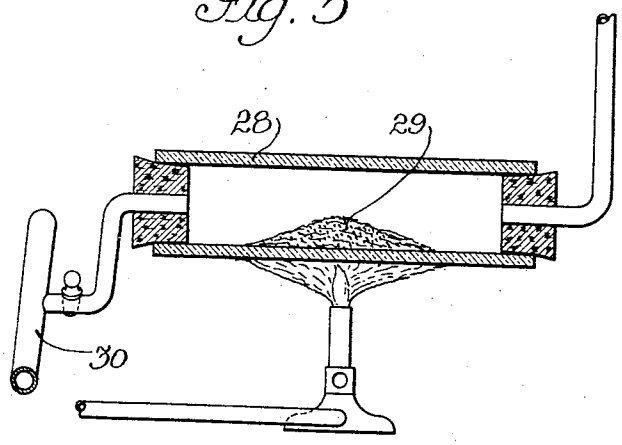
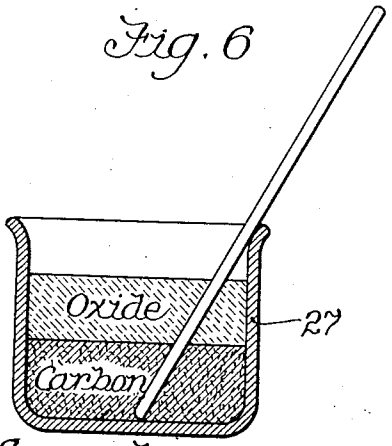


Fig. 6



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UNITED STATES PATENT OFFICE.

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ELECTROLYTIC CELL AND METHOD OF OPERATING THE SAME.

1,402,986. Specification of Letters Patent. Patented Jan. 10, 1922.

Application filed April 13, 1918, Serial No. 228,310. Renewed April 4, 1921. Serial No. 456,389.

To all whom it may concern:

Be it known that I, HUGH H. WIKLE, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a certain new and useful Improvement in Electrolytic Cells and Method of Operating the Same, of which the following is a full, clear, concise, and exact description, reference being had to the accompanying drawings, forming a part of this specification.

My invention relates to an improvement in electrolytic cells and method of operating the same for preparation of oxides and powders of metals and alloys.

While the invention is particularly applicable to the formation of oxides and powders of metals and alloys for use in the manufacture of brushes for dynamos and the like, I do not intend to limit the invention to such use.

The object of the present invention is to provide an improved electrolytic cell and manner of operating the same to secure oxide of copper or the like or oxide of the metals which may make up an alloy of copper, such as brass, bronze, german silver, etc.

A further object of the invention is an improvement in the manner of securing finely divided or powdered metals or alloys such as the powders of copper or alloys of copper or the like.

In the accompanying drawings which form a part of the present specification, I have illustrated diagrammatically one manner in which my invention may be carried out.

Figure 1 is a view partly sectional and partly diagrammatic of an electrolytic vat for carrying out my invention;

Figure 2 is a plan view of the vat;

Figure 3 is a diagram of the connections for a series of cells;

Figure 4 is a diagrammatic layout of a cell and associated mechanism for carrying out the invention;

Figure 5 is a diagrammatic view of a furnace for the reduction of the oxide; and

Figure 6 is a view illustrating the step of mixing the oxide with a reducing agent such as carbon.

In the manufacture of brushes for electrical machinery, particularly brushes of the "metal" and "metal graphite" type, it is necessary to secure metal in a finely subdivided state to form the same into a compact mechanical mass formed of a mixture of carbon, preferably in graphite form, with the finely divided metal. The present invention aims particularly to secure such finely divided metal, but it is apparent to those skilled in the art that the process is not limited to such use and may be applied whereever a finely divided oxide of the metal or a powder of the metal is required.

Incidentally I have found that it is possible to treat alloys of copper in substantially the same manner as pure copper and arrive at the finely sub-divided oxide of the alloy with the same steps and apparatus employed in securing the oxide or powder of copper.

I find also that I can secure the powdered alloy by mixing the proper proportions of the metals either in elementary form or in the form of their oxides and then heating in a reducing atmosphere to the point of reducing the oxides, or of causing the elementary metals to unite to form a powder of the alloy.

The electrolytic cell which I have devised is particularly applicable to carrying out the above process, but it is not to be limited to such use.

The vat 1 shown in Figure 1, comprises a box of wood or other insulating material, provided with a plurality of wooden partitions 2, which extend down into the vat to a point adjacent the bottom wall 3 of the vat. Metallic electrodes 4—5 are mounted on opposite sides of the partitions 2 by means of the bolts or pins 6 which are preferably made of the same material as the electrodes or plates 4—5.

In a vat which I have employed successfully the tank 1 is made approximately 36 feet long by 10 inches wide by 12 inches deep with the partitions reaching down to within 2 inches of the bottom of the vat. Any dimensions desired may be employed and the above are given merely for the sake of illustration. The number of cells which are in series depends upon the voltage which is impressed on the cells. Where a voltage of 125 volts direct current is available, the vat should be divided into 100 cells so that the voltage across each cell is approximately 1¼ volts. The end electrodes 7 and 8 are connected through a reversing switch 9 to a suitable source of current 10. The reversing switch 9 may be manually operated

or may be automatically operated, as by means of the mechanism which I have illustrated. The movable contacts 11—12 are mounted on a rock shaft 13. The rock shaft 13 is connected to a toggle mechanism 14 which is adapted to be periodically thrown from one side to the other by means of a spring 15 and the slotted link 16 which slotted link is controlled by the constantly rotating cam 17.

The bottom of the vat is connected by a pipe 18 through a valve 19 to a filter 20. This filter comprises an open sided box having a screen or filter, preferably a piece of fine cloth 21 on the bottom of the box for filtering out the oxide which is precipitated in the vat 1. The liquid which passes through the filter is collected in a tank 22 from whence it is pumped by means of the pump 23 and the pipe 24 back to the vat 1. The pipe 24 is provided with a suitable valve 25.

The operation of the mechanism thus far described is as follows:

Assuming that the parts are in the condition shown in Figure 1 and that the vat 1 is filled, or substantially filled with an electrolyte of sodium chloride (NaCl), current passes from the source and through the cells in series, electrolyzing the said solution of sodium chloride, causing the sodium atoms to collect at the cathode and the chlorine atoms to pass to the anode of each cell. This action may be represented by the following equation: $NaCl=Na+Cl$.

As explained, the sodium ions collect at the cathode and there combine with the water of the solution, according to the following equation: $2Na+2H_2O=2NaOH+H_2$.

The chlorine ions which have migrated to the anode unite with the metal of the anode to form a chloride or chlorides of the same. Assuming that the electrode is of copper, the following equation takes place: $2Cl+Cu=CuCl_2$.

The current density in the vat is maintained at such a value that heating of the electrolyte occurs. Heating of the cupric chloride in the presence of copper causes the following reaction: $CuCl_2+Cu=2CuCl$.

Cuprous oxide is then formed by hydrolyzing the cuprous chloride with hot water in accordance with the following equation: $2CuCl+H_2O=Cu_2O+2HCl$.

The cuprous oxide forms a very fine heavy precipitate of red color, which precipitate settles to the bottom of the vat in each cell and may there be drawn out. The recombination of the hydrochloric acid with the sodium hydroxide makes the process continuous, as can be seen from the following equation: $HCl+NaOH=NaCl+H_2O$.

Whereas certain other oxides or chlorides or chemical combinations of the elements above set out may occur, I find that on the whole the action is such as to conform with the above reactions which I believe to occur.

The cuprous oxide which is formed in the electrolyte is so finely sub-divided that it remains partly in suspension and can be drawn off by way of the pipe 18 into the filter 20, where the oxide is separated from the liquid and the liquid is returned to the vat. The process of removing and filtering out the oxide may be intermittent or continuous as desired. The cuprous oxide is preferably washed to remove the salt or hydroxide of the solution and may then be dried if desired or used in the wet condition, as will be described later.

In order to carry out the complete process it is necessary to get the sodium hydroxide and the hydrochloric acid into intimate contact with each other so that the process may be carried on as effectively and economically as possible. In order to secure this result in the most advantageous manner I have provided the reversing switch 9, which periodically reverses the polarity of the electrodes so that current flows in the opposite direction and the reactions can occur more easily and efficiently. I have found that the reversal of current at periods of one hour is effective in securing the desired action.

In order to obtain the maximum efficiency the electrolyte should always be kept at the point of saturation, but no free salt (sodium chloride) should be introduced into the vat.

The electrolyte should be kept at a temperature of not lower than 70 deg. C. and not higher than 90 deg. C. This temperature may be maintained by the proper current strength through the electrolyte. The voltage across the vat should not exceed $1\frac{1}{2}$ volts. A current density of approximately 144 amps. per sq. ft. of anode surface gives about as great an output as can be secured without boiling the electrolyte and secures the best effect.

I have discovered that not only does copper pass through the reactions above indicated, but alloys of copper may successfully be reduced to the oxide form by the same process. That is to say, I have found that brass and bronze may be reduced from the solid metallic condition to a condition of an oxide of the alloy, which oxide may be again reduced to the metal, producing a finely divided powder of the alloy.

The exact chemical reactions which occur I am unable to state. It is sufficient to say, however, that observing the above rules, I am able to use brass electrodes in the electrolytic vat or cells above described and secure an oxide or oxides which, when passed through the reducing stage which I shall presently describe, produce finely divided particles of the alloy without a change in the proportions or the property of the alloy.

The powdered oxide which is thus obtained may then be reduced to the metal by subjecting the same to heat in a reducing atmosphere of about 1500 deg. F.

The oxide is mixed with an excess of carbon and heated in a closed chamber in a reducing atmosphere where the material is employed for brushes. To this end the oxide either of copper or of the alloy is mixed with the proper proportion of carbon, preferably in graphite form, to form a graphite metal composition suitable for the material of the brush. This may be done as illustrated in Figure 6 by stirring the two materials in the mixing vessel 27.

I have found it an advantage to mix the oxide in the wet condition with the graphite so that there is less danger from the flying dust and less inconvenience. The batch of oxide and graphite is then placed in the furnace 28, as shown at 29 in Figure 5 and subjected to heat, while a current of gas such as hydrogen or city gas is passed through the furnace from the main 30.

I have found that the resulting material consists of a mixture of graphite and the metal or alloy in very finely sub-divided condition, the metal or alloy being suitably annealed and being preferably in the form of crystals. The metal is of such fineness that it would readily pass through a 200 mesh screen and is in ideal condition to form a homogeneous brush. If desired the metal brush produced may be employed for any other purpose.

I have also found that where powdered metals or their oxides are mixed in proper proportions to form an alloy and are then fired in a reducing atmosphere, that the resultant mass consists of finely divided grains of the alloy. This is of considerable advantage in case it is desired to obtain a powder of an alloy and a powder or an oxide of one of the metals is obtainable or is already secured. This permits of powders or oxides of the metals being secured from various sources and making up a powder of the alloy without going through the stage of melting the metals into a mass of alloys. Due to the extreme fineness of the metal or alloy when produced as above described, there is no noticeable tendency of the metal and the graphite to segregate and a very superior article results.

The electrolytic process may be carried out in a single cell, as illustrated in Figure 4.

The separate cells may be employed in series or in multiple, or in combination of both.

In Figure 3 I have illustrated one manner in which a group of 100 cells may be connected for suitable handling. The cells are arranged in groups of ten and provided with switches so that any group may be cut out for the removing of oxide and refilling the cell. A series of switches S are provided for cutting out by short circuiting, any particular group so that these cells may be emptied individually for filtering out the oxide and for recharging with the filtered liquid or fresh liquid electrolyte. Otherwise the operation of the cells in this arrangement is the same as described in connection with Figures 1–2.

I have found that by keeping the electrolyte cold the nature of the precipitate is changed to the extent that the precipitate consists of a complex cuprous hydroxide which may be drawn off and treated in substantially the manner above described to reduce the same to the metal, or to combine into an alloy. The hydroxide is reducible in substantially the same manner as the oxide. I do not consider this a departure from my invention but only a less advantageous manner of practicing the same.

Instead of sodium chloride, other alkali-halide salts may be employed.

I do not intend to be limited to the precise details of construction and the precise steps of operation above described.

I claim:

1. In a cell, a pair of electrodes, an electrolyte comprising a halide which under electrolysis releases a halogen for attacking said electrodes, a source of current for the electrodes and means for periodically reversing the polarity of said electrodes.

2. In a cell a pair of electrodes made of a metal comprising copper, an electrolyte comprising a solution of sodium chloride, a source of current for said electrodes and a reversing switch for periodically reversing the polarity of the electrodes.

3. The method of operating an electrolytic cell having electrodes of similar material which consists in periodically reversing the polarity of the electrodes, and maintaining the current density at such a value as to heat the electrolyte.

4. The method of precipitating an oxide of a metal, which consists in passing current from an electrode formed of the metal, through an electrolyte consisting of a saturated solution of common salt to an electrode of the same metal and simultaneously generating heat in the electrolyte with said current flow.

5. The method of precipitating an oxide of a metal, which consists in passing a current from an electrode formed of the metal through an electrolyte consisting of a solution of a halide of a metal of the alkali group, to an electrode of the same metal, then heating the solution.

6. The method of precipitating an oxide of a metal, which consists in passing a current from an electrode formed of the metal through an electrolyte comprising a soluble

chloride to an electrode of the same metal, then heating the solution and periodically reversing the polarity of the electrodes.

7. The method of precipitating an oxide of a metal, which consists in decomposing a soluble chloride in the presence of the metal to form a chloride of the metal, then heating the chloride in the presence of the metal and water to precipitate an oxide of the metal.

8. A method of producing cuprous oxide, which comprises electrolyzing a solution of salt with copper electrodes to form copper chloride and then heating the electrolyte containing the copper chloride to hydrolyze the copper chloride and precipitate the copper thereof as cuprous oxide.

9. The method of operating a cell for precipitating oxides of a metal, which consists in passing a curent from a metal electrode through an electrolyte consisting of a soluble chloride to an electrode of the same metal with sufficient current density to heat the electrolyte to between 70 deg. C and 90 deg. C.

10. The method of operating a cell for precipitating oxides of a metal, which consists in passing a current from a metal electrode through an electrolyte comprising a soluble chloride to an electrode of the same metal with sufficient current density to heat the electrolyte to between 70 deg. C. and 90 deg. C., and periodically reversing the direction of current flow.

11. The method of operating an electrolytic cell which consists in periodically reversing the current flow through the cell.

12. The method of operating an electrolytic cell for the production of metallic oxide in flocculent or precipitated form suitable for reduction to a minority subdivided metallic powder, which consists of passing a current from a suitable metallic electrode containing the metal to be precipitated through an electrolyte consisting of a halide of a metal of the alkali group to a second electrode also containing the metal to be precipitated and periodically reversing the flow of current through said electrode and electrolyte.

In witness whereof I hereunto subscribe my name this 4th day of April, A. D. 1918.

HUGH H. WIKLE.