W. K. PAGE.

PRODUCTION OF ELECTRODES.

APPLICATION FILED JAN. 10, 1916.

1,302,959. Patented May 6, 1919.

Fig. 1.

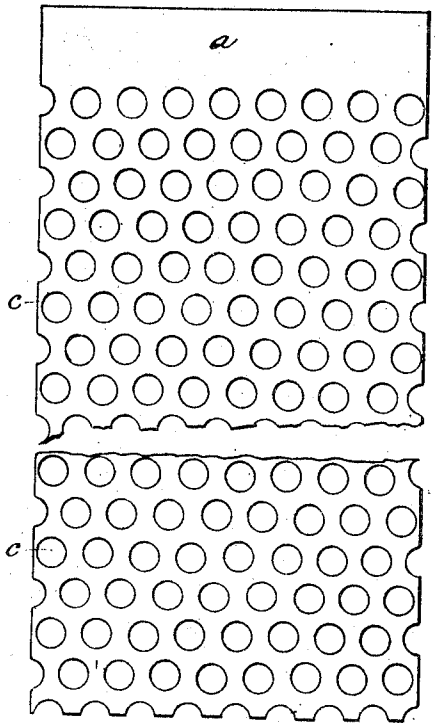


Fig. 2.

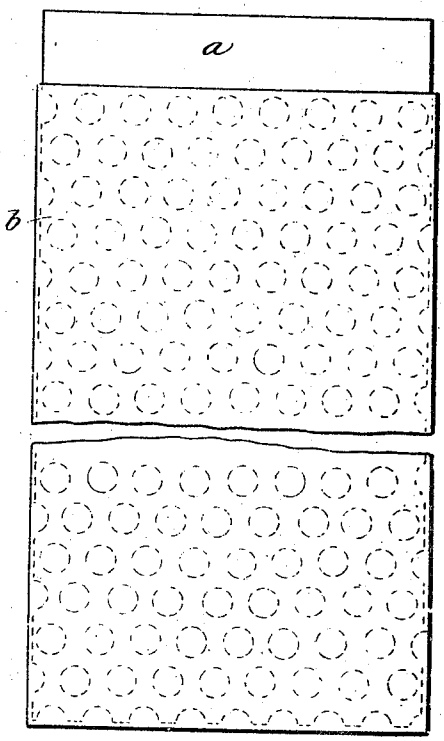


Fig. 3.

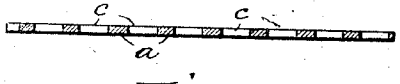


Fig. 4.

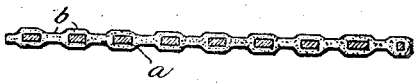
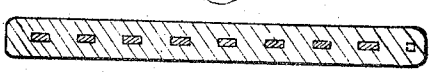


Fig. 5.



Fig. 6.



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PRODUCTION OF ELECTRODES.

1,302,959. Specification of Letters Patent. Patented May 6, 1919.

Application filed January 10, 1916. Serial No. 71,211.

To all whom it may concern:

Be it known that I, WILLIAM KINGMAN PAGE, a citizen of the United States, residing at Chicago, county of Cook, State of Illinois, have invented certain new and useful Improvements in the Production of Electrodes; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the production of an electrode particularly adapted for use in electrolytic operations where it is desirable to have electrodes of ample conductivity to subserve their intended purpose and which will nevertheless be insoluble in the electrolyte in which they are employed. Electrodes made in accordance with the present invention are of particular use in the electrolytic production of caustic soda and in the electrolysis of the leach liquors of ores, as, for instance, the solutions obtained by the leaching of copper or other ores with sulfuric or hydrochloric acid.

In the accompanying drawing, are shown suitable embodiments of the invention. In said drawing—

Figure 1 represents, in side elevation, a metal plate (shown broken away intermediate of its length, for convenience of illustration) suitable for use as a core or main body portion of the electrode;

Fig. 2 represents a like view of the said core with its protecting sheath of insoluble material firmly anchored thereto, the whole constituting a completed insoluble electrode;

Figs. 3 and 4 represent, respectively, cross-sectional views of Figs. 1 and 2.

Fig. 5 represents a cross-sectional view of a modified form of core plate, and

Fig. 6 represents a solid cast electrode with a core plate embedded therein.

Similar letters of reference indicate similar parts in both views.

In carrying out the invention, the core or main body portion of the electrode consists of a metal plate of ample conductivity with which is intimately associated a fused outer coating of material insoluble in the electrolyte for which the electrode is intended. Thus, the core *a* of the electrode shown in the drawing may consist of soft iron or mild steel, or of silicon iron or steel or ferro-silicon, and it is important that the material chosen shall have the same, or approximately the same, coefficient of expansion as the coating material *b* fused thereto, so that, within the range of temperatures to which the electrode is subjected in practical use there will be no tendency for the fused coating to develop fissures or cracks into which the electrolyte could penetrate to attack the metal beneath.

The coating *b* will consist preferably of magnetite containing usually from 5 to 7% of silica most or all of which is derived from the usual silica content of the magnetite. The magnetite is fused in any suitable electric furnace, or the like, and it is preferred to add to it a few per cent. (say 2 to 3%) of alumina for the purpose of toughening it and thereby decreasing any tendency to crack after it has been applied to the core.

To apply the fused material to the core, it is preferred to dip the core in a molten bath of the said material, and to quickly withdraw it from the molten bath so as to permit the dip coating to chill and shrink into close surface union with the metal of the core. To facilitate the adhesion of the fused material to the metal, it is preferred to first pickle the core, in the usual manner employed, for instance, in the tin-plating industry, for the purpose of de-oxidizing and removing the surface scale. To the clean metallic surface left after the pickling operation, the molten magnetite adheres with the most intimate tenacity.

It will be noted that the metallic core plate shown in Figs. 1 to 4 is provided with a series of apertures *c*, of relatively large area, arranged in close proximity to each other throughout. The purpose of these apertures is to serve as a secure anchorage to the coating of fused magnetite. The molten material, during the dipping operation, enters and occupies the series of apertures, and, upon the quick withdrawal of the plate, the molten material sets in said apertures, partly or wholly filling them, and, in any event, locking the coating as a whole to the core. The core is thus incased in a thin, tough and anchored coating of material, insoluble in the electrolyte for which the electrode is intended and of a co-efficient of expansion so closely identical with that of the metal of the core that, within the range of

temperatures met with in the use of the electrode, there will be no tendency to the development of cracks or fissures sufficient to permit the electrolyte to reach the metal core.

It will be preferable and desirable to give the electrode a second coating of the molten material, after it has received its first coating. This second coating may likewise be applied by dipping. It serves, moreover, not only to reinforce the first coating, with which it blends into a homogeneous union, but also covers any parts which may have been left uncoated in the first dipping. Furthermore, the application of the magnetite in two coatings has the additional advantage, of very considerable practical importance, that the first coating may be applied by quickly immersing the core plate and as quickly withdrawing it, so that it may not be in the molten bath for any longer period of time than is necessary for its immersion and immediate withdrawal. Consequently, the tendency for the molten magnetite to burn the iron core plate is correspondingly minimized. In the second dipping operation, any imperfections of the first are cured, and the initial coating serves as a protector to the metal core sheet within. As indicated at the upper part of Fig. 2, it will be convenient to leave uncoated the upper part of the metal core sheet, so that the electrode may be coupled up appropriately in the circuit by the customary connections, not shown.

In order to further toughen the coating, it will be desirable, in some cases, to anneal it for several days in a body of inert pulverulent material, such as kieselguhr (infusorial earth), powdered pumice, powdered quartz, or the like.

Under the conditions of practice of the invention as described, the magnetite may be regarded as fused to the surface of the iron or steel core by a bond which is probably magnetic iron oxid formed on the iron surface itself during the dipping operation. This probability is indicated by the extreme tenacity of union between the iron surface and the magnetite coating, it being impossible to separate the coating from the iron by any clean plane of cleavage. In the completed electrode, nevertheless, the iron core retains its desired conductivity, throughout its entire extent, appropriate to its use as an insoluble anode in the electrolytic art, and the relatively thin coating of magnetite offers no excessive resistance for the uses intended, while it is nevertheless adapted to withstand, without injury, the rough handling usually encountered in industrial operations.

The electrode above described, and illustrated by Figs. 1 to 4, can be used directly as an electrode, or it can be used in the production of cast electrodes having a much larger body of the magnetite cast therewith. In the production of cast electrodes, the coating or coatings of the magnetite protects the core plate in much the same manner that the first layer of magnetite protects the core plate during the subsequent dippings into the molten magnetite.

A cast electrode having a larger body of magnetite cast therewith, is illustrated in cross section in Fig. 6. In the production of this cast electrode, the mold is previously heated to a temperature of about 350° C. and may with advantage have a removable hot top or pouring funnel thereon forming an extension in which the molten magnetite can be poured. In producing the cast electrode, the molten magnetite is poured into the mold through the funnel or hot top until both the mold and the removable top are completely filled, and the mold is then allowed to stand undisturbed for a period which may vary, in practice, for example, from ten to sixty seconds, depending upon the size of the mold. This is for the purpose of allowing a shell of magnetite to form in contact with the walls of the mold. Before removing the hot top or pouring funnel, the iron or steel core may be immersed into the still molten interior and quickly withdrawn. During the short period of immersion a thin layer of the magnetite is deposited upon the core, thereby producing a coated core of a nature similar to that above described. Where the core is a perforated core having holes therethrough, the layers on either side will be united at intervals by means of the holes. This coated core or screen is then buried in a bed of insulating material such as kieselguhr, to prevent its being cooled too rapidly. If the coated cores have been otherwise produced, their production in this manner will not be necessary, but in the rapid production of cast electrodes the coated cores may with advantage be produced in this manner.

After the core or screen has been thus coated, or after the shell of magnetite has been first produced, within the mold, where the coated core has been otherwise produced, the removable pouring funnel or hot top is knocked off with a shearing effect, thereby leaving the mold filled with the magnetite, the outer portion of which is solid and of uniform thickness, and the inner portion of which is still molten. A coated screen or core, which has been coated by a previous operation, is quickly thrust down into the still molten interior of the mold. This core, when a mold of, for example, 1¼ inches thick is used, may be about ¼ inch thick, and of a width giving ½ inch clearance on either side when inserted in the mold. Thus, with a mold 4½ inches wide, the core might be about 3¾ inches wide. The length of the core might, with advantage, be somewhat

greater than the depth of the mold, for instance, 4 inches greater over all, in the case of a 4 ft. mold.

The wall of magnetite which has already formed in the mold, serves to guide and center the coated core, while the coating upon the core protects it from the corrosive action of the molten magnetite. Before this coating upon the core can be penetrated, the temperature of the mass will be so lowered that the whole will be solidified. This is important, both in order to protect the screen or core, and to insure an intimate contact between it and the body of magnetite surrounding it. With an uncoated screen, there is danger of reaction and of destruction if it is immersed and allowed to remain in the molten magnetite without previous coating, and the union between the core and the magnetite body may be of an imperfect nature. It is accordingly of advantage to use a coated core, or a core which is otherwise of a nature so that it will not be injuriously acted upon by the body of molten magnetite.

As soon as the body of the electrode is solidified, it is quickly removed from the mold, and transported by appropriate means, suitably supported throughout its length, to a soaking or annealing furnace, such as a muffle furnace previously heated to an approprate temperature, where it is allowed to remain for a period varying from, for instance, 5 to 15 minutes. This treatment serves to adjust the strains set up by any difference in expansion of the magnetite and its core, and thus prevent cracking during cooling. After this treatment the electrodes are removed and placed in a body or bed of inert pulverulent material such as kieselguhr, etc.

Where the core is of material which does not lend itself readily to punching or perforating, such as ferro-silicon or silicon steel, the core can be cast with ribs, arranged longitudinally thereof, and these ribs may also, with advantage, be undercut, as indicated in the cross section of Fig. 5 in order to make the union between the core and the body or coating of magnetite more secure. The use of cores of ferro-silicon or of silicon iron or steel presents the advantage that by suitably regulating the content of silicon the co-efficient of expansion can be made substantially the same as that of the magnetite so that danger of splitting off or cracking of the coating or body of magnetite will be thereby minimized. Ferro-silicon or silicon steel is furthermore of an acid resisting nature, and when used as a core, is but little attacked by the electrolyte even when exposed. When thus exposed, the results obtained seem to indicate that the current tends to pass from the core through the magnetite to the electrolyte rather than directly from the core to the electrolyte, thereby further reducing the corrosion of the core.

It may be stated generally, that it has been found appropriate and convenient to make the cores of about $\frac{1}{8}$ of an inch in thickness and from 3 to 4 feet in height, and of a width of, for example, 3 to 5 inches, so that the completed electrode, with its coating or body of magnetite, may be readily handled, and so that it may be of moderate weight where it is employed in the electrolysis of copper ore solutions in operations conducted on a large scale. It will be understood, however, that the dimensions of the electrode may vary with the particular purpose for which the electrodes are to be employed, and that the illustrations given are but typical of its many possible embodiments in practice.

What I claim is:

1. An electrode for electrolytic purposes, comprising a core sheet of metal, and an outer body or coating fused thereto of material insoluble in the proposed electrolyte, said core and said body or coating having substantially the same heat co-efficient of expansion; substantially as described.

2. An electrode for electrolytic purposes, comprising a core sheet of metal and an outer body or coating fused thereto and consisting mainly of magnetite; substantially as described.

3. An electrode for electrolytic purposes, comprising a core sheet of soft iron or mild steel, provided with a series of apertures in close proximity to each other, and a body or coating fused thereto consisting mainly of magnetite; substantially as described.

4. An electrode for electrolytic purposes, comprising a core sheet of soft iron or mild steel, provided with a series of apertures in close proximity to each other, and a body or coating fused thereto consisting mainly of magnetite together with silica; substantially as described.

5. An electrode for electrolytic purposes, comprising a core sheet of soft iron or mild steel, provided with a series of apertures in close proximity to each other, and a body or coating fused thereto consisting mainly of magnetite together with silica and alumina; substantially as described.

6. An electrode for electrolytic purposes, comprising a core sheet of soft iron or mild steel, and a flowed dip coating fused thereto consisting mainly of magnetite, said coating having substantially the same heat co-efficient of expansion as that of the core sheet; substantially as described.

7. An electrode for electrolytic purposes, comprising a core sheet of soft iron or mild steel, and a flowed dip coating fused thereto consisting mainly of magnetite, said coating having substantially the same heat co-

efficient of expansion as that of the core sheet, said dip coating consisting of individual layers blended into substantially homogeneous union; substantially as described.

8. An electrode for electrolytic purposes, comprising a core sheet of metal having a flowed dip coating fused thereto consisting mainly of magnetite and a body consisting mainly of magnetite cast around said coating, said coating and cast body having substantially the same heat coefficient of expansion as that of the core sheet; substantially as described.

9. The method of producing electrodes for electrolytic purposes, which comprises immersing a core sheet of metal in a molten body of a coating conductive material insoluble in the proposed electrolyte and withdrawing said sheet before injury thereto, whereby an outer coating of the material is fused to said sheet; substantially as described.

10. The method of producing electrodes for electrolytic purposes, which comprises immersing a core sheet of metal in a molten body consisting mainly of magnetite and withdrawing said sheet before injury thereto, whereby an outer coating of the magnetite is fused to said sheet; substantially as described.

11. The method of producing electrodes for electrolytic purposes, which comprises immersing a core sheet of metal in a molten body consisting mainly of magnetite and withdrawing said sheet before injury thereto, whereby an outer coating of the magnetite is fused to said sheet, and repeating the immersion to form a further coating upon the coated sheet; substantially as described.

12. The method of producing electrodes for electrolytic purposes, which comprises immersing a core sheet of metal in a molten body consisting mainly of magnetite and withdrawing said sheet before injury thereto, whereby an outer coating of the magnetite is fused to said sheet, and casting a body of magnetite around the coated sheet by inserting such sheet in a body of the magnetite and allowing the body to solidify; substantially as described.

13. The method of producing electrodes for electrolytic purposes, which comprises pouring molten magnetite into a heated mold and allowing the same to stand until a sheet of magnetite is formed in contact with the walls of the mold, then inserting a metal sheet coated with magnetite into the still molten interior of the mold and allowing the molten magnetite to solidify, whereby the shell of magnetite first formed serves to guide the metal sheet, and whereby the coating of magnetite upon such sheet protects it from the action of the molten magnetite; substantially as described.

14. The method of producing electrodes for electrolytic purposes, which comprises pouring molten magnetite into a heated mold and allowing the same to stand until a sheet of magnetite is formed in contact with the walls of the mold, then inserting a metal sheet coated with magnetite into the still molten interior of the mold and allowing the molten magnetite to solidify, whereby the shell of magnetite first formed serves to guide the metal sheet, and whereby the coating of magnetite upon such sheet protects it from the action of the molten magnetite, removing the solidified electrode from the mold and holding the same at the high temperature to anneal the same, and then slowly cooling the electrode; substantially as described.

In testimony whereof I affix my signature.

WILLIAM KINGMAN PAGE.