UNITED STATES PATENT OFFICE.

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ELECTRODE ELEMENT FOR GALVANIC BATTERIES AND METHOD OF PRODUCING SAME.

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No Drawing. Application filed November 6, 1919. Serial No. 336,208.

To all whom it may concern:

Be it known that I, THOMAS A. EDISON, a citizen of the United States, and a resident of Llewellyn Park, West Orange, Essex county, New Jersey, have invented certain new and useful Improvements in Electrode Elements for Galvanic Batteries and Methods of Producing the Same, of which the following is a description.

My invention relates to electrode elements for galvanic batteries, and more particularly to an improved negative electrode element for primary batteries employing a caustic alkaline electrolyte and in which the negative electrode consists of an element or elements of oxid of copper and the positive electrode consists of an element or elements of zinc.

My invention also resides in the method of producing my improved negative electrode element.

In primary batteries of the type described, the negative electrode elements are usually made in the form of plates or cylinders molded from a mass of finely divided oxid of copper. At the present time these oxid of copper elements are generally produced as follows: A mass of powdered copper oxid is first moistened with a strong solution of caustic soda. The damp powdered copper oxid is then placed in molds of proper form and consolidated into elements of the desired shape in a hydraulic press. These elements are then baked by subjecting the same to a temperature of approximately 1700 degrees Fahrenheit for a period of about 15 hours or more in a suitable furnace. During this baking operation the particles of oxid of copper are, under the action of the caustic soda, fritted together at their points of contact so that the elements when cold will have sufficient strength to enable them to be shipped and used commercially without serious liability of breaking.

The method of making negative oxid of copper elements as described above, however, is objectionable for the following reasons:

1. The caustic soda being a poor binder for powdered copper oxid, a considerable number of the molded elements are broken and crumble in handling prior to the baking operation.

2. During the baking operation the elements shrink and crack to an appreciable extent, and because of this it is usually necessary to reject a considerable number of the elements.

3. The use of an excessive amount of fuel is required in maintaining such a high temperature for so long a period during the baking operation.

4. The output of the furnaces employed for baking the elements is small.

5. The elements even after being baked, are weak, the particles of oxid of copper being merely fritted together where they happen to be in contact. Moreover, a large percentage of these particles will be in very loose contact. This results in very poor electrical contact between such particles on reduction to metal and consequently the elements will have a high internal resistance and the current generated by cells provided with such elements will have a low and constantly diminishing voltage.

One of the principal objects of my invention resides in the production of an improved porous battery element formed of agglomerated powdered oxid of copper and in which practically all of the particles are firmly bound together and consolidated, thus rendering the element a practically integral structure with the particles thereof in much more intimate contact with each other, whereby cells provided with such elements will generate current having a higher and more constant voltage than cells provided with similar elements produced by the methods now employed.

A further object of my invention resides in the production of my improved copper oxid element in such a manner that the maintenance of an exceedingly high temperature for a very long period of time during the baking operation is unnecessary.

The present invention is based on the discovery that the foregoing objects may be attained by properly combining with the powdered oxid of copper from which the

elements are to be formed, suitable materials which under certain conditions during the agglomerating of the elements will form cupric oxid *in situ* in the latter. Such materials consist of a caustic alkali and any of a number of copper salts, such as sulfate of copper, and preferably I use for these materials a solution of caustic soda and semi-dehydrated sulfate of copper.

In producing electrode elements in accordance with my invention, where sulfate of copper is used as one of the materials to be combined with the oxid of copper, I first dehydrate the sulfate of copper by driving all but a very small amount of the water of crystallization therefrom. The dry powdered semi-dehydrated sulfate of copper thus produced is ground to an impalpable powder and then thoroughly mixed with the dry powdered copper oxid from which the elements are to be formed, preferably in a mixing machine. The proper amount of a solution of caustic alkali, preferably caustic soda, is then gradually added to the mixture and the operation of the mixing machine is continued until the contents thereof are thoroughly mixed. The caustic soda and sulfate of copper will react to form cupric hydroxid and sodium sulfate, and as I preferably employ an excess of caustic soda, a certain amount of free caustic soda will also be present. The moist batch thus produced is then removed from the mixing machine, placed in suitable molds and molded into elements of the desired shape by means of a hydraulic press. The unbaked molded elements thus produced are not very easily broken, being much stronger than the unbaked molded elements produced in the present processes of making battery elements of copper oxid. This is due to the fact that the free caustic soda and the cupric hydroxid and sodium sulfate formed by the reaction of the caustic soda and copper sulfate with which the copper oxid is mixed, comprise a fairly strong, hard binder for the latter, as distinguished from the caustic alkali which is alone employed in the present methods and which has scarcely any binding properties. The dehydrating of the sulfate of copper renders the mixture of copper oxid, caustic alkali and sulfate of copper, after the reaction between the two latter materials takes place as described, of proper consistency for molding, such mixture then being viscous, tenacious and putty-like. In case any other copper salt containing water of crystallization is employed in place of the sulfate of copper, the same is also dehydrated for the reason specified. The molded elements are now placed in a furnace which is brought up to a temperature which while sufficient to drive off all the water and decompose the cupric hydroxid in the elements so as to form cupric oxid and harden the latter, is much lower than that necessary to frit the oxid of copper of which the material from which the elements are formed is principally composed. Accordingly no shrinkage of the elements takes place during this baking operation. Preferably the temperature to which the furnace is brought is from 1000 to 1300 degrees Fahrenheit, which is maintained for a period of from 3 to 5 hours. Both the temperature at which this baking operation is carried on and the period of such operation, however, vary greatly according to the size of the furnace, the proportions of the ingredients in the elements being baked and the size and shape of such elements. At the conclusion of the baking operation the elements are removed from the furnace, allowed to cool and are then ready for use.

The copper oxid elements thus produced are much stronger than those produced by the methods ordinarily employed. Moreover as there is no shrinkage of these elements in the baking operation, no loss is incurred due to rejection of elements because of such shrinkage. The current generated by cells provided with elements produced in accordance with my invention will also have a higher and more constant voltage than the current generated by similar cells provided with copper oxid elements produced by the methods commonly employed. This is a very great advantage in signal work where cells of this type are mostly employed. Also because of the higher and more constant voltage, the efficiency of the copper oxid will be greatly increased.

The reason cells provided with elements embodying my invention generate a current of higher voltage, is due to the fact that the internal resistance of these elements is much less than elements of this character heretofore produced by reason of the particles of oxid of copper being brought into more intimate contact and better agglomerated. This improved agglomeration of the powdered copper oxid is explained as follows: During the baking operation the cupric hydroxid present in the elements and formed as one of the products of the reaction between the caustic soda and sulfate of copper, is decomposed into cupric oxid and water, and the water is driven off, as above described. Cupric oxid being soluble in caustic soda at high temperatures, a considerable amount of this finely divided cupric oxid formed *in situ* in the elements by the decomposition of the cupric hydroxid will as the baking operation is continued, dissolve in the excess free molten caustic soda and enter all the interstices between the adjacent particles of copper oxid in the elements so as to cover practically all the surfaces thereof. For some reason, the cupric oxid formed *in situ* during the baking of the elements is

very strong and upon hardening acts as a very effective binding agent for the oxid of copper of which the elements are principally composed. Accordingly, all of the particles of copper oxid in the elements, will now be cemented and firmly locked together by this finely divided, hard and strong cupric oxid, whereby a very high degree of agglomeration of such particles is effected and the same are rendered practically integral. The sulfate of sodium formed in the mixture from which the elements are produced, is inert and its presence is therefore harmless.

While the proportions of the materials used in forming elements in accordance with my invention may be greatly varied, I have found that in elements designed to meet the conditions of general use and where caustic soda and sulfate of copper are the materials combined with the oxid of copper, the following proportions are most satisfactory: Approximately 100 parts by weight of oxid of copper, approximately 8 parts by weight of powdered semi-dehydrated sulfate of copper, and approximately 6 to 9 parts by weight of a 20% solution of caustic soda.

While as specified above, other salts of copper may be used instead of sulfate of copper, I prefer to use the latter as it is cheapest and I find that it answers every purpose.

It is to be understood, of course, that various other materials than those specifically described herein may be combined with the oxid of copper in making my improved elements, and that the method of making the same is subject to numerous changes and modifications without departure from the spirit of the invention and the scope of the appended claims.

Having now fully described my invention, what I claim as new and desire to protect by Letters Patent is as follows:

1. An electrode element for galvanic batteries comprising an agglomerated mass of finely divided oxid of copper held together by a binder comprising cupric oxid formed *in situ* in said mass, substantially as described.

2. An electrode element for galvanic batteries comprising a baked mass of finely divided oxid of copper, and a binder therefor comprising cupric oxid formed *in situ* in the mass during the baking operation, substantially as described.

3. An electrode element for galvanic batteries comprising an agglomerated mass of finely divided oxid of copper held together by a binder comprising cupric oxid formed *in situ* and disposed in practically all the interstices of said mass and the latter thereby rendered practically integral, substantially as described.

4. An electrode element for galvanic batteries comprising a baked mass of oxid of copper combined with a material comprising a copper salt, substantially as described.

5. An electrode element for galvanic batteries comprising a baked mass of oxid of copper combined with a material comprising a semi-dehydrated copper salt, substantially as described.

6. An electrode element for galvanic batteries comprising a baked mass of oxid of copper combined with a material comprising semi-dehydrated sulfate of copper, substantially as described.

7. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, a caustic alkali and a copper salt, substantially as described.

8. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, caustic soda and a copper salt, substantially as described.

9. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, a caustic alkali, and a semi-dehydrated copper salt, subtantially as described.

10. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, caustic soda, and a semi-dehydrated copper salt, substantially as described.

11. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, a caustic alkali, and semi-dehydrated sulfate of copper, substantially as described.

12. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, caustic soda, and semi-dehydrated sulfate of copper, substantially as described.

13. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, a caustic alkali, and semi-dehydated sulfate of copper in the proportions of approximately 100 parts by weight of oxid of copper, approximately 6 to 9 parts by weight of a 20% solution of the caustic alkali and approximately 8 parts by weight of the semi-dehydrated sulfate of copper, substantially as described.

14. An unbaked electrode element comprising a molded mass of mixed oxid of copper, a caustic alkali and a copper salt, substantially as described.

15. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, caustic soda and a copper salt, substantially as described.

16. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, a caustic alkali and a semi-dehydrated copper salt, substantially as described.

17. An unbaked battery electrode element comprising a molded mass of mixed oxid

of copper, caustic soda and a semi-dehydrated copper salt, substantially as described.

18. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, a caustic alkali and semi-dehydrated sulfate of copper, substantially as described.

19. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, caustic soda and semi-dehydrated sulfate of copper, substantially as described.

20. The method of producing an electrode element for galvanic batteries which consists in forming a mixture of powdered oxid of copper and material from which cupric oxid will be produced on the application of sufficient heat, and then heating the mixture sufficiently to effect the production of such cupric oxid, substantially as described.

21. The method of producing an electrode element for galvanic batteries which consists in agglomerating a mass of oxid of copper and forming cupric oxid *in situ* in said mass during the agglomeration thereof, substantially as described.

22. The method of producing an electrode element for galvanic batteries which consists in mixing oxid of copper, a caustic alkali and a copper salt, forming the mixture into a molded element, and then baking said element, substantially as described.

23. The method of producing an electrode element for galvanic batteries which consists in mixing oxid of copper, a caustic alkali and a copper salt, forming the mixture into a molded element, and then heating said element at a temperature sufficient to drive off all water therefrom but less than that which will effect shrinkage of the oxid of copper, substantially as described.

24. The method of producing an electrode element for galvanic batteries which consists in thoroughly mixing powdered oxid of copper and a copper salt, then adding to and thoroughly mixing with the mixture thus produced a sufficient quantity of a solution of caustic alkali to dampen the same, then molding the mixture into an element of the desired shape, and then baking such element, substantially as described.

25. The method of producing an electrode element for galvanic batteries which consists in driving off water from a copper salt normally containing water of crystallization, then thoroughly mixing powdered oxid of copper, said salt and a solution of caustic alkali, molding the mixture thus produced into an element of the desired shape, and then baking such element, substantially as described.

26. The steps in the method of producing an electrode element for galvanic batteries which consist in thoroughly mixing powdered oxid of copper with a caustic alkali and a copper salt, and then molding the mixture thus produced into an element of the desired shape, substantially as described.

27. The steps in the method of producing an electrode element for galvanic batteries which consist in partially dehydrating a copper salt normally containing water of crystallization, thoroughly mixing powdered oxid of copper and the said semi-dehydrated salt, adding to the mixture thus produced a sufficient quantity of a solution of caustic alkali to dampen the same, and then molding the mixture into an element of the desired shape, substantially as described.

28. An electrode element for galvanic batteries comprising a baked mass of oxid of copper combined with a material comprising sulfate of copper, substantially as described.

29. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, a caustic alkali and sulfate of copper, substantially as described.

30. An electrode element for galvanic batteries comprising a baked mass of a mixture of oxid of copper, caustic soda and sulfate of copper, substantially as described.

31. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, a caustic alkali and sulfate of copper, substantially as described.

32. An unbaked battery electrode element comprising a molded mass of mixed oxid of copper, caustic soda and sulfate of copper, substantially as described.

This specification signed and witnessed this 3rd day of November, 1919.

THOS. A. EDISON.