Aug. 9, 1932. H. SHOEMAKER 1,870,425

ELECTRODE ELEMENTS FOR RECTIFIERS AND PROCESS OF MANUFACTURING THE SAME

Filed Jan. 29, 1929

Fig. 1.

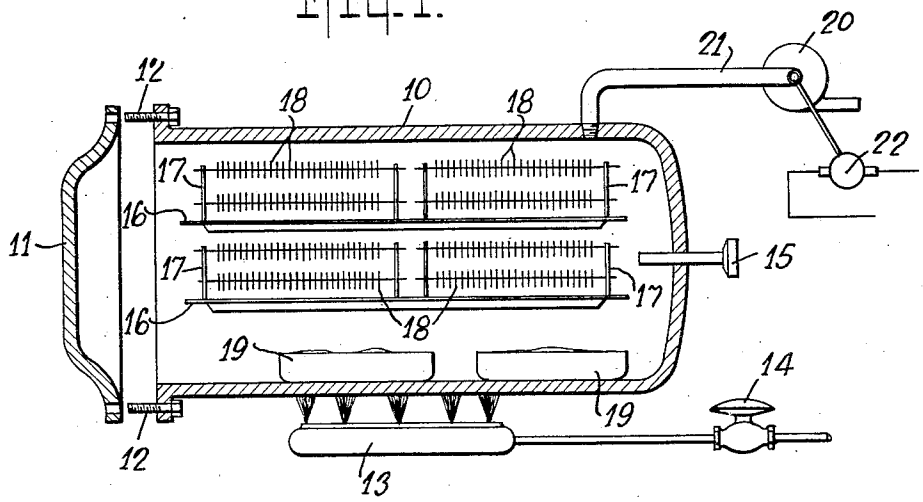


Fig. 2.

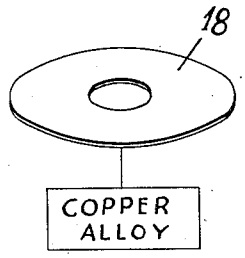
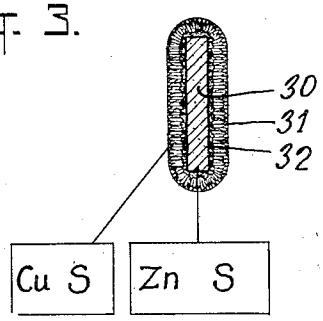


Fig. 3.



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UNITED STATES PATENT OFFICE

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ELECTRODE ELEMENTS FOR RECTIFIERS AND PROCESS OF MANUFACTURING THE SAME

Application filed January 29, 1929. Serial No. 335,932.

This invention relates to electrode elements for rectifiers, more particularly to electrode elements for dry surface contact rectifiers, and to a process of manufacturing the same.

The invention has for its object an improved construction of electrode parts, particularly of composite electrodes, in order to have relatively long life, and to the provision of improved steps whereby such electrodes may be produced continuously on a commercial scale with substantial uniformity in characteristics.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties, and the relation of constituents, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing, in which:

Fig. 1 is a view, mainly in section, showing an arrangement of apparatus adapted for carrying out the process of the present invention;

Fig. 2 shows in perspective one of the raw materials utilized in the process of producing electrode elements in accordance with the present invention; and

Fig. 3 is an enlarged sectional view through a portion of the finished product.

Referring now to the drawing and particularly to Fig. 1, 10 denotes a treating chamber which is of a relatively refractory metal and is adapted to be sealed so as to be substantially gas-tight during the treating period. The treating chamber accordingly has a movable cover 11. A treating chamber constructed of iron or steel and provided with a cover secured in place by means of bolts as shown at 12, is a suitable reaction chamber for carrying out the treating process of the present invention.

A suitable heating means, for example, a gas burner as shown at 13, is disposed in sufficient proximity to the treating chamber 10 to heat the same to the desired reaction temperatures, the heating means being governed by a suitable control device, for example, the diaphragm-controlled valve as shown at 14. In order that the time-temperature cycle may be regulated with precision, as herein desired, the treating chamber is provided with a pyrometer 15, which indicates the temperatures of the treating chamber so that the valve at 14 may be manually controlled, or if desired, a suitable automatic means under the control of the pyrometer may be employed to actuate the valve.

Within the treating chamber are suitable supports, for example, one or more shelves as shown at 16, upon which frames 17 are supported, which contain discs 18 to be treated by the process of the present invention. Below the shelves are placed containers or trays 19, which contain the treating agent that is to be vaporized during the heating cycle. An exhaust pump 20 is also connected with the treating chamber 10 through the pipe connection 21 and is adapted to be driven by any convenient source of power, for example, a direct connected electric motor as indicated at 22.

By operating the treating chamber so as to pass through a desired time-temperature cycle as hereinafter described, electrode elements adapted for use as the electronegative electrode elements in dry surface contact rectifying devices may be produced where the raw materials are relatively thin metallic discs of a metallic alloy, which contains two or more metallic constitutents, each of which is adapted to react with the treating agent, the metallic constituent which has the higher specific gravity comprising the major constituent of the alloy.

A copper alloy wherein copper is alloyed with any lighter metal, reference being had to any improved specific gravity table, is suitable for this purpose. The reaction with the treating agent of both metallic constituents

to give a desired operative electronegative electrode element is accompanied by a migration of the heavier metal, "heavier" being used in the sense of specific gravity, to give defined layers of compounds of the constituents, that of the heavier metal forming the outside layer. It seems probable that this result is dependent chiefly on the relative specific gravities of the constituents.

An example of such an alloy suitable for this purpose which is both workable and cheap is brass, for example, one containing copper 85% by weight and zinc 15% by weight. The discs to be treated may have any desired physical contour but are preferably round perforated discs of the character indicated in Fig. 2. Annular discs punched from ten-mill sheets of brass of the composition above indicated, are particularly suitable for mass treatment by the process of the present invention.

The treatment of the annular discs here shown en masse is readily accomplished in the treating chamber by supporting a plurality of the same on rods disposed in the frames 17, the rods and frames being made of a metal highly resistant to the treating agent.

The treating process of the present invention is adapted to produce electronegative electrode elements for asymmetric couples which are compounds of a chemical element of the oxygen family of the sixth periodic group, particularly of the element sulphur, and is especially adapted to the production of electrode bodies which have an active surface containing a maximum valent compound of copper with sulphur, such as cupric sulphide. The form of this compound which has rectifying characteristics of the character generally desired, is that which has a dark-blue appearance.

In the practice of the present invention, when producing electrode bodies of this character, the trays 19 are filled with flours of sulphur taken in sufficient quantity that there is an excess of sulphur present over that which is vaporized and combined with the metallic discs in the treating chamber. When the chamber has been filled with frames 17 supporting metallic discs to be treated, the chamber is sealed by securing the cover 11 in place, whereupon heating is begun by turning on the heating means. The treating chamber is gradually raised to a temperature of 430° C. at a relatively uniform rate over a period of substantially from six to seven hours. When this temperature is attained, the intensity of the heat applied is diminished, that is, the heating means is turned down, although preferably not completely turned off for a period of an hour or somewhat less.

As soon as the cover 11 is secured to the treating chamber 10, the exhaust pump 20 may be set into operation. It is, however, not essential to start the same immediately, but only to have it operating substantially coinitially with the first evolution of sulphur vapors from the pans 19, for example, the pump may be set into operation substantially at any time within a half hour after the cover is sealed. By this means atmospheric air is removed from the treating chamber, thereby removing oxygen and water vapors that might otherwise react with the sulphur vapors and produce undesirable results. When the pump 20 has been operated sufficiently to remove substantially all the atmospheric air from the treating chamber, it may be stopped, that is, it may be stopped after operating for a period approximating from one-half to one hour. When the pump is stopped, it is preferable that the pressure within the treating chamber shall remain slightly below normal atmospheric, so that when the sulphur vapors are being sublimed from the pans 19 to fill the chamber 10, any tendency for escape to the outside of the chamber 10, which would make it unpleasant for attendants, is thereby avoided.

The temperature rise within the treating chamber does not stop coincidentally with the lowering of the intensity of the heating effect, but may rise a few degrees above that attained when the heating means is turned low, since the process within the treating chamber is exothermic.

After an hour or so of applying heat of low intensity, the heating means may be entirely cut off and the treating chamber allowed to cool gradually for a period of from five to six hours, when the treating cycle is concluded, the chamber opened, and the frames containing the formed electrode elements are removed from the treating chamber. When the chamber is sufficiently cooled, the excess of the sulphur vapors may be removed before opening, if desired.

It is thus seen that the process preferably includes a cycle of heating and cooling over a period of from twelve to sixteen hours, the precise duration of such period being dependent upon the desired effect upon the electrode, both the heating and the cooling requiring suitable periods of time to give the best results. Since these parts of the cycle extend over protracted periods of time they are referred to as "slowly" or "gradually" heating and cooling.

A section of the electrode elements formed by the process above described is shown in Fig. 3, where it is indicated as having a central core 30, which is a relatively homogeneous, though somewhat porous, compound of zinc sulphide, this core being somewhat greater in cross-sectional area than that of the original metallic disc. About this core is an extended crystalline structure of cupric sulphide, which, when made in the manner above described, comprises long, parallel,

crystal needles 31 disposed end-on against the core 30, these crystals, upon analysis, being found to be substantially pure cupric sulphide of the dark-blue variety. Closely disposed about the core 30 and at the base of the standing crystal needles of cupric sulphide, there may be an intermediate structure in which the crystals of cupric sulphide are not quite so regular as that of the outer layer, this layer being indicated at 32, and has a somewhat irregular fracture or hackly; this intermediate layer when present being generally slightly more dense than the outer structure.

The growth of the crystal needle structure about the central core in the electrode elements of the present invention is accompanied by a migration of the heavier component, copper, from within the core to points without, and there appears to be an exchange or metalepsis of sulphur for copper in the space occupied by the original copper-alloy disc, here taken as the basic material for treatment.

Formation of the distinct layers of compounds of the two constituents is thus necessarily relatively slow since the heating and cooling periods must be of sufficient duration to allow the proper migration of the heavier metal and the so-called metalepsis of the treating agent for the heavier compound and the proper growth of the distinct layer of crystals. It becomes apparent that gradual or slow increases in temperature during the heating period and the gradual decrease during the cooling period are essential to the efficient production of the layers of crystals.

The electrode elements, after they come from the treating chamber, are preferably machined in order to give them a smooth plane contacting surface whereby they can be placed in co-operating relation with a metallic electropositive electrode element to form asymmetric couples for rectifying purposes.

Since certain changes in carrying out the above process, and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. The process adapted to produce electronegative electrode elements, which comprises providing a body of an alloy of copper with a lighter metal adapted to react with a chemical element of the oxygen family of the Sixth Periodic Group, exposing the same to the action of vapors of said chemical element in a hermetically-sealed chamber, gradually increasing the temperature of said treating chambers over a protracted period of time, and thereafter gradually cooling the same.

2. The process adapted to produce electronegative electrode elements, which comprises providing a disc to be treated of an alloy of copper with a lighter metal, exposing the same in a hermetically-sealed chamber to the action of sulphur vapors, gradually raising the temperature of the same over a protracted period of time, and thereafter gradually cooling the same in said sealed chamber.

3. The process adapted to produce electronegative electrode elements, which comprises providing a disc to be treated of an alloy of copper with a lighter metal, exposing the same in a hermetically-sealed chamber to the action of sulphur vapors, gradually raising the temperature of the same over a protracted period of time at a substantially sub-atmospheric pressure, and thereafter gradually cooling the same in said sealed chamber.

4. The process adapted to produce electronegative electrode elements, which comprises providing an initial body of a metallic alloy, exposing the same to the action of sulphur vapors in a hermetically-sealed chamber at sub-atmospheric pressure, gradually raising the temperature of the same to a reaction temperature of approximately 430 degrees C., and thereafter gradually cooling the same in said hermetically-sealed chamber.

5. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like, which comprises a core of zinc sulphide having an envelope surrounding the same, comprising crystallized cupric sulphide.

6. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a core of a metallic compound with a chemical element of the oxygen family of the sixth periodic group having a crystallized envelope of a copper compound with an element of the oxygen family of the Sixth Periodic Group, said second metal having a higher specific gravity than the first.

7. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a core of a metallic sulphide having an envelope of a crystalline copper sulphide, said second metal having a greater specific gravity than the first.

8. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a core of a relatively light metallic sulphide having an envelope comprising a maximum valent compound of copper with sulphur having a crystalline form.

9. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a core of a relatively light metallic sul-

phide having an envelope comprising cupric sulphide crystallized in relatively long needles disposed end-on about said core.

10. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a body having a contacting surface composed of crystalline needles of cupric sulphide, said crystals being arranged parallel each to each and adapted to make contact at their ends.

11. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a crystalline cupric sulphide body containing relatively long needles arranged side by side and cut transversely, whereby said crystals are adapted to make end-on contact with an electropositive electrode body.

12. An electrode body adapted for use as an electronegative electrode element in dry surface contact rectifiers and the like which comprises a maximum valent compound of copper with a chemical element of the oxygen family of the Sixth Periodic Group, said compound comprising elongated needle-like crystals disposed parallel and cut transversely to provide an end-on contacting surface with an electropositive electrode body.

In testimony whereof I affix my signature.

HARRY SHOEMAKER.