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METHOD OF MANUFACTURING BLOCKING-LAYER ELECTRODE SYSTEMS

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This invention relates to a method of manufacturing blocking-layer electrode systems of the kind comprising a selenium electrode and also to the blocking-layer electrode system produced thereby.

The invention has primarily for its object to improve the blocking layer of such an electrode system. The quality of this layer is of very high importance as regards satisfactory operation of blocking-layer electrode systems, for example in industrial rectifiers. As is well known, an increased blocking effect ensures that the leakage current is reduced so that the losses are reduced and the efficiency increases. In addition, this leakage current primarily governs the evolution of heat in the rectifier and it is this evolution of heat which generally causes the electrode system to deteriorate. An increase of the blocking effect leads to a decrease of the evolution of heat and thus to an increase of the life, and the loading capacity.

With blocking-layer electrode systems having a non-genetic blocking layer, for example of polystyrol, it has been suggested to limit the leakage current by the provision of a bounding layer of high resistance between the blocking layer proper and the selenium. A lesser number of electrons is thus emitted during the reverse cycle in which the selenium is negative and hence a blocking effect is bound to occur. This method of reducing leakage is particularly important in those cases in which the resistance in the pass-direction may have a comparatively high value. As is well known, the supplementary resistance-layer also increases the resistance in the pass-direction.

The invention is based on recognition of the fact that the condition of the selenium surface at the time of formation of the blocking-layer plays an important part in the obtainment of a satisfactory blocking-layer effect. The invention is characterized in that the selenium layer has a blocking layer formed on it after its transformation, at least at the surface, into the crystalline modification (Se_B) exhibiting poor conductivity but before it is converted completely into the modification (Se_C) of good conductivity.

It is known that selenium after being applied to a carrier and smoothed, generally shows the so-called amorphous structure, which is non-conductive and is referred to hereinafter as SE_A. If this selenium is subjected, if desired under a press, to heat-treatment, for example at about 160°, the amorphous selenium passes into the crystalline modification which, however, is of poor conductivity and which is referred to herein as Se_B. The transformation into the conducting modification, which is finally desired, takes place at a substantially higher temperature, generally at about 200° C. The selenium thus formed is referred to herein as Se_C. Now, according to the invention the blocking layer is not applied until crystalline selenium (Se_B) has been formed at least superficially. Furthermore, the complete transformation of the crystalline selenium Se_B into the conducting form Se_C does not take place until the blocking layer has been applied. Thus, the blocking layer is applied between two treatments the former of which has already led to the formation of Se_B on the surface, whereas the latter completes the process rendering the selenium conductive. It has been found that this is particularly advantageous as regards the density, the uniformity and the firm adhesion of the blocking layer.

This method is particularly important in connection with that kind of blocking-layer formation in which surface treatment of the selenium is conducted to render the substance on the surface (selenium and/or an admixture therewith) non-conducting. Such a method is described in French specification 826,933, it being highly advantageous to carry out several successive forming treatments, each succeeding treatment being preferably performed at a higher temperature than the previous one. As is well known, treatment at high temperature results in a continuous transformation of the selenium because the time of applying the blocking layer is chosen in such manner that the complete transformation into Se_C has not yet taken place. On the other hand, a good basis for the blocking layer is provided because the crystalline selenium Se_B has already been formed, at least superficially.

The selenium is found to be highly sensitive to the action of the substances that serve for the formation of the blocking layer during the progress of transformation. If a second treatment is carried out at a higher temperature than the first this progress in the transformation of the selenium is sure to ensue.

The complete building up of an electrode system according to the invention will now be described and several other measures that may be used with advantage will also be set out.

A quantity of molten selenium has added to it an admixture for increasing the conductivity. A large number of such admixtures are serviceable. Thus, for example from 0.1 to 0.2%, for example 0.12%, of zirconium chloride may be added.

A quantity of this mixture is applied in the liquid state on a rotary aluminium carrier which may be previously roughened for better adhesion and also provided with layers of zinc and carbon (see U. S. Patent No. 2,244,664, issued June 10, 1941). Due to the centrifugal force the selenium is distributed evenly over the surface (see patent application Serial No. 254,508, filed February 3, 1939). The selenium layer formed may have, for example, a thickness of 80 microns.

Next a small roughened mica plate is laid on the carrier comprising the selenium layer, said plate being previously coated on the side adjacent the selenium with a liquid which, due to its action on the selenium layer, forms a blocking layer. Such liquids must have a comparatively high boiling point because the action ensues at a temperature of about 160° and the liquid must be prevented from being vaporised too rapidly. In addition it has been found that use may be made with advantage of a substance in which the selenium is slightly dissolved. Due to the selenium particles on the surface being brought into solution a much more intense action on the selenium and the admixture may result so that it is more easily possible to render the material on the surface non-conductive. Satisfactory results are obtained by means of substances having an alkaline reaction. Both the conversion of the zirconium chloride into the zirconium oxide and an action on the selenium itself may be influential. The exact action on the selenium has, however, not yet been elucidated. As an example of a substance that has the said properties we may mention quinoline.

The selenium layer and the mica plate, jointly with the interposed quinoline, are then compressed in a press having a temperature of about 160°. This treatment takes about 5 minutes. Due to the compression the selenium layer is caused, to an even greater extent than that obtained by centrifuging, to assume a uniform thickness and made compact. Due to the action of the quinoline a first blocking-layer formation also ensues. As may be seen from French Patent 826,933 no other treatment than this blocking-layer formation used to be performed and subsequent treatment was only carried out for converting the Se_B formed under the press into the conducting modification Sec.

In accordance with the invention a further forming treatment is carried out with the selenium which is converted into the crystalline modification (Se_B) but has not yet obtained the final form Sec, since after the aggregate has been withdrawn from the press and the mica plate is removed quinoline is again applied to the surface of the electrode. The quinoline is preferably applied by spraying, so that a fine distribution over the surface is obtained. The intimate contact between the quinoline and the selenium surface which was obtained under the press by the pressure of the press is now produced due to the fact that the quinoline is sprayed in fine drops on to the entire surface.

Secondly, this method of spraying or disintegration has for its object to distribute the quinoline uniformly throughout the surface. In the third place, this method permits of applying an accurately dosed quantity of quinoline. It has been found that the avoidance of an excessive quantity of quinoline is very important in connection with the obtainment of a satisfactory result. This may be due to the fact that when an excessive quantity of quinoline is provided locally or throughout the surface an excessive quantity of selenium is brought into solution so that the uniformity of the selenium layer may be disturbed.

If the blocking layer is to be further intensified this is not effected by applying more quinoline, which involves a longer action, but is preferably effected by using a further independent forming treatment.

The second treatment described is carried out at a temperature between 160° and the melting point of the selenium. The selenium electrode may, for example, be introduced into a furnace having a temperature of 200° C. After the temperature of the plate has reached about 170° the plate, while staying in the furnace, is subjected for 2 minutes to spraying with quinoline. The selenium electrode is then left in the furnace for another three minutes.

To complete the construction of the electrode system the blocking layer then has applied to it by spraying a complementary electrode consisting, for example, of a low-melting alloy of tin, bismuth and cadmium.

By splitting up the forming treatment in this manner and performing at least one stage (in the example quoted the second stage) after Se_B is formed and before the complete conversion into Sec has taken place it is ensured that the blocking-layer formation takes place while the selenium is in a condition which is particularly sensitive to the forming action.

Since this forming stage is independent of the application and smoothing of the selenium layer of the operation of rendering the selenium compact under the press and finally of the final complete conversion into the conducting modification Sec it can be controlled entirely and can be effected in a manner capable of ready reproduction.

The preceding blocking-layer formation under the press has the effect that a single following stage suffices in this case. Instead of carrying out the blocking-layer formation under the press it is, however, possible to add a blocking-layer forming treatment after compression.

Depending on the blocking layer desired to be formed the treatment may be repeated as many times as desired.

Each successive treatment procures an intensification and greater homogeneity of the blocking layer obtained in the previous treatment. Feeble spots which lead to a high leakage current are in effect nullified.

The advantages obtained according to the invention are apparent from the test results given below. The forward current of an electrode system of well-known form and also of a system in which blocking-layer formation has been effected under the press by the action of an alkaline liquid, is, at 2 volts, about 0.25 amp./cm.^{2}. The admissible blocking voltage for such a system is from about 16 to 18 volts. In this case a leakage current of about 8 ma./cm.^{2} occurs; a higher leakage current is regarded as inadmissible.

In a system made by the method of the invention the admissible blocking voltage is, however, from 30 to 45 volts. It is most surprising that under these conditions the same forward current can be obtained so long as care is taken that the conductivity of the selenium is sufficiently high. This is ensured in the embodiment described by the addition of the percentage of zirconium chloride indicated. In spite of the high conductivity thus obtained a leakage current of only 8 ma./cm.^{2} arises at the said blocking voltage.

From this it can be concluded that very high advantages can be obtained. Thus, for example, it was hitherto requisite to connect in series such a number of electrode systems that the blocking voltage per electrode system did not exceed the admissible value and hence the leakage current did not increase to a value exceeding about 8 ma./cm.^{2}. As a first result of the invention it is found that the number of systems to be connected in series can be reduced by approximately half for this blocking voltage.

The effect is also apparent from the following test. Four small plates made by known methods may be loaded in a Grätz circuit with an alternating voltage of 16 volts. In this case 0.05 amp./cm.^{2} can be obtained at a direct output voltage of about 11.5 volts. If cooling plates are used in this case the output current can be increased to 0.1 amp./cm.^{2}.

When using electrode systems made according to the invention and comprising cooling plates it is possible to apply an alternating voltage of 30 volts in the same circuit. In this case it is also possible to obtain 0.1 amp./cm.^{2} but at a direct output voltage of 23 volts. The energy obtained with the use of a corresponding number of electrode systems of corresponding size is consequently doubled.

In all these cases the operating temperature of the rectifiers is comprised between 50 and 55° C.

What we claim is:

1. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming a blocking-layer on the selenium electrode after the selenium at the surface thereof has been converted into its poor-conducting crystalline modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modifications (Sec).

2. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming on the selenium electrode a blocking layer in a plurality of consecutive intensifying treatments after the selenium at the surface thereof has been converted into its poor-conducting crystalline modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modification (Sec).

3. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming on the selenium electrode a blocking layer in a plurality of consecutive treatments after the selenium at the surface of the selenium electrode has been converted into its poor-conducting modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modification (Sec), the first treatment being effected at a lower temperature than the subsequent treatments.

4. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, pressing the selenium electrode, forming a blocking-layer on the selenium electrode in a plurality of treatments after the selenium at the surface of the selenium electrode has been converted into its poor-conducting crystalline modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modification (Sec), one of said blocking-layer forming treatments being effected simultaneously with the pressing step.

5. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming a blocking-layer on the selenium electrode in a plurality of treatments after the selenium at least at the surface of the selenium electrode has been converted into its poor-conducting crystalline modification (Se_B) and before it has been converted into its good-conducting modification (Sec), and heating the system simultaneously with one of the latter of said blocking-layer forming treatments to convert the poor-conducting crystalline selenium (Se_B) into the good-conducting crystalline modification (Sec).

6. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming a blocking-layer on the selenium electrode by applying thereto a dosed quantity of a substance which renders the surface of the selenium electrode non-conductive, the formation of the blocking layer being effected after at least the selenium at the surface has been converted into its poor-conducting crystalline modifications (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modifications (Sec).

7. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming a blocking-layer on the selenium electrode by applying to the surface of the selenium electrode a dosed quantity of a substance which has an alkaline reaction and dissolves selenium, the blocking layer formation being effected after at least the selenium at the surface has been converted into its poor-conducting crystalline modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modifications (Sec).

8. In the manufacture of a blocking-layer electrode system, the steps of applying a selenium electrode to a substratum, forming a blocking layer in a plurality of treatments, the first treatment being effected at a temperature of about 160° C. after the selenium at the surface has been converted into its poor-conducting crystalline modification (Se_B), and converting the selenium at the surface of the electrode into its good-conducting modification (Sec), one of the latter of said blocking-layer formation treatments being effected at a temperature of about 200° C.

9. In the manufacture of a blocking-layer selenium electrode system, the steps of forming a selenium electrode on a carrier plate, placing a pressing plate upon the surface of the selenium electrode with the interposition of a uniformly-distributed layer of a liquid adapted to act upon the selenium to form a blocking layer, pressing the assembly while heating the same to a temperature of about 160° C., removing the press-

ing plate, applying to the so-formed surface a substance in a finely-divided state and adapted to act on the selenium to form a blocking layer, and heating the assembly at a temperature of about 200° C.

10. A blocking-layer electrode system comprising a selenium electrode, the selenium at the surface of the electrode consisting of the good-conducting modification (Se_C), and a blocking-layer formed on the electrode while the selenium at the surface thereof is in its poorly-conducting modification (Se_B), the selenium at the surface of the electrode being converted from its poorly-conducting modification (Se_B) into its good-conducting (Se_C) modification after the formation of the blocking-layer.

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