

Sept. 30, 1947.

A. VON HIPPEL ET AL
COMPOSITE SELENIUM ELECTRODE

2,428,055

Filed Jan. 5, 1943

2 Sheets-Sheet 1

Fig. 1.

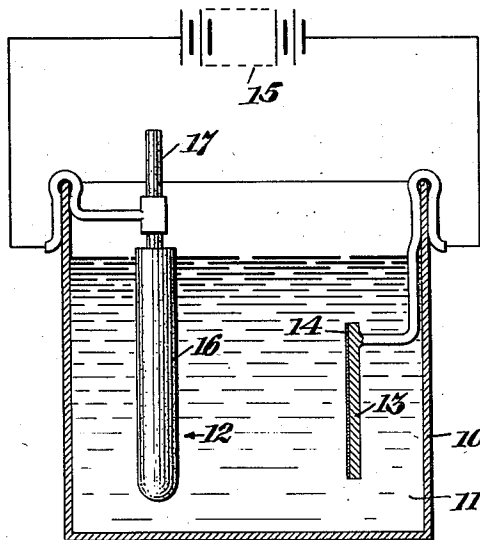


Fig. 2.

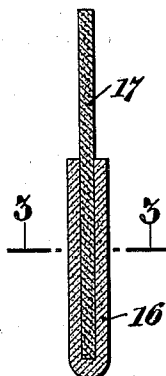


Fig. 4.

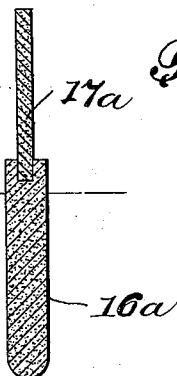


Fig. 3.



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Fig. 5.

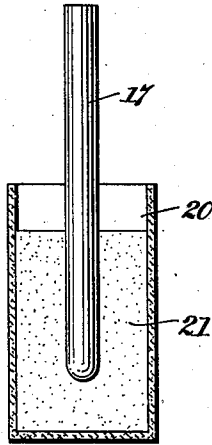


Fig. 6.

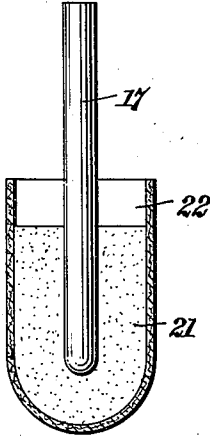
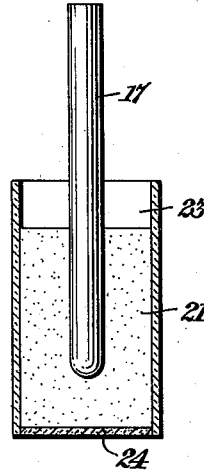


Fig. 7.



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COMPOSITE SELENIUM ELECTRODE

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Application January 5, 1943, Serial No. 471,346

5 Claims. (Cl. 204—282)

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This invention relates to electrodes and a method of making them, of a type used in electro-deposition solutions and has for its object to provide an electrode which can efficiently be used in a solution for electro-depositing selenium.

In the use of selenium plating arrangements in which metallic selenium is deposited on a cathode, we have found

(1) That unless the anode material consists of a substance inactive to the electrolyte and to the anodic products of electrolysis, the anode is attacked and destroyed either by the chemical action of the reagents of the bath alone or by the electro-chemical action when current is passed; and

(2) Even if the anode material does consist of such an inactive material, the passage of current is attended by a copious and undesirable evolution of gas at this anode and it also causes a depletion of the selenium content of the plating solution.

Theoretically these undesirable effects might be eliminated by use of an electrode of pure selenium in which case the passage of electric current causes anodic dissolution of the selenium rather than gas evolution, the dissolved selenium replenishing the concentration of that element in the plating bath as it is used up in the plating. Electrodes of selenium alone, however, have such high electrical resistivity that insufficient current can be sent through the solution for a satisfactory plating.

We have discovered that by using electrodes in which selenium is admixed with an inactive substance of good conductivity, there is little or no bubbling at the electrode and the conductivity is sufficiently high to permit a satisfactory flow of current through the solution, the electro-chemical change taking place at this anode being the same as that obtained with a pure selenium anode, namely, oxidation of the Se to Se^{+4} . We have discovered that carbon, platinum, gold and palladium are suitable materials for mixing with the selenium for this purpose. Of these, carbon is preferable owing to its cheapness. According to the present invention there is provided a selenium-carbon electrode (or alternatively, selenium-platinum or selenium-gold or selenium-palladium) suitable for this purpose. The invention will be better understood from the following detailed description taken in conjunction with the accompanying drawings, of which

Fig. 1 shows an electro-deposition bath containing an electrode in accordance with this invention:

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Fig. 2 shows a cross-sectional view of an electrode in accordance with this invention;

Fig. 3 shows a cross-section view taken at line 3—3 of Fig. 2;

5 Fig. 4 shows a cross-sectional view of a modified form of electrode in accordance with this invention;

Figs. 5, 6 and 7 show alternative forms of electrodes.

10 Fig. 1 shows a container or jar 10 containing a selenium plating solution 11 which may be of a type disclosed in the copending application of Von Hippel and Bloom, Ser. No. 420,906, filed November 29, 1941, which is now abandoned.

15 The solution may be made, for example, by dissolving selenium dioxide (SeO_2) in large quantities in an aqueous bath which also contains an acid, for example sulphuric acid, H_2SO_4 . The positive hydrogen ions from the acid tend to favor the production of quadrivalent selenium cations by combining with the oxygen of the selenium dioxide and forming water. We have found that such acids as sulphuric acid (H_2SO_4), selenic acid (H_2SeO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) are especially suitable for enhancing the concentration of quadrivalent selenium cations. Immersed in the bath there is an anode 20 25 30 12 and a cathode 13. The cathode may be in the form of a suitable disc on which the deposition of selenium is to be made at 14, when a source of voltage 15 is connected between the cathode and the anode.

In accordance with the preferred form of this invention the anode electrode is constructed as shown in the cross-sectional views of Figs. 2 and 3. An electrode 16 composed of a mixture of selenium and carbon, is fitted with a suitable conducting wire or rod 17, which may be one of the group platinum, gold or graphite, and which serves merely as a mechanical holding device or handle and as a point of connection to the source of current. The electrode 16 is preferably made of a mixture of selenium powder and carbon powder, which may be shaped in a suitable mold. This mixture is heated to a temperature causing sintering or preferably above the melting point of the selenium so that the selenium melts and upon cooling forms a solid block throughout which the carbon is evenly distributed. The selenium is then preferably annealed by heating it up to a temperature kept below the melting point of selenium to form the metallic or grayish form although this step is not essential. In such an arrangement the proportion of carbon to selenium has not been found critical as per-

tages of carbon in the mixture varying from about 10% to 75% by weight have been found satisfactory.

An alternative way of making the anode is to place the mixture of selenium and carbon with or without simultaneous heating under sufficient pressure to produce an electrode of good mechanical strength. When such an arrangement is used it has been found that the percentage of carbon required for good electrical conductivity can be as low as 2.5% by weight. When pressure without heat treatment is employed it has been found that the anode tends to disintegrate more rapidly in the solution than does the sintered or molten and annealed type anode described above.

Fig. 4 shows a construction of the electrode which is somewhat different from that shown in Fig. 2. In Fig. 4 the conducting wire or rod 17a intrudes only a little way into the top of the electrode, instead of almost all the way through it as shown in Fig. 2. The arrangement of Fig. 4 has the advantage of enabling the electrode mixture 16a to be practically entirely consumed without attacking the rod 17a. This may be done by inserting the electrode into the bath up to a level which is below the bottom of the rod 17a. This is illustrated in Fig. 4 wherein the dotted line 18 represents the surface of the bath.

The conductivity of the anode may be made to have any desired value by selection of the ratio of carbon to selenium and the proportions of the anode. For example, a mixture of 71.5% of selenium and 28.5% of graphite, by weight, formed into a rod-shaped electrode 4 inches long and $\frac{1}{8}$ inch in diameter and fitted with a $\frac{1}{4}$ inch diameter graphite rod as a core, has a resistance of about 1 ohm.

The efficiency of the anode in respect to the proportion of the current flow consumed in forming the desired Se^{+4} cations, depends somewhat on both the proportions of the ingredients and on the current density at the anode. For example, a mixture of 20% carbon and 80% selenium has been found to have a current efficiency of about 90%, and the efficiency has been found to change if the proportions and/or current density are greatly varied from this.

By the use of an electrode in accordance with this construction, it has been found that a fairly rapid deposition of the desired metallic grayish form of selenium may be obtained on the cathode 13, with little or none of the undesired bubbling of oxygen gas from the anode. The carbon, even though in relatively small proportions in the anode, serves to provide a high conductivity needed for the rapid plating and the selenium passes into solution to replace that which is deposited on the cathode. Thus the solution is maintained at its desired concentration of quadrivalent selenium.

It will be understood that while the invention has been described in detail with respect to the mixture of carbon with selenium, which is a preferred mixture in view of the cheapness of carbon, either gold or platinum or a mixture of both might be substituted for some or all of the carbon in the mixture in so far as electrical and chemical operation and efficiency are concerned. Furthermore, the electrode is not necessarily limited to use as an anode as shown in the example described; it might in some instances be used as a cathode. For example when used in a cathode in a dilute H_2SO_4 solution, hydrogen selenide (H_2Se) will be generated which is useful in the anodic electro-deposition of selenium. Such an

anodic electro-deposition is described in copending application Serial No. 467,562, filed December 1, 1942, by Mortimer C. Bloom, now Patent No. 2,414,438, January 21, 1947.

Figs. 5, 6 and 7 show some different forms in which an electrode containing selenium powder might be constructed. In Fig. 5 the electrode material is cast or compressed and held within a porous cup 20 such as a porous ceramic cup within which there is inserted the rod 17 which is preferably of carbon but could be one of the other inactive materials such as platinum or gold. The cast or compressed mixture of selenium and carbon 21 is placed within the cup and the rod provides the connection. This may be used as an anode in place of that shown in Fig. 1. The porosity of the ceramic cup allows the plating solution to come into contact with the selenium.

In Fig. 6 the rod 17 and the cast or compressed selenium substance 21 is placed within a bag 22 of fiber glass so constructed that it is porous and allows the plating solution to enter into contact with the selenium.

Fig. 7 shows a modification in which the container for the selenium and the conducting rod is a glass tube 23 having a porous end piece 24 made of sintered glass which allows penetration of the solution to the selenium substance 21.

In each of the embodiments of Figs. 5, 6 and 7 the electrode material may either be cast directly within the porous container which may then be fitted with the connecting rod or wire, or the electrode material may be cast first and then have the porous container loosely fitted over it.

The embodiments of Figs. 5, 6 and 7 has the advantage of keeping floating particles from the electrode from filling up the bath. In operation, the carbon tends to fall off the electrode as it is used up and if these floating particles were allowed to float all over the bath they would be objectionable. But by the use of the surrounding porous container no such particles may get out into the bath.

What we claim is:

1. An electrode comprising a porous container, a conductor within the container and a conductive solid body comprising coherent compressed selenium-carbon powder within the container around the conductor.
2. An electrode according to claim 1 in which the conductor is a non-reactive material of good conductivity from the group consisting of platinum, gold and graphite.
3. An electrode according to claim 1 in which the container is of fiber glass.
4. An electrode according to claim 1 in which the porous container is of ceramic material.
5. An electrode according to claim 1 in which the porous container comprises sintered glass.

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