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SELENIUM RECTIFIER AND PROCESS FOR MAKING SAME

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Fig. 1

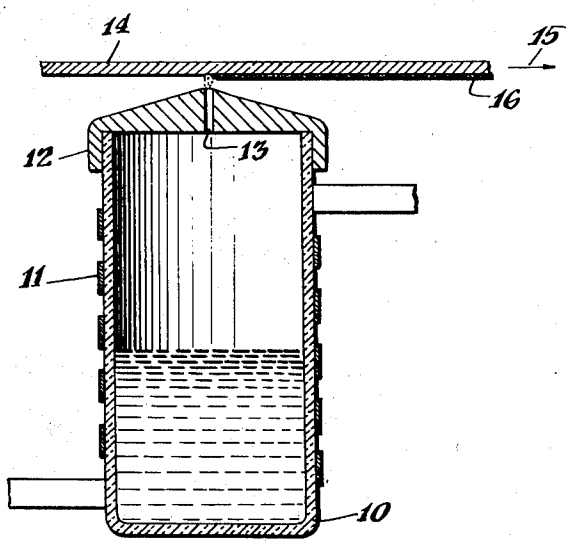
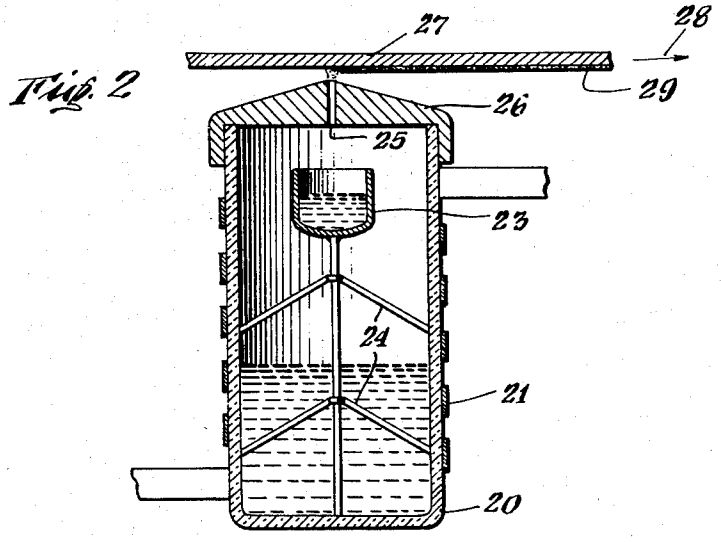


Fig. 2



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SELENIUM RECTIFIER AND PROCESS FOR MAKING SAME

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8 Claims. (Cl. 175—366)

1

This invention relates to selenium rectifiers and to a process for the manufacture thereof, and has for an object to provide an improved method for forming the selenium element of the rectifier.

Another object is to provide a selenium layer having novel and improved characteristics.

Another object is to facilitate the formation of the blocking layer.

Other objects and advantages will be apparent as the nature of the invention is more fully disclosed.

In the manufacture of selenium rectifiers it is necessary to form a blocking layer on the surface of the selenium in contact with the counter electrode and to so condition the same that a high resistance is obtained in the reverse direction. At the same time, the selenium should have a low resistance in the forward direction.

It has been found that by incorporating halogens in the selenium, the resistance thereof is greatly reduced, but at the same time the presence of halogens at the surface of the selenium layer is undesirable as they interfere with the formation of the blocking layer thereon.

It has been proposed to form the selenium in two layers, a first relatively thick layer of selenium containing halogen and a second relatively thin layer of halogen-free selenium which is suitable for the formation of a blocking layer. However, the selenium requires heat treatment to convert the same into the crystalline condition suitable for rectification, and during the heat treatment the halogen diffuses into the second layer so that it is difficult in any event to obtain a pure selenium surface. In addition, the heat treatment tends to cause the selenium layer to crack or crinkle due to the contraction in volume during crystallization. This condition will be partially or completely avoided if the crystallization can be made to take place rapidly.

In accordance with the present invention, I have found that both of the above difficulties can be overcome by incorporating an alkali metal in the selenium layer. The presence of the alkali metal in the selenium layer permits the selenium to crystallize rapidly without appreciable cracking or wrinkling and the alkali metal at the surface counteracts the effect of the halogen on the formation of the blocking layer.

It is accordingly a further object of the present invention to provide a process for incorporating the desired percentage of alkali metal in the selenium layer.

Although the novel features which are believed to be characteristic of this invention are pointed

2

out more particularly in the claims appended hereto, the invention will be better understood by referring to the following description taken in connection with the accompanying drawings in which specific embodiments thereof have been set forth for purposes of illustration.

In the drawings:

Figs. 1 and 2 are diagrammatic views illustrating suitable apparatus for carrying out the process.

One method of depositing a selenium layer on a base plate is set forth in my co-pending application Serial No. 513,265, filed December 7, 1943, for Selenium rectifier, now Patent No. 2,426,377. In that application a process is disclosed which comprises vaporizing the selenium at or above atmospheric pressure and passing the base plate through the selenium vapor in such a manner that a uniform deposit is obtained. This deposit may be built up to any desired thickness by making repeated passes through the selenium vapor or by vaporizing the selenium in a series of boilers and passing the base plate in succession through the vapors thus produced.

In carrying out the present invention, the halogen, chlorine, bromine, iodine, or fluorine may be added to the selenium boiler in the proper quantity to deposit therewith in the form of a selenium halide. In the case of a plurality of boilers, the halogen may be added to all of the boilers or to only the boiler depositing the first layer, or, if desired, the halogen may be added to the different boilers in varying quantities so as to produce a greater concentration thereof in the first layer and lower concentrations in succeeding layers, preferably being entirely omitted from the last layer.

The alkali metals, sodium, potassium or lithium may likewise be incorporated in the boiler. Lithium is preferred because of its greater solubility in selenium. Lithium in the form of a lithium selenide may be dissolved in the selenium in at least the final boiler until the saturation point is reached. The lithium will then vaporize with the selenium and will deposit therewith. Since there is some tendency for the lithium selenide to precipitate out of the molten selenium it is desirable to so design the boiler that the selenium is vaporized as soon as possible after the injection of the lithium selenide therein.

Another method for incorporating the alkali metal is to allow the selenium vapor to pass over a receptacle containing either the alkali metal selenide or the alkali metal halide. Potassium iodide is particularly suitable for this purpose

as it possesses sufficient vapor pressure at the temperature of boiling selenium to permit the desired quantity of potassium to be dissolved by the selenium vapor. Potassium iodide has also been found to corrode the receptacle at a much slower rate than other materials such as lithium selenide.

When a layer of selenium having the halogen and the alkali metal uniformly dispersed therein is heat-treated the halogen concentration is caused to decrease progressively toward the surface of the layer. The alkali metal, however, is not appreciably changed except at the surface and at the surface appears in a much greater concentration than before heat treatment due to its low vapor pressure which causes the selenium to vaporize from the surface whereas practically no alkali metal selenide vaporizes from the surface. The alkali metal remaining dispersed within the layer causes crystallization to proceed at a rate sufficiently rapid to prevent the selenium from crinkling during the heat treatment, even in layers .002 inch thick or more which are required in rectifiers and, due to its extra concentration at the surface tends to counteract the deleterious effects of any halogen that may be present and facilitates the production of the blocking effect.

One aparatus for carrying out this invention is illustrated in Fig. 1 which shows a retort 10 containing the selenium and having heating means such as an electrically heated coil of resistance ribbon 11 disposed thereabout. The retort 10 is provided with a cap 12 having a transverse slit or opening 13 through which the selenium vapors emerge. A base plate 14 of suitable material on which the selenium is to be deposited is moved across the slit 13 in the path of the vapors issuing therefrom in the direction indicated by the arrow 15. The vapors issuing from the slit 13 thus deposit a layer 16 of selenium on the under surface of the plate 14. A plurality of passes may be made to build up a deposit of the desired thickness.

The halogen is preferably dissolved in the selenium. The alkali metal selenide, for example lithium selenide, may be introduced into the selenium and stirred therein with the cap 12 removed, although introduction of the alkali metal selenide is preferably accomplished as a prior step. The selenide is introduced until a saturated solution is obtained after which the selenium may be diluted to any desired alkali metal concentration. The cap 12 may then be replaced and the base plate 14 passed across the path of the vapor as indicated above. The layer of selenium 16 thus deposited will contain the halogen and the alkali metal in proportions determined by the concentration of the materials within the container 10.

It is to be understood of course that a plurality of such containers may be used and that the base plate 14 may be passed in succession thereover in order to deposit successive layers of selenium on the under surface thereof. If desired, the halogen may be introduced into the first container only so as to deposit a first layer containing halogen and the alkali metal may be introduced into the various containers to deposit a suitable proportion of the alkali metal with the selenium.

Fig. 2 shows an apparatus for introducing the potassium iodide, or other alkali metal compound, directly into the selenium vapor. In this embodiment a retort 20 is provided with a heating

coil 21 such as a resistance ribbon for vaporizing the selenium therein. The selenium vapors are passed over a cup 23 which may contain the alkali metal as the selenide or halide, such as potassium iodide, lithium chloride, sodium bromide or sodium, potassium, or lithium selenide, and then through an orifice 25 in a cap 26 past which a base plate 27 is passed in the direction indicated by the arrow 28, so as to deposit on the exposed surface of the base plate a layer 29 of selenium containing a suitable concentration of alkali metals. The cup 23 may be supported by suitable brackets 24 in the container 20.

The apparatus is preferably made of Vycor or quartz glass in order to resist reaction with the selenium vapor. The concentration of the alkali metal in the selenium vapor may be controlled by varying the area exposed to the vapors in the cup 23 or by varying the temperature of container 23.

The base metal is preferably cleaned and prepared to receive the deposit as set forth more fully in my co-pending application above-identified. The selenium layer after deposition may be heat-treated in the usual manner, as for example first at a temperature of from 100° C. to 150° C. for from 0 to 45 minutes and finally at a temperature of about 210° C. for a period of from 15 minutes to an hour, in order to convert the same to the proper crystalline form. Thereafter the blocking layer and counter electrode are formed in the usual manner and the final forming operation may take place to produce the desired rectification characteristics.

The halogen may be evenly distributed throughout the entire layer before the heat treatment. After the heat treatment the halogen concentration decreases toward the free surface of the selenium. However, there will still be a substantial concentration of halogen at the surface. The selenium may be deposited in two layers with the halogen evenly distributed through only the first layer before heat treatment. After the heat treatment the halogen concentration in the first layer decreases toward the free surface but a substantial portion of the halogen diffuses into the second layer, and an appreciable portion may appear at the surface thereof.

The first layer may contain halogen evenly distributed therein and both the first and second layers may contain alkali metal before heat treatment. After heat treatment, the halogen content varies in the same manner as above set forth, whereas the alkali metal concentration is practically unchanged except at the surface where a substantial increase appears. This alkali metal concentration at the surface, as pointed out above tends to offset the deleterious effect of the halogen at the surface and permits the blocking layer to be formed readily thereon. If only a single layer is involved both the halogen and the alkali metal may be present in equal quantities and uniformly distributed in the layer before heat treatment. After heat treatment the halogen content is substantially reduced whereas the alkali metal content is increased at the surface.

As a specific example, I found that one part of potassium to 2000 parts selenium (atomic ratio) before heat treatment yields a suitable concentration of alkali metal. The proportion may be varied however from about 1 to 1000 to 1 to 4000 or even less according to the results desired. After heat treatment the surface concentration of the alkali metal will be somewhat in excess of the initial average concentration. The other

alkali metals may be used in equivalent atomic ratios. The halogen concentration before heat treatment may vary from one part halogen to one thousand parts selenium to one part halogen to two thousand parts selenium atomic ratio.

Although certain specific embodiments of the invention have been shown for purposes of illustration, it is to be understood that changes and modifications may be made therein as will be readily apparent to a person skilled in the art. The invention is only to be limited in accordance with the scope of the following claims.

What is claimed is:

1. A selenium rectifier unit comprising, in combination, a base plate and a layer of selenium containing a selenium halide and an alkali metal compound selected from the group consisting of alkali metal selenides and alkali metal halides, the portion of said selenium layer adjacent the outer surface thereof having a substantially higher amount of alkali metal compound therein than the portion adjacent said base plate, the outer portion of said selenium layer being substantially free from selenium halide.

2. A selenium rectifier unit comprising, in combination, a base plate, and a layer of selenium deposited on said base plate, the portion of said selenium layer adjacent the base plate containing a relatively small amount of an alkali metal compound selected from the group consisting of alkali metal halides and alkali metal selenides and a relatively large amount of a selenium halide, the portion of said selenium layer adjacent the outer surface thereof containing a relatively large amount of said alkali metal compound and a relatively small amount of said selenium halide.

3. A selenium rectifier unit comprising a base plate, and a plurality of selenium layers deposited on said base plate including an inner layer adjacent said base plate and an outer layer defining the outer surface of said rectifier unit, said outer layer containing a relatively large amount of an alkali metal compound selected from the group consisting of alkali metal halides and alkali metal selenides and a relatively small amount of selenium halide, said inner layer containing a relatively small amount of said alkali metal compound and a relatively large amount of said selenium halide.

4. The method of making a selenium rectifier having a plurality of layers containing selenium which comprises depositing on a base plate an inner layer of selenium containing a selenium halide, depositing an outer selenium layer containing an alkali metal compound selected from the group consisting of alkali metal halides and alkali metal selenides and a substantially smaller amount of selenium halide than said first layer, and heat treating the resulting rectifier unit to increase the concentration of said alkali metal compound adjacent the outer surface of the second selenium layer.

5. The method of making a selenium rectifier having a plurality of layers containing selenium which comprises depositing upon a base plate a first selenium layer containing a relatively large amount of selenium halide and a relatively small amount of an alkali metal compound selected from the group consisting of alkali metal halides and alkali metal selenides, depositing a second selenium layer containing a relatively small amount of said selenium halide and a relatively large amount of said alkali metal compound, and heat treating the resulting rectifier unit to increase the concentration of said alkali metal compound adjacent the outer surface of the second selenium layer.

6. A selenium rectifier unit constructed in accordance with claim 1 in which the alkali metal is lithium.

7. A selenium rectifier unit constructed in accordance with claim 1 in which the alkali metal is potassium.

8. A selenium rectifier unit constructed in accordance with claim 1 in which the alkali metal is sodium.

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