United States Patent

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[54] **ARTICLES PLATED WITH OR COMPRISED OF SILVER-PALLADIUM ALLOYS**
3 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **313/146,** 313/178
[51] **Int. Cl.** **H01j 1/02**
[50] **Field of Search** 204/37, 40; 252/181.1; 313/174, 176, 178, 181, 159; 316/25

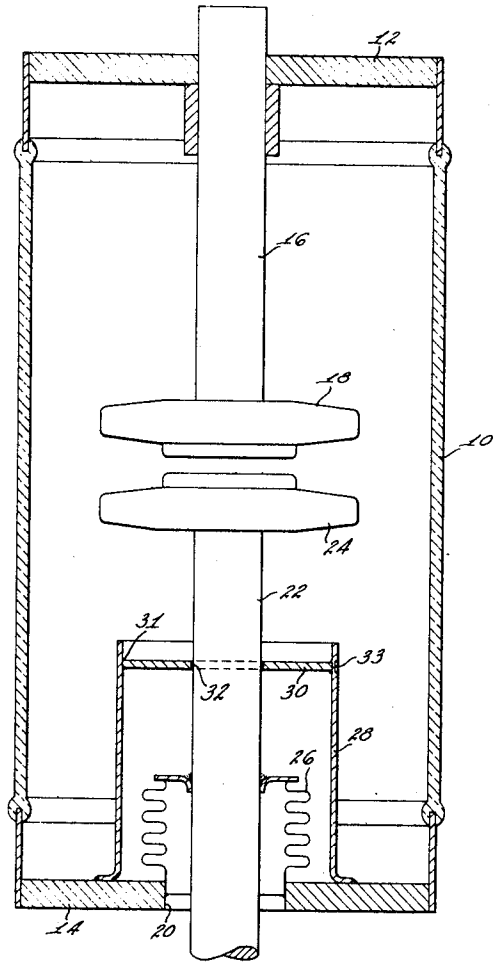
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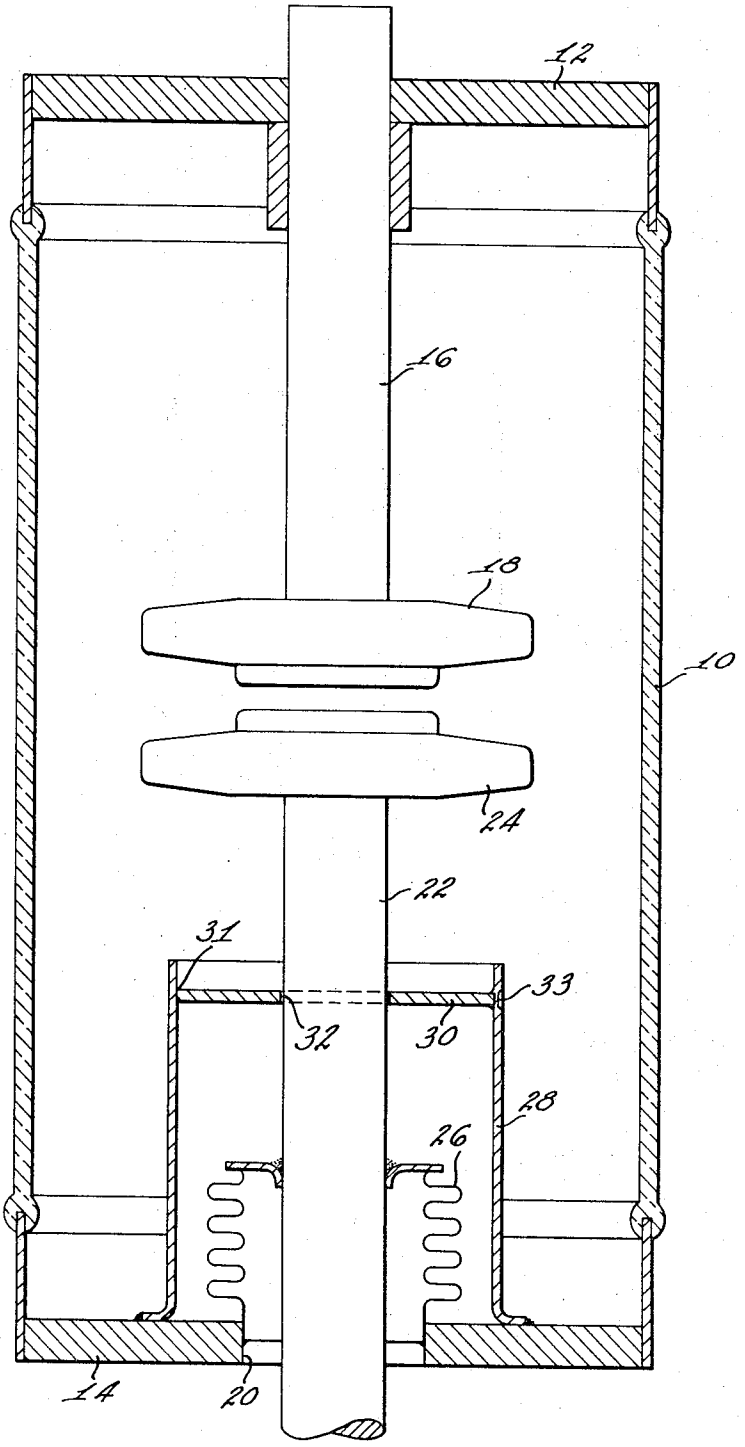
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ABSTRACT: A high voltage vacuum switch having a sealed envelope with a pair of relatively movable electrodes within the envelope between which arcing occurs. One of the electrodes is reciprocably movable in an axial direction within the envelope and is guided by a rigidly supported washer during axial movement, the washer having a plating of silver-palladium alloy for gettering gas within the envelope. The alloy is formed by depositing silver on the washer and depositing palladium on the silver and heat treating both of the metals to effect diffusion.



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3,562,574



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ARTICLES PLATED WITH OR COMPRISED OF SILVER-PALLADIUM ALLOYS

This is a division of application Ser. No. 453,009, filed May 4, 1965 and now abandoned.

This invention relates to articles plated with silver-palladium alloys and processes for plating the same.

Silver-palladium alloys have the property of absorbing gases and are presently available in sheet and ingot form for use as getters in evacuated electrical devices such as vacuum switches and electron tubes and for use as roll-on or dipped protective coatings for base and precious metals. When using this alloy as a getter to remove traces of free hydrogen and other gases in evacuated electrical devices, it was formerly the practice to cut a small piece of the alloy from sheet stock and mechanically mount it on a support within the evacuated device. This practice is undesirable because of the risk of the piece breaking loose and causing a short circuit or mechanical failure. More elaborate mounting means to prevent this risk are to be avoided because additional costs would be imposed on an already expensive component. When used as a roll-on or dipped protective coating to provide a tarnish resistant coating of good appearance on tableware and jewelry, expensive machinery and processes are required to bond the sheet alloy to the base member and dip coating results in a coating of uncontrolled thickness.

It is desirable from the standpoint of cost reduction to electroplate silver-palladium alloys on articles for gettering and other gas absorption purposes. It is also desirable to electroplate silver-palladium to provide tarnish resistant coatings having certain desirable qualities as regards texture and appearance. However, it is not known at present how to electroplate such an alloy directly since dissimilar metals cannot ordinarily be plated simultaneously.

Accordingly, it is an object of the present invention to provide articles plated with silver-palladium alloys and to provide improved processes for making the same.

Another object is to provide silver-pallidium plated articles which exhibit desirable characteristics depending on the silver-palladium ratio.

Another object is to provide improved getters for use in vacuum type devices, particularly getters which take the form of a silver-palladium alloy plated on parts within such devices, which parts already serve some other function within the device.

Another object is to provide a tarnish resistant plate for metal articles, such as silver.

Other objects and advantages of the invention will hereinafter appear.

The drawing illustrates a preferred embodiment of the invention but it is to be understood that the embodiment illustrated is susceptible of modifications with respect to details thereof without departing from the scope of the appended claims.

In accordance with the present invention an article is first provided with a plating of silver of desired thickness, then with a plating of palladium of desired thickness over the the silver, and then the article so plated is subjected to heat treatment at a temperature below the fusion points of the article, the silver and the palladium to effect diffusion between the silver and palladium to provide a plating of a true silver-palladium alloy on the article. For purposes of illustration, the invention is hereinafter described as applied, first, to provide a getter for a vacuum switch and, secondly, to provide a tarnish resisting plating on an article.

Referring to the drawing, there is shown a portion of a vacuum switch which is used in the high voltage electrical transmission art for switching high voltage, high amperage circuits. The vacuum switch has a glass envelope **10** which is understood to be sealed at each end by means of metal plates **12** and **14** and has a high vacuum maintained therein and an internal volumetric capacity of approximately 65 cubic inches. Plate **12** affords mechanical support for an electrical connection to a stationary contact support rod **16** on which is

mounted a stationary contact **18**. Plate **14** is provided with aperture **20** for accommodating a movable contact support rod **22** on which is rigidly mounted a movable contact **24**. A flexible metal bellows **26** is connected in sealed relationship as by brazing to the inner surface of plate **14** around aperture **20** and to the exterior of movable contact support rod **22** to permit relative movement of contacts **18** and **24** to open and close position as movable contact support rod **22** is moved. A hollow cylindrical sleeve **28** surrounds bellows **26** and a portion of contact rod **22** and is rigidly secured as by brazing to plate **14**. Sleeve **28** mechanically supports a washer **30**, preferably of copper, which is brazed as at **31** and crimped in place as at **33** near one end of the sleeve. Washer **30** has an aperture **32** for accommodating movable contact support rod **22** and serves to support the rod against axial misalignment as it moves back and forth.

In the vacuum switch hereinbefore described it is necessary to maintain a high vacuum and an uncontaminated environment to assure a minimum of arcing and rapid arc extinguishment as the contacts **18** and **24** separate under load. Most impurities are removed during various steps in manufacture and assembly of the switch and substantially all impurities normally in gaseous form are removed during the establishment of the vacuum within glass envelope **10**. However, trace impurities still remain after the tube is sealed and some impurities appear as a result of gases released from the contact materials during arching.

Accordingly, means are usually provided to getter the impurities which are present in gaseous form, such as hydrogen and methane.

Formerly, a small piece of silver-palladium alloy cut from sheet stock was rigidly secured to one end of a small piece of wire as by brazing and the other end of the wire was secured as by brazing to a suitable member within glass envelope **10** of the vacuum switch. However, such an assembly was rather delicate because of its necessarily small size and was subject to detachment which created a risk of damage to or shorting of the vacuum switch.

In accordance with the present invention, it is proposed to provide a member already within glass envelope **10** of the vacuum switch and normally serving another function with a silver-palladium plating to serve as a getter. In the embodiment shown washer **30** which supports movable contact support rod **22** is provided with a silver-palladium plating to also serve as the getter in the following manner.

In the particular embodiment shown, only one side of washer **30** needs to be plated since it has sufficient surface area with respect to the envelope volume to absorb impurities which might be present. To plate only one side of washer **30**, the other side is coated with a substance to resist deposition of plating, such as "Microstop" lacquer.

Washer **30** which is, for example, made of copper is chemically cleaned by dipping in a suitable cleaning solution such as trichloroethylene or tetrachloroethylene in a still or ultrasonic bath. It is then thoroughly water rinsed in cold running water before putting into a solution such as 50 percent HNO_3 by volume for 10 seconds.

It is preferable at this stage to provide washer **30** with a prior silver strike to improve the adhesion of the subsequent silver plating. This is accomplished by passing a very high current, on the order of 40 to 50 amperes per square foot, for 30 seconds while the washer is submerged in a weak silver plating solution. Washer **30** is then submerged in an aqueous silver cyanide plating bath and connected as a cathode with a source of silver for deposition submerged in the same bath and connected as an anode. A plating current having a current density of about 10 amperes per square foot of the surface area to be plated is then passed through the cathode, bath and anode to deposit a plating of silver on washer **30**. For each minute of plating time at the current density specified, a layer of silver 25 millionths of an inch thick will be deposited on the surface of washer **30**. A layer of silver one-two thousandths of an inch thick deposited after 20 minutes on a washer about 2⅛ inches

in diameter and having a hole thirteen-sixteenths inches in diameter was found to be suitable for use in a getter for a vacuum switch rated at 15.5 KV and 12,000 amperes.

After the silver is plated on washer **30**, the washer is submerged in an aqueous plating bath comprising palladium chloride in a ratio of 50 grams per liter of distilled water, ammonium chloride in a ratio of 50 grams per liter of distilled water and an acid for maintaining the acidity of the bath below 0.5 pH. The tank for the bath is, for example, made of glass or plastic lined steel. Washer **30** is connected as a cathode with an anode made of platinum (such as "Platanode") or stainless steel (such as 316 stainless steel) in the same bath. A suitable anode to cathode surface area ratio was found to be 2 to 1.

A plating current having a current density of about 4 amperes per square foot of the surface area to be plated is then passed through the cathode, bath and anode to deposit a plating of palladium on the plating of silver already on washer **30**. During plating of the palladium the plating bath should be agitated vigorously as by means of a mechanical impeller. For each minute of plating time at the current density specified, a layer of palladium 12.5 millionths of an inch thick will be deposited on the silver plated surface of washer **30**. A layer of palladium 1½ thousandths of an inch thick deposited after eight hours on one side of washer **30** having the dimensions described was found to be suitable for use as a getter. In practice, then, a ratio of silver and palladium of 1 to 3 is suitable.

Since the palladium plating on the silver plating of washer **30** is porous, the washer is then subjected to heat treatment to cause diffusion of the silver into the palladium and alloying of them. Thus, the plated washer is heated for 8 hours at a temperature between 300 and 400° C. Since the temperature at which washer **30** is heated is below the fusion points of the copper, the silver plating and the palladium plating, it is apparent that solid state diffusion occurs to produce the desired alloy rather than actual melting. Thus, desired tolerances can be maintained by the method disclosed which may be a critical factor in some devices.

An alloy as specified hereinbefore (25 percent silver and 75 percent palladium) has excellent properties as a getter when applied in the amount specified in he vacuum switch described particularly in absorbing hydrogen.

Experiment has shown that by changing the ratio of silver to palladium to 75 percent silver and 25 percent palladium (by weight) produces an alloy or plating which resembles silver in appearance and texture but is extremely tarnish resistant in that sulphides are not readily absorbed. Heretofore, it has been the practice to add chromium oxide or chromium trioxide to silver cyanide electroplating baths to plate out an alloy of silver chrome but the resultant product does not have the soft color of silver and tends to resemble chromium. Furthermore, this product has a relatively high electrical resistance and is not desirable as an electrical conductor. Chromate conversion coatings are used to keep silver from tarnishing before customer use but are very thin. A rhodium flash coating over silver has antitarnishing qualities but has a hard, cold appearing surface which could tend to peel.

In accordance with the present invention an article is provided with 75 percent silver plate and 25 percent palladium thereover (by weight of coating) in the manner hereinbefore described. The resultant product is then heated for 8 hours at between 300° to 400° C. to effect solid state diffusion and alloying between the silver and palladium.

I claim:

1. In a high voltage vacuum tube device, in combination, a sealed envelope having a vacuum maintained therein, a pair of electrodes within said envelope between which arcing occurs, a member within said envelope which is required to perform a predetermined function, and a plating of silver-palladium alloy on said member for gettering gas within said envelope, said alloy formed by depositing silver on said member and depositing palladium on said silver and heat treating both said metals to effect diffusion.

2. In a high voltage vacuum switch, in combination, a sealed envelope having a vacuum maintained therein, a pair of relatively movable electrodes within said envelope between which arcing occurs, a member for supporting a movable one of said electrodes, and a plating of silver-palladium alloy on said member for gettering gas within said envelope, said alloy formed by depositing silver on said member and depositing palladium on said silver and heat treating both said metals to effect diffusion.

3. In a high voltage vacuum switch, in combination, a sealed envelope having a vacuum maintained therein, a pair of relatively movable electrodes within said envelope between which arcing occurs, one of said electrodes being reciprocably movable in an axial direction within said envelope, a rigidly supported washer for guiding said one electrode during axial movement, and a plating of silver-palladium alloy on said washer for gettering gas within said envelope, said alloy formed by depositing silver on said washer and depositing palladium on said silver and heat treating both said metals to effect diffusion.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,562,574 Dated February 9, 1971

Inventor(s) Henry J. Wesoloski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The cover sheet should have included:
"[73] Assignee Allis-Chalmers Manufacturing Company
Milwaukee, Wisconsin"

Signed and sealed this 6th day of July 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents