

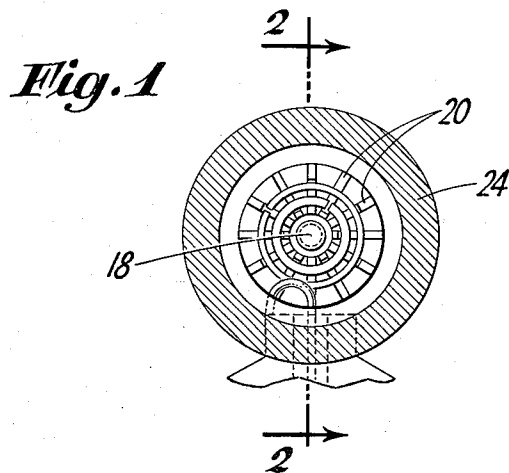
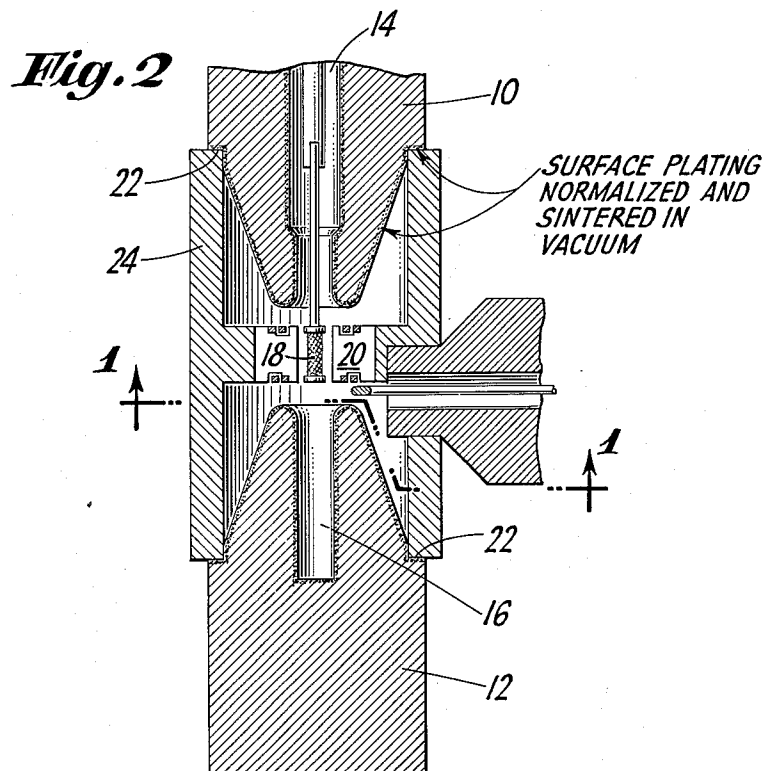
May 29, 1956

M. C. PEASE III, ET AL

2,748,067

PROCESSING PLATED PARTS

Filed July 20, 1951



INVENTORS
JOHN P. JASIONIS
MARSHALL C. PEASE III
BY *Paul S. Martin*
ATTORNEY

1

2,748,067

PROCESSING PLATED PARTS

Marshall C. Pease III, Needham, and John P. Jasionis, Belmont, Mass., assignors to Sylvania Electric Products Inc., a corporation of Massachusetts

Application July 20, 1951, Serial No. 237,766

9 Claims. (Cl. 204—37)

The present invention relates to the processing of metal parts, especially for electric discharge devices and to such devices incorporating parts so processed.

It is frequently required that parts for a vacuum tube or for a tube that is evacuated and filled with a particular gas at low pressure be plated with another material. This is desirable in the case of tubes having an envelope whose wall is of a particular metal which might, except for the plating, be leaky so as to permit gas from outside the tube to enter its interior, or so as to permit the escape of gas that has been deliberately introduced into the tube.

Metal parts used either for the metal tube wall or for an internal electrode or other structure are plated for other reasons as well. In the course of plating some of the nascent hydrogen that is liberated is quickly absorbed into the bulk of the metal, so as to be a threat to the condition of the discharge device in which that part is used. Plated metals have heretofore been subjected to a sintering operation for forming a continuous seal against the flow of gas through the plate, whether from the exterior of the device into the evacuated space from the interior to the exterior, or from the bulk of the metal into the discharge space.

It has also been the practice of plating parts of metal-walled electric discharge devices with a metal to make it easier for that part to be joined to another in a brazing operation. When this is done, there again exists the possibility of nascent hydrogen being absorbed by the base metal during the plating operation and forming a pocket between the base metal and the plated film during the sintering operation. This pocket could provide a leakage path, in some instances, between the exterior of the tube and the interior, in case the pocket appeared in the region of a braze.

In a particular instance which is discussed in detail below, the pole piece of magnetron (a highly evacuated type of tube used as a microwave oscillator) is plated and later brazed to other metal parts, the brazing being facilitated by the metal plating and the pole piece having been sintered with the intention of insuring the plating against leakage. When such tubes have been so processed there have developed a large number of gassy tubes due to leakage past the brazed joints and due to the presence of hydrogen which, in conjecture, was liberated from the bulk of the pole-piece material or possibly from pockets or blisters in the plating.

An object of the present invention is to provide greater assurance against penetration of gases through plate on a part exposed to the internal space of an electric discharge device. More generally, an object of the present invention is to improve the construction of electron discharge devices. A further object is to provide improved methods of plating such as to insure uniformity of the bond between the plating and base metal, thereby to eliminate blisters, pockets, and the like.

The principles of the invention will be described in connection with the manufacture of a magnetron where

2

the invention has particular merit, but those skilled in the art will recognize other and more general applications of its various features and aspects.

In the construction of magnetrons, pole pieces made of cold rolled steel have heretofore been plated, covering the surface that is later to be exposed to the evacuated interior of the tube and the surfaces later to form brazed joints to other metal parts of the envelope wall that seals off the evacuated interior. Such tubes are of well known construction and are shown, for example, in "Microwave Magnetrons," vol. 6 of the Radiation Laboratory Series, published in 1948 by McGraw-Hill Book Company, and shown at pages 773, 774, and 781. A typical tube structure is shown in the accompanying drawings, Fig. 1 being a cross-sectional view thereof along the line 1—1 in Fig. 2, and Fig. 2 being a fragmentary longitudinal cross-section along the line 2—2 in Fig. 1. These tubes have a pair of pole pieces 10 and 12, one of which in the illustrations referred to is formed with a bore 14 through which the cathode structure extends, the other also having a bore 16 to make it symmetrical with the first piece and to permit centering of the cathode 18 in the anode structure 20, so that both the pole pieces have large surfaces exposed to the internal highly evacuated space. An electric discharge takes place in this space between the anode and the cathode of the magnetron. The pole pieces have circular seats 22 that are brazed to cylindrical metal wall structures 24, that are unitary with the anode itself. This piece is customarily of oxygen-free copper. In order that the seats of the steel pole pieces may be effectively bonded as vacuum-tight seals to the copper portion of the evacuated envelope, the pole pieces are usually plated with copper, or more particularly, with a triple layer of copper, nickel, and copper.

With such construction, it is desirable that the plated surface, both at the inside area exposed to the evacuated space and the seat where the brazing is to be effected, shall be free of blisters and entrapped gas, shall have a firm bond to the base metal, shall be everywhere continuous so as to avoid leaky pores, and shall not entrap any gas or volatile contaminant that may be contained in the base metal.

In applying the present invention, the steel pole piece is plated in conventional manner as with copper, nickel, and then copper again. The nickel prevents puddling due to excessive flow that might take place were a simple thick copper plating used alone. This plated part is normalized in a vacuum of a high order and at a temperature well below the melting or sintering temperature of the plating, a suitable range for copper and nickel being 450 to 700° C., at 10⁻⁵ mm. of mercury, for example. This has the effect of driving off the gases, particularly hydrogen and other volatile contaminants that might be absorbed in the bulk of the steel or in the plate, or trapped in or under the plate. These may be driven off at this stage of the processing since the plate has not yet been sintered and is, therefore, highly porous. The absorbed or trapped gases might, except for this vacuum normalizing operation, later form a blister separating the plating locally from the base metal. After this has proceeded long enough for the vacuum gauge to show that there is no further appreciable release of gas, the temperature is raised to sintering temperature or to a point just below or even just above the melting temperature of the plating, 1125–1150° C. for the copper-nickel-copper plating in this example. The introduction of the normalizing under vacuum or the pre-sintering bakeout operation has the effect of greatly improving the plating so as virtually to eliminate blisters, and this in turn reflects on the manufacture of magnetrons having brazed joints in the envelope wall and plated parts exposed to

the interior, in reducing costly losses due to leakage and accumulation of hydrogen in the discharge space.

In an illustrative procedure for making magnetrons with plated pole pieces, pole pieces which have been machined to their final shape are cleaned and degreased in the customary manner, as by successive treatment in hot carbon tetrachloride, then in a detergent bath, followed by a water rinse, and then an electrolytic cathodic and anodic cleaning sequence. The preparation process also includes firing at 1200° C. in a wet hydrogen atmosphere to remove surface carbon and other contaminants, and as a novel step, in this sequence, firing the parts in vacuum at 1200° C.

The plating of copper on the pole pieces includes further surface preparation with hydrochloric acid, a water rinse, and a sodium cyanide dip followed by copper plating. The bath may, for example, be a conventional Rochelle salts plating solution of 57.0 grams per liter sodium cyanide, 45.0 grams per liter CuCN, 30.0 grams per liter Rochelle salts, and 20.0 grams per liter Na₂CO₃. The plating is carried out in a bath of 60–70° C., at a pH of approximately 12.5 and with a current density of approximately 20 amperes per square foot for two minutes to produce a plating thickness of about .00005 inch.

Nickel plating is next effected after suitable preparation with water rinse and acid dips in a bath of 240 grams per liter of NiSO₄·6H₂O; 45.0 grams per liter of NiCl₂·6H₂O; and 30.0 grams per liter of H₃BO₃. This plating is carried out in a bath of 60–70° C. for approximately 17 minutes with an approximate current density of 20 amperes per square foot and a pH of 4.5 to yield a thickness of approximately 0.00025 inch.

Subsequently after suitable rinse and cyanide dipping, the copper plating is repeated for a thickness of 0.0002 inch under the same conditions as above. Thereafter the pole pieces are rinsed, washed, and dried.

This practice is purely illustrative and is entirely unchanged so far as previous plating practice on magnetron pole pieces is concerned, except for the vacuum firing step in the preparation.

The pole pieces are next subjected to the following novel treatment. The parts are racked on suitable support in a vacuum of approximately 10⁻⁵ millimeters of mercury, and heated by radio frequency induction. The heating is controlled at 550–650° C. for a period long enough to insure expulsion of gases through the plating which is relatively porous at this stage, usually for 20 minutes. Thereafter the heating is increased to approximately 1125° C.–1150° C. to produce sintering or hot flow of the plated metal. This temperature as given in the illustrative example is sufficient to produce molten flow of copper in vacuum, but a lower temperature for a longer time would produce a comparable sintering even if the temperature were not enough to allow molten flow. The critical requirement is that sufficient flow be produced by heating so that a gas tight skin free of blisters and pores will result upon cooling. This heating is continued for approximately 10 minutes, controlling the pressure to prevent an increase above 10⁻⁴ mm. of mercury. The pieces are then allowed to cool, and the cooling can be expedited through the use of anhydrous helium or other inert cooling gas.

The fact that the type of normalizing and sintering process described yields parts of greatly improved plating characteristics, especially by obtaining good adherence of the plated metal to the base metal and by the virtual elimination of blisters and by the effective elimination of absorbed gas is of great importance to the art of tube fabrication.

The pole pieces of the magnetron used as an illustrative but important example have an area machined to form a circular seat which is designed to mate with and be brazed to a corresponding area of a cylindrical copper body part which, together with other parts of the tube form the vacuum envelope. This joint is commonly formed by brazing the parts together with a copper-silver

eutectic alloy in a hydrogen furnace. Such a braze is difficult to make directly to the steel. It is much more easily and reliably made if the steel is plated by a process whereby a surface layer of sintered copper-nickel-copper alloy is formed. It is essential, however, that said layer of alloy be well adherent to the base metal so that no leak may occur there. Any leak in the joint, even though it be under the sintered plated alloy, will cause the destruction of the tube.

Blisters on the surface of any area internal to the vacuum envelope will also be sufficient, in general, to destroy the tube. Such blisters normally are filled with gas, thought to be usually hydrogen. During the process of exhausting the tube it will normally be baked at a somewhat elevated temperature for some time at the same time as it is being pumped to a high vacuum. Two hours at 450° C. at a pressure below 10⁻⁵ mm. of mercury may be taken as illustration. In as much as the gas enclosed in a blister is enclosed by a dense and relatively impervious alloy of the sintered plate, said gas will not, in general, be removed by said process of baking out. After the tube is finished, however, and is sealed off, it is expected not to lose the degree of vacuum required for satisfactory operation which, by way of illustration may be of the order of 10⁻⁵ mm. of mercury, even though the tube be kept for several months or even years. Over such a long period of time the gas contained in a blister will diffuse through the metal into the supposedly evacuated region of the tube causing the tube to fail to operate satisfactorily.

In addition to the slow process of diffusion described above, the gas contained in a blister on an interior surface may be released into the supposedly evacuated region and prevent satisfactory operation by the rupture of the blister at any time. This may be the result, for example, of the occurrence of a momentary arc at the blister.

Finally, even if said plating adheres well to the base metal and no blisters have been formed anywhere on the internal surface there is still the possibility of gas being entrapped under the sintered plating by direct solution in the base metal. This gas may originate from impurities present in the base metal, from the nascent hydrogen present during the plating operation, or from the hydrogen atmosphere used during the brazing and other operations of assembly. This hydrogen or other gas may be present under the sintered layer of alloy and may not be removed by the usual exhaust procedures. It is thought, in fact, that the hydrogen is the cause of the blistering observed in the methods of processing prior to this invention. It is thought that these blisters are formed as the result of the pressure generated by hydrogen absorbed in the base metal. But even if no blisters occur the hydrogen or other gas may remain entrapped under the sintered plated alloy and by slow diffusion into the evacuated space, ultimately prevent the tube from operating satisfactorily.

Control of gas in a vacuum tube is, therefore very important. If excess gas develops in the evacuated region after the tube has been sealed off, the tube is no longer satisfactory. It can not usually be salvaged and may fail under hazardous circumstances. Any method of processing the parts, therefore, that helps to reduce the incidence of gas in finished tubes by eliminating one or more possible source of gas is valuable.

The present invention is not necessarily identified with the metals and conditions described, although the plating metal or metals should have a lower sintering temperature than the melting point of the base metal. The process is used to best advantage to make parts from metals which have a pronounced tendency of absorbing hydrogen, such as iron, nickel, cobalt and various alloys thereof. The plating metals including plated metal alloys should be such as form a relatively hydrogen tight surface seal, including as examples the copper-nickel plating described, gold, gold alloys including gold-indium. To those skilled in the art, some metals are known to pass hydrogen freely at elevated temperatures (pal-

5

ladium for example) and such metals would naturally not be chosen as platings to form the desired surface seal.

While described in connection with a high-vacuum tube electric discharge devices such as transmit-receiver tubes containing hydrogen or other gas at low pressure can also be made to advantage with the novel features described.

Various other applications may be made of the foregoing novel concepts and a variety of modifications and substitutions will occur to those skilled in the art; and therefore the appended claims should be allowed a broad latitude of interpretation, consistent with the spirit and scope of the invention.

What we claim is:

1. The method of processing a plated metal part to be exposed to the interior of an electric discharge device, including the steps of electroplating the part of a base metal with a porous layer of a different metal whose melting temperature is lower than that of said base metal, heating the plated part in vacuum over a period and at a temperature sufficient to remove the gasses contained in the part without however sintering the plating, and thereafter raising the temperature sufficient to sinter the plating while maintaining a vacuum of a high order.

2. The method of processing plated metal whose plating has a lower sintering temperature than the melting temperature of the base metal, which includes the steps of treating the plated metal in vacuum at a high temperature inadequate to produce sintering for a sufficiently extended period to reduce the rate of removal of occluded gas to a negligible level, and thereafter raising the temperature at least to the sintering temperature of the plating but below the melting temperature of the base metal while maintaining a vacuum.

3. The method of assembling a vacuum tube, the envelope of which includes multiple metal parts joined together by brazing, one of which parts is of steel, which

6

method includes the steps of plating the steel part to be brazed, heating the plated steel part to 450-700° C. in a high vacuum for a period sufficient to draw out the free gasses, without sintering the plating, thereafter sintering the plating at approximately 1125° C., and cooling the part in an inert atmosphere.

4. The method in accordance with claim 1 in which said part is electroplated with copper.

5. The method in accordance with claim 1 in which said part is electroplated with nickel.

6. The method in accordance with claim 1 in which said part is of steel and is electroplated with copper and nickel.

7. The method in accordance with claim 4 wherein the removal of gases is effected at a temperature in the range 450° C. to 700° C. and in which the sintering is effected at a temperature in the range 1125° C. to 1150° C.

8. The method in accordance with claim 6 wherein the removal of gases is effected at a temperature in the range 450° C. to 700° C. and in which the sintering is effected at a temperature in the range 1125° C. to 1150° C.

9. The method in accordance with claim 3 in which copper is a metal electroplated on the steel part.

References Cited in the file of this patent

UNITED STATES PATENTS

30	2,077,633	McMaster et al. -----	Apr. 20, 1937
	2,128,234	Dallenbach -----	Aug. 30, 1938
	2,424,576	Mason -----	July 29, 1947
	2,478,534	Kather -----	Aug. 9, 1949
	2,490,700	Nachtman -----	Dec. 6, 1949
35	2,512,141	Ma et al. -----	June 20, 1950
	2,535,713	Wooten -----	Dec. 26, 1950
	2,556,864	Apker -----	June 12, 1951