METHOD FOR PRODUCING COATINGS OF HIGH OHMIC RESISTANCE IN THE INTERIOR OF VACUUM TUBES

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6 Claims. (Cl. 250—27.5)

This invention relates to a method for producing electrically conductive coatings of high ohmic resistance in the interior of vacuum tubes and particularly relates to the production of extremely homogeneous coatings which maintain their resistance values over long periods of time at the operating temperatures of such vacuum tubes.

It has heretofore been proposed to use current-carrying electrodes or wall coatings, for example in cathode ray tubes, across which a large potential drop is developed in the direction of the flow of the current. The electrical fields produced in this manner are utilized in the operation of the tube. Such electrodes or wall coatings must have as high a resistance as possible in the direction of the current flow in order to enable the development of the proper potential drop by means of weak currents. The use of metals or metallic alloys is excluded because the value of the resistance obtainable is considerably too small. The use of insulating materials upon which a very thin metal coating is applied by evaporation or spraying frequently causes difficulties because the surfaces which are to be coated are so shaped that a completely homogeneous coating cannot be applied by application by spraying or evaporation owing to poor accessibility. If the coatings are irregular, however, the resistance of the surface will not be the same at every point taken in a cross section perpendicular to the direction of the flow of current, and consequently the distribution of the lines of force of the electrical field produced will not have the desired shape.

In accordance with the present invention a method is used which essentially makes use of gaseous compounds only for producing the high resistance coating. Broadly considered, a homogeneous metallic deposit is produced on the member supporting the coating by means of thermal decomposition of gaseous metallic compounds, and, in order to increase the ohmic resistance of the coating, the deposit is converted into a semi-conductor, preferably with the aid of gaseous reagents. Metallic carbynls are particularly suited for the manufacture of the metallic coating, these being caused to decompose at a suitable temperature. Aside from the metallic coating, only gaseous decomposition products are formed in addition thereto and these can readily be withdrawn and expelled from the tube. If the metallic coating is then allowed to enter into reaction with a liquid or a gas, e.g. oxygen, a progressive reaction with the metallic coating will produce an increase in ohmic resistance which depends on the depth of the coating to which the reaction proceeds.

In practising the method, the gaseous metal compound, e.g. nickel carbonyl, or iron, cobalt, molybdenum, chromium, tungsten, or ruthenium carbonyl, is introduced into the interior of the previously evacuated tube. These metallic carbynls are liquid or solid substances at room temperature and have a rather high vapor pressure. In storing them, and in shutting off carbonyls from the apparatus to be coated, special safety precautions must be taken, since they decompose slowly in contact with grease, such as is used for sealing stopcocks, as well as in contact with mercury. It is therefore preferable to use glass valves for shutting off the carbonyls from the apparatus. Such valves need not be greased and they permit the admission of the carbonyls into the apparatus in a controllable manner. The portions of the apparatus which are to be coated with the layer are first carefully cleaned and then heated to 120—180° centigrade. This causes these portions to become covered with a rigidly adhering metallic mirror. The thickness of the metallic mirror depends upon the temperature of the member to be coated, the duration of the decomposition and upon the concentration or the pressure of the gaseous carbynls. In order to produce a homogenous metal coating having a resistance of several hundred ohms, upon a surface of several square centimeters, a decomposition period of a few seconds is ample, using the gaseous carbonyls at a pressure of a few millimeters of mercury. The carbon monoxide formed as a decomposition product presents no difficulties during the evacuation and degasification of vacuum tubes treated in this manner. It is also quite feasible to heat individual parts of the electrodes or the tube wall for a longer period or to higher degree than the remaining portions so that a thicker metal coating is produced thereon. A substance, preferably a gas, is thereafter introduced into the tube, which enters into combination with the metal. A gaseous, liquid or solid solution or compound is thus produced. In the case of oxidation a decrease in the thickness of the metal layer is produced. If the resulting compound is a solid non-conductor, a metal layer will be left behind having merely a very small effective cross section. In most cases, however, the reaction products are solid semi-conductors possessing a resistance which is higher to the extent of a number of magnitudes than the metal itself and which in many cases has an appreciably lesser absorption capacity, so that the coating can
be made transparent to light. If the metal layer is allowed to react to the extent that it is completely changed into a semi-conductor, a coating will be obtained having very high resistance and which, due to the manner of its preparation, is completely homogeneous. The reaction may be influenced by suitably proportioning the quantities of material used, or the gas pressure, temperature, and duration of the reaction. This method also has the advantage that the resistance may be brought to the desired value by operating on the tube while it is attached to the pump and prior to melting the same off.

If a nickel mirror surface is treated with oxygen, e.g. at 400° centigrade, a nickel oxide, stable at ordinary temperature, is formed. Such a nickel coating of several square centimeters of surface, having an initial resistance of a few ohms, may, by being converted into nickel oxide have, for example a resistance of 300,000 ohms. This resistance does not change even if the coating later comes in contact with air.

What is claimed is:

1. The method of producing high resistance wall coatings within a vacuum tube which comprises evacuating the tube, introducing a metallic gaseous carbonyl, heating the wall of said tube to cause depositing of a metallic coating thereon from said metallic gaseous carbonyl, re-evacuating said tube, and oxidizing said metallic layer.

2. The method of producing a high resistance wall coating in a cathode ray tube which comprises cleaning the wall of said tube, evacuating said tube, introducing a metallic gaseous carbonyl, heating the wall of said tube to cause condensation thereon of metallic elements from said carbonyl, re-evacuating said tube, and introducing into a quantity of oxygen sufficient to convert said metallic layer to an oxide layer and finally re-evacuating said cathode ray tube.

3. The method of producing a high resistance wall coating in a cathode ray tube which comprises cleaning the interior of said tube, evacuating said tube, introducing a metallic gaseous carbonyl therein, heating said tube to cause metallic condensation therein, evacuating said tube, introducing a quantity of oxygen therein, and evacuating said tube after reaction of said oxygen with said metallic wall coating.

4. The method of producing a high resistance wall coating in a cathode ray tube which comprises cleaning and evacuating said tube, introducing a metallic gaseous carbonyl containing nickel therein, heating the wall of said tube to produce condensation thereon, re-evacuating said tube, introducing a quantity of oxygen therein to cause oxidation of said condensed metal layer, and finally evacuating said tube.

5. The method of producing high resistance wall coatings in a cathode ray tube which comprises cleaning and evacuating said tube, introducing gaseous nickel carbonyl therein, heating the wall of said tube to the condensation point of nickel from said carbonyl, re-evacuating the tube, oxidizing said condensed nickel, finally evacuating and sealing off said tube.

6. The method of producing high resistance wall coatings in a cathode ray tube which comprises cleaning and evacuating said tube, introducing therein a gaseous nickel carbonyl, heating the walls of said tube to a degree corresponding to the desired thickness of a nickel coating to be deposited thereon, evacuating said tube after condensation of nickel from said gaseous carbonyl, oxidizing said nickel layer, re-evacuating and sealing off said tube.

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