

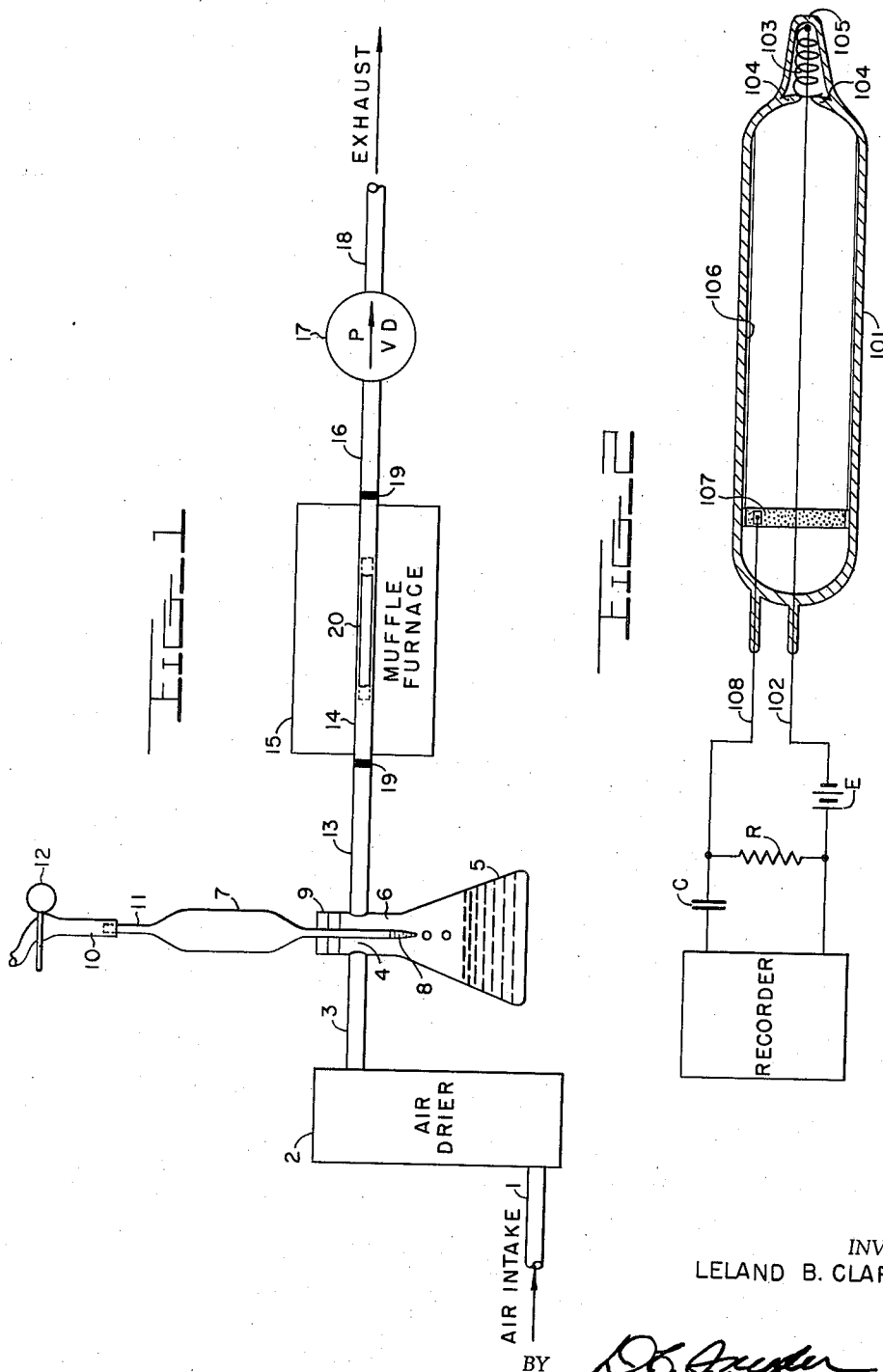
Aug. 4, 1959

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2,898,496

ELECTRICALLY CONDUCTIVE FILMS AND METHOD FOR PRODUCING SAME

Filed Nov. 20, 1953



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2,898,496

ELECTRICALLY CONDUCTIVE FILMS AND METHOD FOR PRODUCING SAME

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Application November 20, 1953, Serial No. 393,526

14 Claims. (Cl. 313—93)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The present invention relates to a method for producing electrically conductive films on impervious surfaces of solids, to the coated surfaces and to articles employing the same. A particular application of the method of the invention is the production of cathode-envelopes for ionization detection devices which are to contain a halogen in the ionizable gas filling.

Ionization detection devices to which the present invention relates have as their prototype the well-known Geiger-Mueller counter or tube. The counter comprises an envelope in which is sealed the anode and the ionizable gas filling which generally is provided with an admixture of a small proportion of a gaseous or vaporous quenching agent to render the counter self-quenching. The envelope is usually made of metal and thus also serves as the cathode for the counter. Polyatomic organic compounds, such as alcohol, and the halogens, chlorine and bromine, have been used as quenching agents. The halogens have the advantage that, unlike polyatomic organic compounds, they will not permanently break down into smaller molecules of no quenching activity under the action of overvoltages in the counter. The halogens have the disadvantage, however, of being reactive toward the metals out of which the usual cathodes are made and will combine therewith to reduce the content of free halogen in the counter. This reactivity of the halogens militates against their use as quenching agents since the life of a counter depends upon the maintenance of an adequate level of concentration of the quenching agent therein.

It has been heretofore proposed to use vitreous envelopes for Geiger-Mueller counters in which the cathode is a halogen-resistant, non-metallic conductive film on the inner surface of the envelope. The conductive film is obtained by spraying a solution of a metal halide in alcohol on the inner surface of the vitreous tube out of which the envelope is made while the tube is maintained at a temperature of from about 400 to 700° C. Counter tubes made up with a glass envelope on which the cathode film has been provided by the above spray method using tin tetrachloride in alcohol as the film-forming solution have given unsatisfactory performance. The films possess an optical haze and have been found to contain a considerable amount of moisture as is evidenced by a milky, opalescent appearance of the film. This moisture is present in bound form, either chemically combined with the particles of the film or adsorbed thereon. Released into the ionizable gas filling as water vapor during operation of the counter, it causes the slope of the plateau of the counter to be increased to such an extent as to render the tube useless for accurate counting purposes. Plateau slopes of more than 35% have been commonly encountered in the use of these prior art cathode-envelopes. This moisture has also been found to produce variable pulse heights in operation of the counter. Cathode films prepared by the above spray method have the additional disadvantage of being non-uniform in thickness, with the greatest uniformity obtained being

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a thickness variation of about 20 to 30% for the individual film. For best results, the cathode film should have a uniform resistance per unit length which would be provided by a level thickness of the film. Spray application of the film-forming solution to the inner surface of a tube, the envelope of Geiger-Mueller counter is usually tubular in geometry, is not suited to producing a film of level thickness.

It is an object of the present invention to provide a method for producing clear, moisture-free, electrically conductive films on impervious surfaces of solids. It is a further object to provide a method for producing a clear, moisture-free, halogen-resistant, electrically conductive film on the inner impervious surface of tubes suitable for forming envelopes for ionization conduction devices. It is a still further object to provide a method of this kind which is productive of a level thickness in the film. It is another object to provide solid articles having an impervious surface coated with a clear, moisture-free, halogen-resistant, electrically conductive film of level thickness, especially tubes having an inner impervious surface coated with such a conductive film. It is also an object to provide ionization detection devices in which the envelope is coated on its inner surface with a clear, moisture-free, halogen-resistant cathode film.

These and other objects of the invention which will become apparent hereinafter are accomplished in accordance with my invention by a method which is relatively simple in its application to the production on impervious surfaces of solids of a clear, moisture-free, halogen-resistant, electrically conductive film of a uniform thickness. By impervious surfaces as used herein and in the claims is meant one which is nonporous or substantially so, for example, vitreous solids, such as glass and fused quartz, vitreous-surfaced solids, such as glazed ceramics and enamelled metals, natural materials of little or no porosity, such as mica and quartz, metals polished to a level or continuous surface, such as highly polished steel, or which have been cast in smooth-faced molds, and metals of fine grain which as such or by virtue of having been worked have a level or continuous surface.

In the practice of the method of my invention a dry aerosol comprising the product of mixing dry air in calculated proportions with the vapors from the addition of a liquid metal polyhalide to dry methanol is passed over the impervious surface to be coated while the latter is maintained under dry conditions and is heated to a temperature sufficient to cause deposition of film-forming particles from the aerosol onto the impervious surface. A suitable range of temperatures for this purpose is from about 300 to 700° C. and preferably is from about 500 to 700° C. Higher or lower temperatures may also be used with some change in the rate of deposition from the aerosol. The higher temperatures favor a faster rate of deposition of the film-forming particles. Obviously, the surface to be coated should not be heated to temperatures which would cause sagging or other deformation of the same. The films which can be produced by the method of the invention are transparent, may be of various colors, and are formed of metal in a non-metallic state, most probably in the form of the finely crystalline higher oxide of the metal which in the crystal lattice contains an excess of the metal or oxygen in elemental form, most probably the metal.

The aerosol is formed in a dry atmosphere and the addition of the liquid metal polyhalide to the methanol is carried out in discrete fashion, suitably dropwise, whereby to control the rate of production of the vapors. Liquid metal polyhalides which may be employed in the method are antimony pentachloride, antimony pentafluoride,

germanium tetrachloride, tin tetrachloride, titanium tetrachloride and vanadium tetrachloride, of which tin tetrachloride constitutes a preferred species. The air employed in forming the aerosol may be dried in any suitable fashion, for example, by passing it through a drying tower having a packing of porous ceramic tile covered with a body of concentrated sulfuric acid as the desiccant.

In the accompanying drawing forming part of the description of the present invention:

Figure 1 is a schematic showing of an apparatus suitable for carrying out the method of the invention, and

Figure 2 is a showing of a typical ionization detection device provided with an envelope and cathode of the invention.

The apparatus shown in Figure 1 is designed as a closed system with the exception of an inlet for supply of the air to be dried and used in the method and an outlet for discharge of aerosol exhaust from the system. A tube 1 serves as the air intake into the system and is connected for flow of the air into and through the drier 2 containing a packing of porous ceramic tiles covered with a body of concentrated sulfuric acid, for example, 90% H_2SO_4 . The drier may be of conventional design and provided with feed and take off outlets (not shown) for replenishing the supply of acid of drying strength. A tube 3 leads from the drier into a mixing zone 4 at the top of a glass vessel 5 which is designed to hold a supply of dry methanol. The vessel 5 is formed with a neck 6 at its upper end and, as shown, has the configuration of the well-known Erlenmeyer flask. Arranged above the vessel 5 is a glass pipette 7 of conventional construction for containing a supply of the liquid metal polyhalide. The lower tube 8 of the pipette extends down through a gasket 9 of rubber or of Tigon (an expansible plastic) into the neck 6 of the vessel 5 and terminates at a point which is below the juncture of the tube 3 with the neck 6 but is substantially above the bottom of the vessel 5. The tube 8 is tapered at its lower end from which the liquid metal polyhalide is allowed to issue in the form of drops. A length of rubber or expansible plastic tubing 10 is attached to the upper tube 11 of the pipette 7 and is provided with a pinchcock 12 thereon for controlling the rate of flow of the liquid from the tube 8. Extending from the mixing zone 4 of the vessel 5 is a tube 13 which is coupled to a tubular muffle 14 of an electrically heated muffle furnace 15 which is capable of operating to heat the muffle to operating temperatures for the method. The size of the tubular muffle 14 is so chosen that the diameter thereof is only a shade larger than that of the tube which is to be coated on its inner surface by treatment with the dry aerosol, whereby the latter can be slid into position in the tubular muffle and held there by a tight fit. The muffle 14 is coupled with a tube 16 which leads to a variable speed exhaust pump 17 which is provided with an exhaust discharge tube 18. The coupling between the tubular muffle 14 and the adjacent tubes 13 and 16 is made outside of the furnace by means of a gasket 19 of an expansible plastic such as Tigon. The tubes employed in the apparatus should be of the same inner diameter in order to promote easy flow of the air and aerosol in the system and may be made of metal or glass.

For a more complete understanding of the invention, the method will be described as it is carried out in an apparatus as shown in Figure 1. A tube 20 which is to be coated on its inner surface with the conductive film is slid into position in the tubular muffle 14. This arrangement of the tube and muffle is illustrated in the drawing wherein the muffle is shown as being partly broken away in the area of the tube. The tube 20 having been arranged in the muffle, the furnace is set to heat to and maintain the temperature to be used during the operation of the method. The tube and muffle having been brought to temperature, air is drawn into the system at 1 by operation of the variable speed exhaust

pump 17. The exhaust pump is operated at low delivery rates, sufficient to cause the air entering at the inlet 1 to move in gentle flow through the system. This gentle flow of air may be movement of the air at a rate just sufficient to cause it to progress through the system or one at rates which are moderately higher. Variation in the rate of flow of the air will depend upon the factors of travel time required for the air to pass through the desiccant and come out in dry condition, the concentration of the dispersed phase desired in the aerosol, and the rate at which it is desired to deposit the film on the impervious surface to be coated. The concentration of the film-forming or dispersed phase in the aerosol is not critical, the more dilute dispersions giving a slower rate of build-up of the film. The liquid metal polyhalide is fed from the pipette 7 through the tube 8 and enters in the form of drops into the body of dry methanol in vessel 5. The methanol is warmed by any suitable heating means (not shown) to promote reaction between it and the entering liquid metal polyhalide, for example, to a temperature in the region of 25 to 30° C. The rate of addition of the latter is controlled by means of the pinchcock 12 on the expansible tubing 10 attached to the tube 11 of the pipette. By adjusting the rate of addition of the liquid metal polyhalide to the methanol, the volume of the vapors generated can be controlled to vary the concentration of the film-forming or dispersed phase in the aerosol for a set rate of air intake. The vapors from the addition of the liquid metal polyhalide to the methanol rise into the zone 4 at the top of the vessel 5 and from there are swept out into the tube 13 by the stream of dry air entering from the tube 3. Mixing of the dry air and vapors with production of the dry aerosol takes place in the tube 13. As a section of a continuously flowing fluid mass, the dry aerosol is moved into the hot muffle and through the heated tube 20. In flowing over the inner surface of the tube 20, the aerosol is caused to deposit a film of the conductive material thereon by the action of the applied heat. Flow of the aerosol over the inner surface of the tube is continued until the desired thickness of film has been attained. Discharge of the spent or partially spent aerosol from the system is made through the exhaust pump 17 and exit tube 18. The snug fit between the muffle 14 and the tube 20 precludes deposition of a film on the outside surface of the tube.

The method of the present invention which operates from the gas phase to deposit the film on the impervious surface of the solid makes possible the production of conductive films which are of a uniform thickness in the individual layer as shown by the reflection interference color of the film in white light. The color of the film is indicative of its thickness and a single color therein of the uniformity in thickness. The electrical resistance of the film can be related to the color thereof. The color of the film and, accordingly, its thickness will depend upon the concentration of the dispersed phase in the aerosol, the rate of flow of the aerosol over the surface to be coated and the duration of the exposure of the surface to the aerosol. The optimum conditions for producing any particular film color can be found by trial and error and once determined can be readily duplicated.

Following the method and employing apparatus as described above, an electrically conductive film was deposited on the inner surface of a glass tube using tin tetrachloride as the liquid metal polyhalide for the production of the aerosol. The tube was made of Pyrex glass No. 7740 and measured 25 mm. in diameter and 16.25 cm. in length. Deposition of the film was made at a muffle temperature of 500° C. The pump was operated to induce a gentle flow of air through the system. The tin tetrachloride was fed dropwise to 10 ml. of dry methanol warmed to approximately 25° C., and at a rate such that approximately 2 ml. thereof was

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added to the methanol over a period of 25 to 30 seconds. The coating operation having been completed within this time period (the operation is quite short), the pump was stopped and the muffle and tube removed from the electric furnace. After having cooled down to room temperature, the treated glass tube was removed from the muffle. The inner surface of the tube was coated with a film for a length of 15 cm. The film was clear, free from bound moisture, of a single color, indicating a uniform thickness, and non-metallic in appearance. Although the exact chemical identity of the film is not known, an analysis of such films has disclosed them to be formed of finely crystalline tin dioxide, of the nature of cassiterite, in which the crystal lattice contains excess tin or oxygen in the elemental or uncombined form. The film is not chemically combined with the glass but is held thereon by some physical force or forces. The electrical resistance of the film, end to end of the tube, was 250 to 600 ohms. In this same way, films of the color series, gray, brown, lavender, blue and green which in the order named have a decreasing electrical resistance are readily produced in areas up to 18 square inches on the inner surface of the glass tube by modifying the rate of flow of the aerosol through the tube or the duration of the exposure of the tube to the flowing aerosol. Color is given herein as reflection interference color in white light. If the films have been allowed to stand in the air whereby moisture has collected on the surface of the films, they can be effectively dried to give satisfactory performance in the counter tube by wiping the surface with a soft absorbent material.

Films prepared as in the above example were evaluated for behavior as the cathode in a halogen-quenched Geiger-Mueller counter of the type shown in Figure 2 which is hereinafter described. A one mil wire of platinum-10% iridium alloy was used as the anode. The glass envelopes carrying the conductive film on the interior thereof were evacuated, subjected to positive ion bombardment, heated to 310° C. for 15 to 20 minutes, allowed to cool to approximately room temperature and then filled with neon at a pressure of 550 mm. (mercury) and chlorine at a pressure of 6 mm. (mercury). A characteristic was run which showed that the tubes (envelope and film) started counting at 920 volts and had a good plateau for 360 volts. The tubes can be filled with neon up to pressures of 700 mm. (mercury) without showing a very large increase in starting voltage. In spite of the transparency of the envelope, the tubes showed no increase in the counting rate on exposure to sunlight or to lighted matches. This alone is a feature not shared by the conventional metal counting tubes. The response of the tubes along their axis showed uniform sensitivity. Over 9 cm. of the total active length of the tubes lies on the flat portion of the sensitivity curve. These tubes are capable of operating at temperatures as high as 200° C. in contrast to the conventional counting tube which fails at 100° C. by the loss of the plateau. The dead time-recovery time envelope for a particular tube design can be readily shortened or lengthened by varying the magnitude of the overvoltage applied to the tube.

In the Geiger-Mueller counter shown in Figure 2, the envelope 101 may be made of glass or of other vitreous material or of a vitreous-surfaced ceramic, such as porcelain. The tube from which the envelope is formed is sealed at the one end and provided with a pair of exterior supporting lugs through which the cathode and anode wires extend in gas-tight relationship for connection with the counting circuit. The wire anode 102 is made of halogen-resistant metal, suitably platinum-10% iridium alloy, and extends along the major or longitudinal axis of the envelope. The diameter of the wire anode may vary but should be substantially less than 50 mils and preferably is from about 1 to 10 mils. An anode diameter of 50 mils has failed to function prop-

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erly in the tubes. The anode wire is supported at its opposite end in known way by means of the helical spring 103 to which it is spot-welded. The spring 103 is tensioned against the opposed intumed, spaced ends 104 of the envelope and housed in the cap 105 which seals this end of the envelope. The inner surface of the envelope carries a moisture-free, halogen-resistant, electrically conductive film 106 produced thereon by means of the method of the invention while the envelope is in the form of a glass tube (open-ended envelope). This conductive film serves as the cathode for the counter. A band 107 of colloidal platinum is provided on the inner surface of the envelope 101 and by contiguity makes electrical contact with the cathode 106. The band 107 is painted on the inner surface of the tube in known way and prior to the coating of the tube with the cathode film. A tungsten wire 108 is electrically connected to the band 107 in known way, by spot welding to a platinum spring contact plate which presses onto the surface of the band, and passes through the adjacent end of the envelope to serve as the cathode wire or lead. The atmosphere of the envelope 101 may be maintained at the usual reduced pressures of from about 50 to 650 millimeters (mercury) and is made up of an ionizable gas and a small proportion of a halogen. The ionizable gas is suitably neon or argon or mixtures of these rare or noble gases. A typical gas filling for the envelope is an admixture of neon 500-600 mm. (mercury) with chlorine 5-6 mm. (mercury).

The electrical circuit schematically shown in Figure 2 includes in addition to the anode 102 and cathode 106, a recorder, such as an electrometer, oscillograph, etc., for registering as a signal the impulse from the ionization produced in the gas-filled envelope 101 by the received radiation. A source of potential E is supplied in series with the gas-filled envelope to maintain the atmosphere therein at a potential gradient which will cause rapid production of ion pairs upon the reception of the ionizing radiation. Resistance R and capacitance C in series completes the circuit from the gas-filled envelope to the recorder.

The application of the teachings of the present invention is productive of counter tubes (envelope and cathode) which have an extended operating life using halogen quenching agents and which may be repeatedly thrown into violent discharge without affecting the normal tube operation with its even pulse heights. An interesting observation in the case of the tubes which have a clear glass envelope, is to view the anode wire in the tube in approximately darkened surroundings while the tube is operating normally. Due to the transparency of the cathode and envelope, one will observe that the ion sheath (Townsend Avalanche) about the anode wire is glowing and that its apparent glow intensity is quite sensitive to change in the amount of radiation falling upon the tube. This requires only a very simple circuit, i.e., the counter tube, a series resistance and a high voltage source.

Various changes and modifications may be made in the invention herein described without departing from the spirit or scope thereof. While I have described my invention with reference to the production of moisture-free, non-metallic cathode films in ionization tubes, it will be obvious that the gas phase deposition method of the invention is of general application for the production of moisture-free, non-metallic, electrically conductive films of level thickness on impervious surfaces of various heat-resistant solids.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

What I claim is:

1. A method of coating an impervious surface of a heat-resistant solid with a clear, moisture-free, electrically

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conductive film which comprises, forming a dry aerosol comprising the product of mixing dry air with the vapors from the addition of a liquid metal polyhalide to dry methanol and flowing the dry aerosol over the impervious surface while it is maintained under dry conditions and is at a temperature sufficient to cause deposition from the aerosol and formation of the film thereon.

2. The method as defined in claim 1, wherein the liquid metal polyhalide is tin tetrachloride.

3. A method of coating the inner impervious surface of a tube of heat-resistant material with a clear, moisture-free, electrically conductive film which comprises, forming a dry aerosol comprising the product of mixing dry air with the vapors from the addition of a liquid metal polyhalide to dry methanol and flowing the dry aerosol through the tube while the latter is maintained under dry conditions and is at a temperature sufficient to cause deposition from the aerosol and formation of the film thereon.

4. The method as defined in claim 3, wherein the tube is made of vitreous material.

5. A method of coating the inner surface of a glass tube with a clear, transparent, moisture-free, electrically conductive film which comprises, forming a dry aerosol comprising the product of mixing dry air with the vapors from the addition of tin tetrachloride to dry methanol and flowing the dry aerosol through the tube while the latter is maintained under dry conditions and is at a temperature of from about 300 to 700° C.

6. A heat-resistant solid having a vitreous surface coated with a clear, transparent, moisture-free, halogen-resistant, electrically conductive film of a finely crystalline metal oxide, said film being of uniform thickness as shown by its single reflectance interference color in white light.

7. A ceramic tube having a vitreous inner surface coated with a clear, transparent, moisture-free, halogen-resistant, electrically conductive film of a finely crystalline tin oxide, said film being of uniform thickness as shown by its single reflectance interference color in white light.

8. A vitreous tube having the inner surface thereof

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coated with a clear, transparent, moisture-free, halogen-resistant, electrically conductive film of a finely crystalline tin oxide, said film being of uniform thickness as shown by its single reflectance interference color in white light.

9. A vitreous tube as defined in claim 8, wherein the tube is made of glass.

10. An ionization device comprising a rigid tubular envelope having an impervious inner surface coated with a clear, transparent, moisture-free, halogen-resistant, electrically conductive film of a finely crystalline metal oxide, said film being a cathode and of uniform thickness as shown by its single reflectance interference color in white light, an anode of small diameter and an ionizable, halogen-containing gas filling in said envelope.

11. An ionization device comprising a vitreous tubular envelope coated on the inner surface with a clear, transparent, moisture-free, halogen-resistant, electrically conductive film of a finely crystalline tin oxide, said film being a cathode and of uniform thickness as shown by its single reflectance interference color in white light, an anode of small diameter and an ionizable, halogen-containing gas filling in said envelope.

12. An ionization device as defined in claim 11, wherein the vitreous tubular envelope is made of glass.

13. An ionization device as defined in claim 12, wherein the halogen is chlorine.

14. A method of coating the inner surface of a glass tube with a clear, transparent, moisture-free, electrically conductive film which comprises, forming a dry aerosol comprising the product of mixing dry air with the vapors from the addition of tin tetrachloride to dry methanol and flowing the dry aerosol through the tube while the latter is maintained under dry conditions and is at a temperature of from about 500 to 700° C.

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