

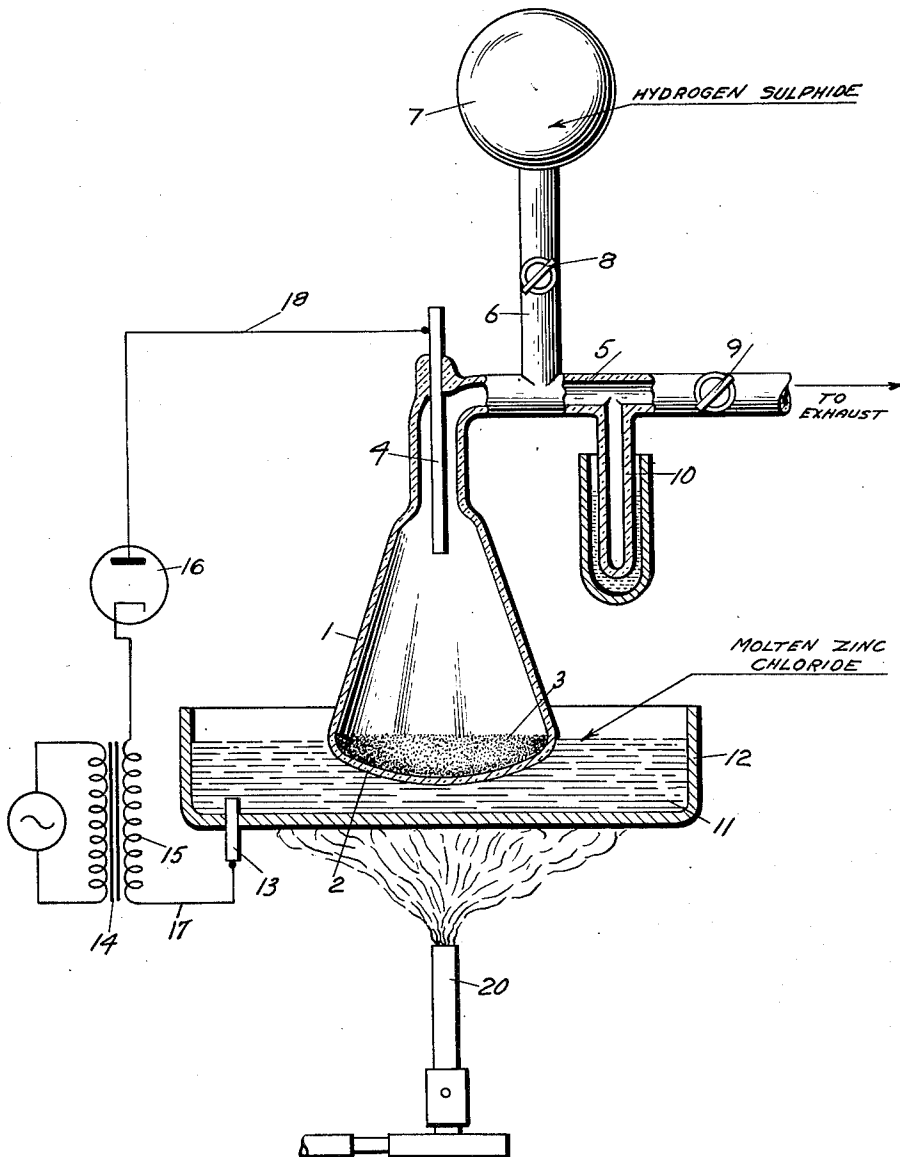
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METHOD FOR PRODUCING FLUORESCENT SCREENS

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METHOD FOR PRODUCING FLUORESCENT
SCREENS

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This is a continuation-in-part of my copending application, Serial No. 634,364, now abandoned, filed December 11, 1945, entitled Method and Apparatus for Producing Fluorescent Screens.

This invention relates to a method of making fluorescent screens such as are used, for example, in cathode-ray tubes.

In the production of cathode-ray tubes for use, for example, in television, it is necessary to produce a fluorescent screen of the desired type with substantially no flaws and a high degree of uniformity of covering of the glass.

In settling processes where uniformity is relatively difficult to achieve, relatively thick coats of fluorescent material are required to completely cover the end of the tube.

This invention discloses a novel method for producing a fluorescent surface on the inside of a glass envelope, such as a cathode-ray tube, whereby an extremely uniform covering of fluorescent material may be applied to said envelope. Because the covering is extremely uniform, a relatively thin layer of fluorescent material need be applied to completely cover the tube face. As a result, objectionable glare light or light from an external source which impinges on the cathode-ray tube surface and is reflected by the fluorescent material to partially mask information presented on the screen will, to a large degree, pass through the fluorescent material and not be reflected thereby. This results in a dark tube effect wherein higher contrast and clarity of picture on the fluorescent screen are obtained.

Briefly, the invention comprises placing the end of the tube envelope, whose interior surface is to be coated, in a bath of a compound comprising an element of the fluorescent coating. The bath is preferably heated, thereby causing a softening of the portion of the envelope immersed therein, such that, if a potential is applied between the bath and the interior of the envelope, current will flow through the envelope. During the manufacture of the envelope, a quantity of the element of the fluorescent coating which occurs in the bath is also placed in the envelope such that, by the application of a suitable polarity voltage between the interior of the envelope and the bath, said element is carried to the inner surface of the envelope by an electrolytic action.

By placing a suitable substance inside the envelope, a chemical reaction may be made to occur with this element on the interior surface of the tube which will form the fluorescent com-

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pound. While the particular embodiment illustrated in the drawing shows a bath comprising molten zinc chloride and a gaseous substance within the tube envelope comprising hydrogen sulphide, it is clearly understood that this invention is not limited thereto.

When hydrogen sulphide is used within the envelope, any of the fluorescent metallic sulphides wherein the metallic component is above hydrogen in the displacement series may be formed. These comprise the sulphides of calcium, barium, strontium, magnesium, beryllium, sodium, potassium, lithium, caesium, cadmium, or zinc.

Particularly, this invention is useful for producing fluorescent sulphides which are used on television screens and comprise the sulphides of calcium, barium, strontium, cadmium and zinc. For any desired metallic fluorescent sulphide to be formed, the molten bath is made up of the chloride of the metal, and a quantity of the metal is placed in the glass envelope during the manufacture thereof.

In addition, other fluorescent compounds may be formed by this process, for example, the fluorescent metallic tungstates and the fluorescent metallic silicates. In particular, calcium tungstate may be formed by the use of a bath of calcium chloride, a tungsten electrode and a filling of oxygen within the envelope. With the bath heated and a potential applied between the electrode and the bath, tungsten from the electrode will be sputtered toward the inner surface of the cathode-ray tube screen. The sputtered tungsten will combine with the oxygen and with the calcium being electrolyzed through the glass envelope to produce calcium tungstate.

In the formation of fluorescent metallic silicates, the tube is placed in a bath of the metal of the silicate and a potential is applied between the electrode within the tube and the bath. The silicates which are in the glass nearest the inner surface of the glass envelope have metallic components concentrated therein to a greater degree than those near the outer surface of the tube. Concentration of the metallic components produces the necessary contamination or activation necessary to produce a good fluorescent compound.

In the other processes wherein fluorescent metallic sulphides and fluorescent metallic tungstates are formed, the contaminators or activators, which may be, for example, minute quantities of silver or copper, may be included in the composition of the electrode within the tube. These contaminators are then sputtered to the

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surface of the envelope on which the fluorescent screen is being produced and combined with the fluorescent screen crystals to activate them. If desired, the activators or contaminators may be placed in the glass tube envelope, and, indeed, it has been found that the commercial glass used contains various minute impurities, including silver and copper, which were sufficient to activate the fluorescent screen.

The glass envelope may be made of a mixture of ordinary commercial glass, such as soft soda glass, which may contain, for example, seventy-five per cent silica dioxide, sodium oxide fifteen per cent, calcium oxide eight per cent, and aluminum oxide two per cent. To this mixture, an additional ten per cent by weight of an oxide of the metallic element of the fluorescent coating is added. The percentages given above are not critical and may be varied widely with good results in accordance with standard glass-making practice.

Referring now to the drawing, a particular fluorescent coating and the apparatus used in the production thereof will be described.

There is shown a glass envelope 1 for a cathode-ray tube, having an end 2 on which there is desired to be provided a fluorescent coating such as, for example, zinc sulphide coating 3 which, as is well known, fluoresces when it is struck by an electron stream. The glass composition of envelope 1 contains a substantial proportion of zinc oxide which may constitute 10 per cent or more of the glass composition. Within the end of the envelope opposite end 2 there is sealed a metallic electrode 4. Communicating with the interior of envelope 1 by means of lateral tube 5 and branch tube 6 is a source or reservoir 7 of gaseous hydrogen sulphide, a valve 8 being provided in order to control the admission of hydrogen sulphide to said interior. Also communicating with the interior of the envelope by means of tube 5 is an exhaust or vacuum pump, not shown, by means of which the interior of the envelope may be evacuated. A valve 9 is provided in this exhaust connection so that the envelope may be readily connected to and disconnected from the vacuum pump. A low temperature trap 10 may be provided in the exhaust line for the purpose of condensing undesirable vapors which may be present in said line.

End 2 of tube 1 is immersed in a bath 11 of molten zinc chloride, which bath is confined in a suitable container 12 and is maintained in the molten condition by any suitable heating means, such as that indicated at 20. End 2 of the envelope is completely immersed in bath 11, so that the bath entirely surrounds and intimately engages the entire exterior surface of end 2 of envelope 1. Metallic electrode 13 is so placed in bath 11 as to be in electrical conducting relation therewith.

A source of high direct potential is provided comprising a high voltage secondary 15 of a transformer 14 and a half wave rectifier 16 connected as shown. Lead 17, therefore, serves as the positive terminal for the high direct potential and is connected to electrode 13, while lead 18 serves as the negative terminal for the high direct potential and is connected to an electrode 14. The high voltage is, therefore, applied between electrode 4 and the bath 11 when the primary of transformer 14 is energized. It is to be clearly understood that this invention is not limited by any particular voltages. It has been found that the process will operate with

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voltages ranging from a few volts to many thousand volts. Excellent results have been achieved where the high voltage secondary has a peak voltage on the order of 20,000 volts, thereby applying substantially that potential between the electrode 4 and the bath 11. However, the process will occur at lower voltages of the clipped sinusoidal wave which results from rectifying the secondary potential of transformer 14 by rectifier 16. These potentials which may be, for example, as low as a hundred volts, will still produce fluorescent coating on the end of the envelope although at a considerably reduced rate.

In the method of this invention, end 2 of envelope 1 is placed in molten zinc chloride bath 11. The envelope is then exhausted as completely as possible by means of the vacuum pump and valve 9, after which a low pressure (of the order of 2 to 10 millimeters of mercury) atmosphere of hydrogen sulphide is provided in the envelope from source 7 through valve 8. A high voltage direct current from the source 14—16 is then applied between electrode 4 and the outer surface of end 2 of the envelope. As the fluorescent zinc sulphide surface or coating 3 is formed on the inside of end 2, it fluoresces due to the passage of electrons or the flow of current through it. When a screen of sufficient brilliancy has been formed, which condition may readily be ascertained by observation, the process is stopped by disconnecting the high voltage source from both electrodes or from either of them.

The explanation of this process is thought to be as follows. As is well known, glass has substantial electrical conductivity at elevated temperatures, such as that of molten zinc chloride. When the glass of envelope 1, which contains zinc oxide, approaches a molten state, zinc ions will be produced on the inner surface of end 2 of the envelope. The hydrogen sulphide is also ionized under the action of the electrical discharge, producing sulphur ions which combine with the zinc ions present to form zinc sulphide which is deposited as a coating 3 on the inside of end 2 of the envelope. Since the flow of electrical current through glass is mainly an ionic flow, the zinc ions used for the formation of the coating are replaced in the glass by the travel of zinc ions, present in bath 11, into and through the glass envelope.

By the method of this invention, a highly uniform fluorescent screen or coating of zinc sulphide may be produced on a cathode-ray tube. Also, since the brilliancy of the screen is readily observable during the process of manufacture, substantially perfect control of the screen may be had.

Of course, it is to be understood that this invention is not limited to the particular details as described above, as many equivalents will suggest themselves to those skilled in the art. It is accordingly desired that the appended claims be given a broad interpretation commensurate with the scope of this invention within the art.

What is claimed is:

1. The method of producing a zinc sulphide coating on a glass envelope which comprises forming said envelope of a composition containing zinc oxide, immersing said envelope in a bath of molten zinc chloride, evacuating said envelope, providing a low pressure atmosphere of hydrogen sulphide within said envelope, and simultaneously applying a direct electrical potential between an electrode in said bath and

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an electrode in the interior of said envelope such that said bath is positive with respect to said envelope to produce by ionic combination a coating of zinc sulphide on the immersed portion of said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

2. The method of producing a fluorescent sulphide coating on an envelope comprising forming said envelope of a composition having a first element of said fluorescent sulphide coating, said element being of the class consisting of calcium, barium, strontium, cadmium and zinc, immersing said envelope in a molten bath consisting essentially of a salt of said first element, providing a quantity of hydrogen sulphide within said envelope, and applying an electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that said bath is positive with respect to said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

3. The method of producing a coating of fluorescent zinc sulphide on a glass envelope comprising forming said envelope of a composition containing zinc oxide, immersing said envelope in a molten bath comprising zinc chloride, providing a quantity of hydrogen sulphide within said envelope, and applying a direct electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that the electrode in said bath is positive with respect to the electrode in said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

4. The method of producing a coating of fluorescent calcium sulphide on a glass envelope comprising forming said envelope of a composition containing calcium oxide, immersing said envelope in a molten bath comprising calcium chloride, providing a quantity of hydrogen sulphide within said envelope, and applying a direct electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that the electrode in said bath is positive with respect to the electrode in said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

5. The method of producing a coating of fluorescent barium sulphide on a glass envelope comprising forming said envelope of a composition containing barium oxide, immersing said

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envelope in a molten bath comprising barium chloride, providing a quantity of hydrogen sulphide within said envelope, and applying a direct electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that the electrode in said bath is positive with respect to the electrode in said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

6. The method of producing a coating of fluorescent strontium sulphide on a glass envelope comprising forming said envelope of a composition containing strontium oxide, immersing said envelope in a molten bath comprising strontium chloride, providing a quantity of hydrogen sulphide within said envelope, and applying a direct electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that the electrode in said bath is positive with respect to the electrode in said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

7. The method of producing a coating of fluorescent cadmium sulphide on a glass envelope comprising forming said envelope of a composition containing cadmium oxide, immersing said envelope in a molten bath comprising cadmium chloride, providing a quantity of hydrogen sulphide within said envelope, and applying a direct electrical potential between an electrode in said bath and an electrode in the interior of said envelope such that the electrode in said bath is positive with respect to the electrode in said envelope, said potential being sufficient to produce a discharge through said hydrogen sulphide.

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