April 24, 1945. V. J. SCHAEFER 2,374,310

METHOD OF PRODUCING SOLIDS OF DESIRED CONFIGURATION

Filed June 27, 1941

Fig. 1.

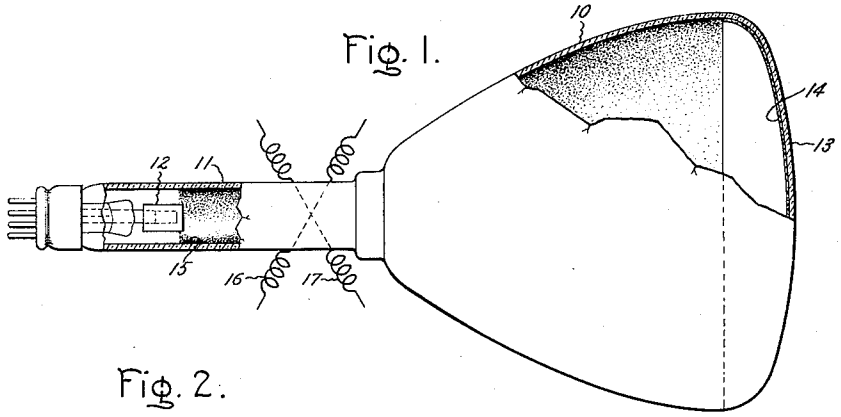


Fig. 2.

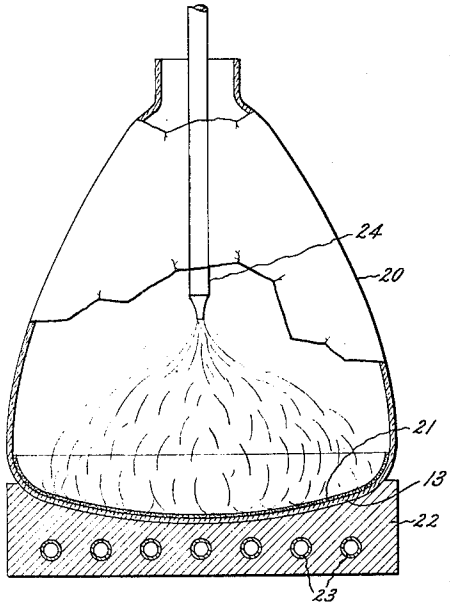


Fig. 3.

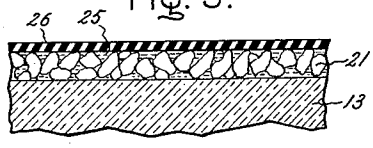


Fig. 4.

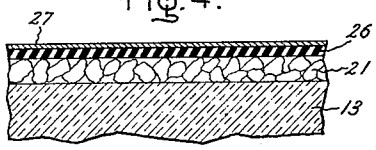


Fig. 6.

Fig. 5.

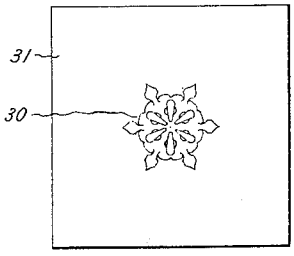
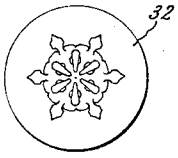


Fig. 7.



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UNITED STATES PATENT OFFICE

2,374,310

METHOD OF PRODUCING SOLIDS OF DESIRED CONFIGURATION

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Application June 27, 1941, Serial No. 400,069

8 Claims. (Cl. 117—34)

The present invention comprises a method of producing a stable solid having a desired surface configuration.

The invention is capable of numerous applications, but is considered to be of special utility in connection with the problem of providing a smooth covering layer on a relatively granular surface such as the surface of a fluorescent screen contained in a television picture tube. This particular problem arises from the desirability of providing such a screen with a smooth reflecting metal coating adapted to prevent light and secondary electrons generated in the screen from being projected back into the free space of the cathode ray tube. The granular character of a screen of the type specified makes it impracticable to obtain a reflecting coating of the desired quality by depositing metal directly on the screen surface. While it has been proposed to overcome this difficulty by first covering the screen with a film of a synthetic resin or the like, even this expedient, as heretofore practiced, has not yielded the desired results.

By the use of the present invention a smooth and strongly adherent coating of appropriate characteristics may be obtained by a procedure which includes the following steps: (1) forming on the screen surface a frozen layer of a normally liquid or gaseous substance, (2) flowing over the frozen liquid a film of an appropriate resin dissolved in a volatile solvent, (3) evaporating the solvent from the resin to cause it to solidify, (4) raising the temperature of the screen sufficiently to cause the frozen liquid to be dissipated by passage in the vapor phase through the resin film, and (5) finally depositing metal on the smooth resin surface thus provided. This procedure, and certain other applications of the technique involved, is explained more fully in the following description which is to be considered in connection with the accompanying drawing. In the drawing Fig. 1 shows a partially sectionalized cathode ray tube in connection with which the present invention may be usefully applied; Fig. 2 illustrates a particular step in the practice of the invention; Figs. 3 and 4 are enlarged fragmentary sectional views showing a fluorescent cathode-ray tube screen in successive stages of treatment, and Figs. 5, 6 and 7 illustrate an alternative application of the invention.

Referring particularly to Fig. 1, there is shown a television picture tube having an envelope which comprises an enlarged bulbous portion 10 and an elongated shaft portion 11, the latter portion containing an electron gun 12 for generating a stream of electrons adapted to be projected longitudinally of the envelope. A conductive coating 15 (e. g., an aqueous suspension of graphite) applied to the inner surface of the envelope and extending to within a short distance of the electron gun provides an accelerating electrode by means of which an appropriate axial field may be created within the envelope. The end of the envelope remote from the electron gun 12 is in the form of a flattened transparent window 13 which is provided on its inner surface with a layer 14 of a fluorescent substance adapted to be excited to visible luminescence by the impingement of electrons. Electron deflecting means, illustrated diagrammatically as deflecting coils 16 and 17, may be provided adjacent an intermediate portion of the tube for the purpose of causing the electron beam to scan sequentially the various elemental areas of the fluorescent screen so as to develop a television picture on the screen.

It is obvious that a portion of the light developed by the screen 14 will, if not impeded, be projected back into the interior of the tube rather than out through the window 13. The light which is thus projected is in a sense lost or, if not lost, tends to produce objectionable internal reflections within the tube. In addition, secondary electrons released from the components of the fluorescent material which are successively struck by the electron stream tend to travel across the surface of the screen to the more positively charged parts thereof and hence to produce a spurious excitation of the screen. In order to overcome these effects, it has been suggested to provide the surface of the fluorecsent screen 14 with a thin coating of a highly reflecting metal which, while capable of penetration by the high velocity electrons in the scanning beam will, nevertheless, prevent light and low velocity secondary electrons from escaping into the interior of the tube. However, as has been previously stated herein, there are numerous practical difficulties which have prevented any extensive use of this expedient.

In Fig. 2 hereof, there is shown the first step of a method by which a fluorescent screen of the type under consideration may be provided with a metallic coating of the desired character. In this figure, 20 represents the bulbous portion of a cathode-ray tube envelope before the same has been joined to the shaft portion of the envelope. In the condition illustrated the end-wall of the envelope 20 is assumed to be provided with a granular adherent coating of fluorescent material (e. g., willemite) which is indicated at 21

and which in the completed form of the tube is intended to perform the function ascribed to the coating 14 of Fig. 1.

According to the present invention, the coated end wall of the tube is first placed in contact with a cooling plate 22 having a surface which conforms to the outer surface of the tube wall. The cooling plate is brought to a temperature slightly above the freezing temperature of water by circulating a suitable refrigerant through ducts 23 provided in the body of the plate. After the tube structure has been adequately cooled by this me ns, water vapor is introduced into the interior of the envelope by a nozzle indicated at 24. The vapor which reaches the end wall of the tube will be condensed because of the low temperature at which the wall is maintained. The condensate fills the interstices which separate the various granular particles of the fluorescent coating 21. The surface is then lowered to a temperature below the freezing point of the liquid to solidify the condensed film. In this way the irregularity by which the coating is initially characterized will be eliminated, and the coating in combination with the adhering deposit of ice (indicated at 25 in Fig. 3) will present a smooth external surface.

After this step is completed, one may flow over the surface of the frozen screen a very thin layer of a film-forming resin dissolved in a volatile solvent and introduced by spraying or otherwise. In this latter connection one may employ numerous resinous materials including, among others, cellulose esters, such as nitro cellulose and cellulose acetate, and resinous compounds of the polyvinyl type, as exemplified by plasticized polyvinyl halides; by the copolymer of vinyl chloride and vinyl acetate, or by one of the reaction products of an aldehyde with a hydrolyzed polymerized vinyl ester. The last named reaction products are described fully in Reissue Patent 20,430, Morrison et al., and are designated generally as "polyvinylal resins." A typical polyvinylal resin and one which is considered especially suitable for the present invention is that which is prepared by condensing formaldehyde with the product of hydrolysis of polyvinyl acetate, the resultant resin being conveniently designated as "polyvinyl formal."

The solvent to be used will, of course, vary with the particular resin selected. In the case of nitro-cellulose and cellulose acetate, acetone may be used as an appropriate solvent; with polyvinyl chloride one may use monochlortoluene; with polyvinyl formal, chloroform or ethylene dichloride, etc. After the particular resinous material selected has been spread to the desired thickness, the resin should be allowed to set by evaporation of the solvent, this latter step preferably taking place while the tube wall is maintained at a relatively low temperature. Under these conditions, the resultant resin film, which is preferably of a thickness between 500 and 10,000 Angstrom units, will be of essentially smooth character as indicated at 26 in Fig. 3. After the resin has set (i. e., by evaporation of its solvent), the temperature of the assembly may be slowly raised in order successfully to melt the liquid on which the resin is superimposed and finally to cause the liquid to be evaporated by passage in the vapor phase through the resin film. If this is done, the resin film may next be coated (e. g., by an evaporating process) with a thin deposit of a highly reflecting metal such as silver or aluminum, the resultant structure being illustrated in Fig. 4. This figure shows in successive layers the fluorescent material 21, the resinous film 26 and a metallic coating 27. Due to the manner of its formation and, more specifically, to the nature of the base on which it is formed, the coating 27 will be uniform and of a highly reflecting nature, a result heretofore substantially unattainable in a system of the type in question.

The procedure described in the foregoing comprises only a specific application of a method which in its broader aspects comprises a new means for obtaining stable solid bodies of desired surface configuration. The invention is further illustrated in Figs. 5 to 7 which depict a procedure which has been used to obtain a permanent mold of an extremely fragile crystalline substance, such as a snow flake.

In this case, the snow flake, indicated at 30 in Fig. 5, is deposited on a receiving surface 31, which has been precooled to a temperature below the freezing point of water. Next, there is deposited on the snow flake a single drop of a suitable resin (e. g., polyvinyl formal) dissolved in a volatile non-aqueous solvent and precooled to a temperature also below the freezing temperature of water. This is illustrated in Fig. 6, the resin drop being shown at 32. After the solvent contained in the resinous material has been allowed to evaporate, the temperature of the various parts is raised to melt the snow flake and to cause the resultant liquid to be evaporated and diffuse in the vapor phase through the mass of resinous material. Thereafter, the solidified resinous body may be removed from the surface 31 and will be found to comprise a permanent mold showing in clear detail the outlines of the snow flake as illustrated in Fig. 7.

In the foregoing, reference has been made to the use of water as the freezable liquid to be employed simply because this substance is ordinarily available and can be caused to pass from its solid to its vapor stage within a range of temperatures practicably attainable. It should be understood, however, that other normally liquid or gaseous substances may be used in this connection. For example, benzene, acetone or alcohol may be employed.

While the invention has been described by reference to particular uses thereof, it will be understood that other applications may be made by those skilled in the art without actually departing from the invention. I, therefore, aim in the appended claims to cover all such equivalent uses as come within the true spirit and scope of the foregoing disclosure.

An application Serial No. 541,401, filed June 21, 1944, constituting a continuation-in-part hereof, is directed to cathode ray tubes in which a reflecting layer of metal is superimposed on a screen of electron-responsive material as herein described.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of producing a solid having a desired physical configuration, which comprises preparing a solution of a selected solidifiable material in a volatile solvent, flowing the solution over a forming member which possesses the desired configuration and which consists of a substance having both solid and vapor phases in a range of temperatures throughout which the said material can exist as a solid, the said substance

being maintained in its solid phase during the aforementioned flowing operation, evaporating the solvent from the said material to cause its solidification, and finally raising the temperature of the forming member to cause its evaporation.

2. The method of producing a stable solid of desired surface configuration, which method comprises preparing a solution of film-forming resin in a volatile solvent, flowing the solution over a forming substance which has a surface conforming to the desired configuration and which exhibits both a solid and a vapor phase in a range of temperatures throughout which the said material can exist as a solid, the said substance being maintained in its solid phase during the aforementioned flowing operation, evaporating the solvent from the resinous material to cause it to solidify, and finally heating the forming substance to a temperature sufficiently high to cause it to be dissipated by passage in the vapor phase through the mass of the resinous material.

3. The method of producing a solid of desired surface configuration, which method comprises preparing a solution of a film-forming resin material in a volatile solvent, flowing the solution over a frozen liquid having a surface which conforms to the desired configuration and having a degree of volatility less than that of said solvent, evaporating the solvent from the resin material to cause it to set, and finally heating the frozen liquid to a temperature sufficiently high to produce a vapor which may diffuse through the resin material.

4. The method of producing a stable, hollow, solid body having an interior configuration corresponding to the exterior configuration of a forming member consisting of ice, which consists in enveloping said forming member with a solution of a water-insoluble resin in a volatile, non-aqueous solvent, evaporating the solvent thereby causing the resin to set about said forming member, and raising the temperature sufficiently to remove said forming member by evaporation and diffusion.

5. The method of producing on an irregular support a thin layer of metal having a desired surface configuration, which comprises forming a body of frozen liquid having the desired configuration, flowing resinous material dissolved in a solvent of greater volatility than the said liquid over the frozen body, evaporating the said solvent to set the resinous material, raising the temperature sufficiently to melt the frozen body and to cause evaporation of its constituent liquid and diffusion of the resulting vapor through the resinous material and depositing a metal film on said resinous material.

6. The method of producing a smooth layer of metal on a wall surface of irregular form, which comprises providing a selected, readily evaporable substance in vapor phase in proximity to the said wall surface to cause the substance to condense on the surface so as to fill in its irregularities, maintaining the wall temperature below the solidification point of the said substance to freeze the substance in situ, flowing over the said surface a film of the resin material dissolved in a solvent of greater volatility than said substance, permitting the solvent to evaporate to set the resin while still maintaining the wall temperature below the point of solidification of the said substance, raising the wall temperature materially above said point to cause the substance to be dissipated through the resin film by evaporation and depositing a layer of metal on said resinous film.

7. The method of producing a smooth layer of resin material on a wall surface having an adherent granular coating, which comprises providing water vapor in proximity to the said wall surface to cause the interstices between the various granular elements adhering thereto to be filled in by a deposit of condensed water, fixing the temperature of the said wall below zero degrees centigrade to solidify the said deposit, flowing over the resultant superficies a film of the resin material dissolved in a volatile solvent, evaporating the solvent to set the resin material while maintaining the wall still at a low temperature, and raising the temperature of the wall surface sufficiently to cause the ice deposit to be dissipated by passage in vapor phase through the resin film while leaving the said film intact.

8. The method of providing with a reflective backing a granular fluorescent coating applied to an extended wall surface which includes the following steps: providing a normally liquid or gaseous substance in vapor phase in proximity to the said wall surface, thereby to cause the substance to condense on the surface so as to fill in its irregularities, fixing the temperature of the wall surface below the freezing point of the said substance to solidify the condensed deposit, flowing over the said surface a film of resin material dissolved in a volatile solvent, evaporating the solvent to set the resin while still maintaining the wall temperature below the point of solidification of the said substance, subsequently raising the wall temperature materially above said point to cause the substance to be dissipated through the resin film by evaporation, and finally depositing on the said film a thin layer of a highly reflecting metal.

VINCENT J. SCHAEFER.