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PROCESS FOR APPLYING PHOSPHOR PARTICLES TO A DIELECTRIC LAYER OF A GASEOUS DISCHARGE DEVICE

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ABSTRACT OF THE DISCLOSURE

There is disclosed a process for embedding phosphor particles in the surface of at least one dielectric member to be assembled in a multiple gaseous discharge display/memory panel such that the phosphor particles are partially exposed to the gaseous medium of the assembled panel and are capable of being excited by radiation from the gaseous discharges of such assembled panel. Any suitable luminescent phosphor which is compatible with the dielectric may be used; however, photoluminescent phosphors are highly preferred. One embodiment comprises partially embedding the phosphor particles by means of a photosensitive material.

This invention relates to the manufacture of multiple gas discharge display/memory panels which have an electrical memory and which are capable of producing a visual color display including the representation of data such as numerals, letters, television display, radar displays, binary words, etc. More particularly, this invention relates to applying phosphor particles to one or more dielectric layers of a multiple gas discharge device such that the device is capable of producing a visual color display in a color other than that characteristic of the color exhibited by the particular gaseous medium utilized in the device.

Multiple gas discharge display and/or memory panels of the type with which the present invention is concerned are characterized by an ionizable gaseous medium, usually a mixture of at least two gases at an appropriate gas pressure, in a thin gas chamber or space between a pair of opposed dielectric charge storage members which are backed by conductor (electrode) members, the conductor members backing each dielectric member being transversely oriented to define a plurality of discrete discharge volumes, each of which constitutes a discharge unit. In some prior art panels the discharge units are additionally defined by surrounding or confining physical structure such as by cells or apertures in perforated glass plates and the like so as to be physically isolated relative to other units. In either case, with or without the confining physical structure, charges (electrons, ions) produced upon ionization of the gas of a selected discharge unit, when proper alternating operating potentials are applied to selected conductors thereof, are collected upon the surfaces of the dielectric at specifically defined locations and constitute an electrical field opposing the electrical field which created them so as to terminate the discharge for the remainder of the half cycle and aid in the initiation of a discharge on a succeeding opposite half cycle of applied voltage, such charges as are stored constituting an electrical memory.

Thus, the dielectric layers prevent the passage of any conductive current from the conductor members to the gaseous medium and also serve as collecting surfaces for ionized gaseous medium charges (electrons, ions) during the alternate half cycles of the A.C. operating potentials, such charges collecting first on one elemental or discrete dielectric surface area and then on an opposing elemental or discrete dielectric surface area on alternate half cycles to constitute an electrical memory.

An example of a panel structure containing non-physically isolated or open discharge units is disclosed in U.S. Letters Patent 3,499,167 issued to Theodore C. Baker et al.

An example of a panel containing physically isolated units is disclosed in the article by D. L. Bitzer and H. G. Slottow entitled "The Plasma Display Panel—a Digitally Addressable Display With Inherent Memory," Proceeding of the Fall Joint Computer Conference, IEEE, San Francisco, Calif., November 1966, pp. 541–547.

In the operation of the panel, a continuous volume of ionizable gas is confined between a pair of dielectric surfaces backed by conductor arrays forming matrix elements. The cross conductor arrays may be orthogonally related (but any other configuration of conductor arrays may be used) to define a plurality of opposed pairs of charge storage areas on the surfaces of the dielectric bounding or confining the gas. Thus, for a conductor matrix having H rows and C columns the number of elementals discharge volumes will be the product $H \times C$ and the number of elemental or discrete areas will be twice the number of elemental discharge volumes.

The gas may be one which produces light (if visual display is an objective) and a copious supply of charges (ions and electrons) during discharge. In an open cell Baker et al. type panel, the gas pressure and the electric field are sufficient to laterally confine charges generated on discharge within elemental or discrete volumes of gas between opposed pairs of elemental or discrete dielectric areas within the perimeter of such areas, especially in a panel containing non-isolated units.

As described in the Baker et al. patent, the space between the dielectric surfaces occupied by the gas is such as to permit photons generated on discharge in a selected discrete or elemental volume of gas to pass freely through the gas space and strike surface areas of dielectric remote from the selected discrete volumes, such remote, photon struck dielectric surface areas thereby emitting electrons so as to condition other and more remote elemental volumes for discharges at a uniformly applied potential.

With respect to the memory function of a given discharge panel, the allowable distance or spacing between the dielectric surfaces depends, among other things, on the frequency of the alternating current supply, the distance typically being greater for lower frequencies.

While the prior art does disclose gaseous discharge devices having externally positioned electrodes for initiating a gaseous discharge, sometimes called "electrodeless discharges," such prior art devices utilize frequencies and spacings or discharge volumes and operating pressures such that although discharges are initiated in the gaseous medium, such discharges are ineffective or not utilized for charge generation and storage in the manner of the present invention.

The term "memory margin" is defined herein as

$$\text{M.M.} = \frac{V_f - V_s}{V_s}$$

where V_f is the magnitude of the applied voltage at which a discharge is initiated in a discrete conditioned (as explained in the aforementioned Baker, et al. patent) volume of gas defined by common areas of overlapping conductors and V_s is the magnitude of the minimum applied periodic alternating voltage sufficient to sustain discharges once initiated. It will be understood that basic electrical phenomena utilized in this invention is the generation of charges (ions and electrons) alternately storable at pairs of opposed or facing discrete points or areas on a pair

of dielectric surfaces backed by conductors connected to a source of operating potential. Such stored charges result in an electrical field opposing the field produced by the applied potential that created them and hence operate to terminate ionization in the elemental gas volume between opposed or facing discrete points or areas of dielectric surface. The term "sustain a discharge" means producing a sequence of momentary discharges, one discharge for each half cycle of applied alternating sustaining voltage, once the elemental gas volume has been fired, to maintain alternate storing of charges at pairs of opposed discrete areas on the dielectric surfaces.

In accordance with the practice of this invention, there is provided a process for applying and attaching phosphor particles to the charge storage surface of at least one dielectric member to be assembled in a gaseous discharge device such that the applied particles are partially exposed to the gaseous medium of the panel and are capable of being excited by radiation from at least one gaseous discharge unit of the panel.

More particularly, there is provided a process for partially embedding phosphor particles in the surface of at least one dielectric member, which surface is to be exposed to the gaseous medium within an assembled gaseous discharge device, which process comprises:

Applying phosphor particles to at least a portion of the dielectric surface;

And then heating the dielectric to a temperature sufficient to soften the dielectric surface such that the phosphor particles sink and partially embed therein.

The phosphor particles may be applied to the dielectric alone or in combination with other suitable ingredients, e.g. solvents, binders, adhesives, etc.

In one specific practice hereof the phosphor particles are mixed with a pyrolizable polymer, such as poly alpha methyl styrene, and then applied to the dielectric. The dielectric and applied mixture are then heated so as to embed the particles in the dielectric and pyrolize the polymer.

In a further practice hereof, excellent results have been obtained by the preliminary conditioning or preparation of the dielectric surface with an adhesive substance so as to temporarily bind the phosphor particles prior to the embedding thereof in the dielectric.

One particularly preferred embodiment comprises the use of a photosensitive material by:

applying a photosensitive material to at least a portion of the dielectric surface;

exposing a selected portion of the applied photosensitive material to appropriate radiation so as to harden the radiation exposed photosensitive material whereby subsequently applied phosphor particles will not adhere thereto;

heating the applied photosensitive material in an amount sufficient to soften that portion of the photo-sensitive material not exposed to radiation such that subsequently applied phosphor particles will adhere thereto;

applying phosphor particles to the dielectric surface such that a portion of the particles adhere to the softened photosensitive material;

removing non-adhered phosphor particles from the dielectric surface;

and then heating the dielectric and photosensitive material in an amount sufficient to vaporize and remove substantially all of the photosensitive material from the dielectric surface and also soften the dielectric surface such that the phosphor particles partially embed within such softened surface.

As used herein, photosensitive material is defined as including both inorganic or organic substances which are capable of changes in chemical structure and/or physical properties (such as hardness, tackiness, solubility, susceptible to softening upon application of heat, etc.) when subjected to radiation of appropriate wavelength.

Specific photosensitive materials contemplated herein include the photopolymerizable monomers and photocross-linking polymers as defined and described in "Photopolymerization and Photocrosslinking of Polymers" by Dr. J. L. R. Williams, Fortschr. Chem. Forsch, vol. 13, No. 2 (1969), pages 227 et seq.

Typical inorganic and organic photosensitive materials include not by way of limitation vinyl cinnamate monomers and poly (vinyl cinnamate) polymers as disclosed by Williams, ferric hydroxide, ferric chloride, benzoyl peroxide, benzophenone, reversible oxygen carriers, and light-sensitive polymers containing recurring styryl ketone groups as disclosed in U.S. Letters Patent 3,453,237.

Where the process comprises the use of auxiliary materials, e.g. solvents, adhesive, photosensitive materials, etc., it is contemplated that intermediate drying steps may be desirable.

In the radiation hardening of the photosensitive material, the material is radiated until it is thermally nontackifiable and non-adhesive relative to phosphor particles applied thereto. The selected radiating of the photosensitive material may be by any suitable means, typically with a mask using ultraviolet radiation.

In the softening of the non-radiated photosensitive material, the material is typically heated to its softening temperature for a short period of time, e.g. about 5 to 10 minutes, until it is thermally tackifiable and capable of receiving and binding applied phosphor particles to the dielectric surface. The exact time and temperature of heating will vary with the photosensitive material.

The removal of excess phosphor particles, such as in the photosensitive material embodiment, may be by any suitable means such as washing (with water, alcohol, etc.), air blow, etc.

In the preferred practice hereof, the phosphor is photoluminescent. The term photoluminescent phosphor includes quite generally all solid and liquid, inorganic and organic materials which are able to convert an input of absorbed photons into an output of photons of different energy, said output comprising visible light of a brightness and intensity sufficient for visual display.

Typical photoluminescent phosphors contemplated include not by way of limitation both activated and non-activated compounds, e.g. the sulfides such as zinc sulfides, zinc-cadmium sulfides, zinc-sufo-selenides; the silicates such as zinc silicate, zinc beryllo-silicate, Mg silicates; the tungstates such as calcium tungstates, magnesium tungstates; the phosphates, borates, and arsenates such as calcium phosphates, cadmium borates, zinc borates, magnesium arsenates; and the oxides and halides such as self-activated zinc oxide, magnesium fluorides, magnesium fluorogermanate. Typical activators include not by way of limitation Mn, Eu, Ce, Pb, etc.

The phosphor particles may be applied to the dielectric alone or in combination with solvents, binders, or other convenient materials.

The phosphor particles are applied to the dielectric surface by any convenient method including not by way of limitation vapor deposition; vacuum deposition; chemical vapor deposition; wet spraying or settling upon the dielectric a mixture or solution of the phosphor suspended or dissolved in a liquid followed by evaporation of the liquid; silk screening; dry spraying of the phosphor upon the dielectric; electron beam evaporation; plasma flame and/or arc spraying and/or deposition; in situ preparation of the phosphor by applying to the dielectric the components or reactants necessary for formation thereof; and sputtering target techniques. Likewise, similar means may be used to apply the photosensitive material and/or other substances (adhesive and non-adhesive) to the dielectric.

It is further contemplated in the practice hereof that two or more phosphors may be combined so as to produce a multicolor display, each phosphor being excited by the same or different source. In such embodiment, the radiation from one phosphor may be used to excite another phosphor.

As an extension of this embodiment it is possible to produce multicolor displays by the use of two or more phosphors with a different colored phosphor at adjacent electrode intersections. This allows control of the discharge so as to excite only the color desired. In this manner, one could produce red characters on a green background for a more striking visual display.

Another extension is the use of three color dots, as commonly used in cathode ray tubes, to obtain multicolor displays. To get true color pictures a means of controlling the intensity of the light from each color is necessary. Possible ways of doing this are varying the voltage applied to the discharge exciting a particular color; varying duration of discharge; use of multilayers of glass and phosphor, possibly with transparent electrodes; and addressing the various layers independently.

One preferred embodiment of this invention comprises exciting the photoluminescent phosphor with photons, for example ultraviolet radiation, emitted from one or more panel discharge units. In the practice of such embodiment, it is contemplated using any gaseous medium which will emit (upon panel discharge) photons, especially UV radiation in the range of about 500 to about 2500 angstrom units, sufficient to excite the photoluminescent phosphor.

In one highly preferred embodiment hereof, the photon emitting gaseous medium is selected from the rare gases of helium, neon, argon, krypton, xenon, and mixtures thereof. In the practice of such embodiment, it has been discovered that the phosphor exciting effectiveness of such rare gases increases with atomic weight, e.g. from neon to argon to krypton to xenon. With krypton and xenon, practically all of the visible light emitted from the panel comes from the excited phosphors, e.g. relative to color emitted by the gaseous medium during the gaseous discharge.

It is further contemplated that other gases may be useful in the practice of this invention including not by way of limitation nitrogen; hydrogen; oxygen; carbon dioxide; carbon monoxide; the halogens, water vapor; hydrocarbons; boron fluoride; acid fumes; Group VIII gases; H_2O_2; vapors of sodium, mercury, thallium, cadmium, rubidium, caesium; carbon disulfide; N_2O; NO; NO_2; N_2O_3; H_2S; phosphorus vapors; C_2H_2; CH_4; naphthalene vapor; anthracene; freon; ethyl alcohol; methylene bromine; sulfur hexafluoride; tritium; radioactive gases; electron attaching gases; electron free gases; and mixtures thereof.

The operation of a gaseous discharge display/memory panel comprises consideration of many operating parameters. In the practice of this invention, two important parameters are the gaseous medium pressure and the frequency of the A.C. supply.

The gaseous medium must be at a pressure sufficient to give a panel memory margin, the exact gas pressure being a function of the particular gaseous medium and other parameters of the system. For example, a pressure of about 50 torr to about 400 torr is contemplated for 100% xenon. For mixtures of neon-argon or neon-argon-xenon, pressures up to about 800 torr may be utilized. Thus for rare gases and mixtures thereof, an overall pressure of about 50 torr to about 800 torr is contemplated.

The frequency of the A.C. supply must be sufficient for both memory margin and display purposes. Typically the higher the frequency, the greater the average light output. However, for optimum memory margin the frequency ranges from about 25 kilohertz to about 300 kilohertz depending upon other parameters, e.g. pressure and wave shape.

In the prior art the color of a display from a gaseous discharge device has been limited to a color characteristic of the particular gas in use, for example red with neon or blue with argon. However, the use of phosphors in accordance with this invention allows other colors to be obtained from the discharge of a particular gas. For example a display using a xenon discharge can be made to appear red, green, blue or almost any other color. This invention also shows that desirable electrical properties, such as memory margin, can be maintained.

In one further embodiment hereof, these is used at least one light absorbing dielectric layer in lieu of and/or in addition to the existing dielectric material charge storage member. Preferably, the light absorbing dielectric layer is in direct contact with the phosphor. However, it is also contemplated that the light absorbing dielectric layer not be in direct contact. In still another embodiment, one or both of the substrates may be of a light absorbing material.

As used herein, color is broadly intended to include all phosphor electromagnetic output and emission in the visible range including various combinations thereof such as white light. Color is also intended as used in the sense of color television.

The practice of this invention also minimizes changes in the panel dielectric since the only material added is the phosphor. Furthermore, the phosphor may be simultaneously attached and embedded to the dielectric during the dielectric heat curing cycle without requiring any additional curing time. Also, once the phosphor particles are attached, the phosphor-dielectric bond is not sensitive to solvents, light abrasion, moisture, normal temperature changes, etc.

The following examples are intended to illustrate some of the best embodiments contemplated by the inventor in the practice of this invention.

EXAMPLE I

A soda lime glass substrate with electrodes and a cured dielectric layer (for use in a gaseous discharge device) was cleaned with alcohol and acetone.

The cured dielectric composition composition comprises by weight 15.5% SiO_2, 69.9% PbO, 12.63 B_2O_3, 1.26% Na_2O, and .59 CaO.

After cleaning (above) and drying, a photosensitive material (poly vinyl cinnamate) is sprayed onto the dielectric surface using a Model 62 spray gun from Binks Mfg. Co. under 40 lbs. of N_2 pressure. This is dried under an I.R. lamp for about 20 minutes and is then exposed to a Sylvania "Sun Gun" for about 3 minutes through a positive mask. The light struck areas of the photosensitive material become hard and are unaffected by mild solvents or heat. The substrate is then heated in an oven at about 160° C. for about 10 to 15 minutes. The dielectric is then dusted with a Zn_2SiO_4:Mn phosphor (Sylvania 160) which sticks to the heat softened-non-light struck areas of the photosensitive material. The substrate is then slowly (1–2 hours) heated to 290° C. and held for 1 hour; then it is slowly (1–2 hours) increased to about 510° C. for 6 minutes. During this time the organic photosensitive material burns off and at higher temperatures during the cycle the dielectric softens allowing the phosphor to partially sink into the dielectric surface. The total heat cycle including cool-down takes about 11 hours.

EXAMPLE II

A mixture of 1 part poly alpha methyl styrene (Dow 276–V2):1 part zinc silicate:Mg phosphor (Sylvania No. 161) is made and thoroughly mixed. A layer of this mixture is coated onto the surface of a dielectric (same as in Example I) to a uniform depth of approximately 20 mils. The dielectric substrate is put into an oven and the temperature is slowly raised to 1150° F. during which time the poly alpha methyl styrene completely pyrolizes. The

temperature is held at 1150° F. for 6 hrs. and is then cooled slowly to room temperature. The excess phosphor is blown off and the result is a thin layer of exposed phosphor particles which adhere to the dielectric and appear uniform and continuous to the naked eye.

The materials and techniques described in Examples I and II are not meant to be exhaustive. Another material other than poly alpha methyl styrene could be used as the vehicle or possibly none used at all. Another printing technique could be used, for example, screen printing or a decal method. The heat cycle used will of course depend on the substrate and dielectric. The temperature must increase such that the vehicle, if one is used, is slowly burned or vaporized away and a plateau must be incorporated at the softening point of the substrate for the length of time required for the phosphor to partially sink into the surface.

I claim:

1. In a process for manufacturing and assembling a gaseous discharge display/memory device characterized by an ionizable gaseous medium in a gas chamber formed by a pair of dielectric material members having opposed charge storage surfaces, which dielectric material members are respectively backed by an array of electrode members, the electrode members behind each dielectric material member being transversely oriented with respect to the electrode members behind the opposing dielectric material member so as to define a plurality of discrete discharge volumes constituting a discharge unit, and wherein the gas is selectively ionized within each discharge unit by operating voltages applied to the transversely oriented electrode members, the improvement wherein phosphor particles are attached to the charge storage surface of at least one dielectric member, which improvement comprises:

applying phosphor particles to at least a portion of the dielectric surface;

and then heating the dielectric to a temperature sufficient to soften the dielectric surface such that the phosphor particles sink and become partially embedded therein.

2. The process of claim **1** wherein an adhesive substance is selectively applied to the dielectric surface in order to bind the phosphor particles thereto and wherein the dielectric is heated to a temperature sufficient to burn off the adhesive substance.

3. The process of claim **2** wherein the adhesive substance is a pyrolyzable polymer.

4. The process of claim **2** wherein the adhesive substance is an organic solvent.

5. The process of claim **3** wherein the polymer is poly alpha methyl styrene and wherein the phosphor particles are mixed with the polymer prior to the applying of same to the dielectric surface.

6. The process of claim **1** wherein said heating step is carried out at atmospheric pressure.

7. A process for applying and attaching phosphor particles to a surface of at least one dielectric member to be assembled in a multiple gaseous discharge memory/display device, said surface of the dielectric member stores charged particles emitted by the gaseous discharge during each half cycle of applied alternating current to give said device a memory and the phosphor particles are partially exposed to the gaseous medium of the device and are capable of being excited by radiation from at least one gaseous discharge unit of the device, which process comprises.

applying a photosensitive material to at least a portion of the dielectric surface;

exposing a selected portion of the applied photosensitive material to appropriate radiation so as to harden the radiation exposed photosensitive material whereby subsequently applied phosphor particles will not adhere thereto;

heating the applied photosensitive material in an amount sufficient to soften that portion of the photosensitive material not exposed to radiation such that subsequently applied phosphor particles will adhere thereto;

applying phosphor particles to the dielectric surface such that a portion of the particles adhere to the softened photosensitive material;

removing non-adhered phosphor particles from the dielectric surface;

and then heating the dielectric and photosensitive material in an amount sufficient to vaporize and remove substantially all of the photosensitive material from the dielectric surface and also soften the dielectric surface such that the phosphor particles partially embed within such softened surface.

8. The process of claim **7** wherein the photosensitive material is a photopolymerizable monomer.

9. The process of claim **7** wherein the photosensitive material is a photocross-linking polymer.

10. The process of claim **7** wherein said heating step is carried out at atmospheric pressure.

11. The process of claim **7** wherein the photosensitive material is a vinyl cinnamate monomer or poly (vinyl cinnamate) polymer.

12. The process of claim **7** wherein the photosensitive material is ferric hydroxide, ferric chloride, benzoyl peroxide or benzophenone.

13. The process of claim **7** wherein the photosensitive material is a light-sensitive polymer containing recurring styryl ketone groups.

14. In a process for manufacturing and assembling a gaseous discharge display/memory device characterized by an ionizable gaseous medium in a gas chamber formed by a pair of dielectric material members having opposed charge storage surfaces, which dielectric material members are respectively backed by an array of electrode members, the electrode members behind each dielectric material member being transversely oriented with respect to the electrode members behind the opposing dielectric material member so as to define a plurality of discrete discharge volumes constituting a discharge unit, and wherein the gas is selectively ionized within each discharge unit by operating voltages applied to the transversely oriented electrode members, the improvement wherein phosphor particles are attached to the charge storage surface of at least one dielectric member, which improvement comprises:

applying a photosensitive material to at least a portion of the dielectric surface;

exposing a selected portion of the applied photosensitive material to appropriate radiation so as to harden the radiation exposed photosensitive material whereby said hardened photosensitive material is made thermally non-tackifiable and non-adhesive and subsequently applied phosphor particles will not adhere thereto;

heating the applied photosensitive material in an amount sufficient to soften that portion of the photosensitive material not exposed to radiation such that subsequently applied phosphor particles will adhere thereto;

applying phosphor particles to the dielectric surface such that a portion of the particles adhere to the softened photosensitive material;

removing non-adhered phosphor particles from the dielectric surface;

and then heating the dielectric and photosensitive material in an amount sufficient to vaporize and remove substantially all of the photosensitive material from the dielectric surface and also soften the dielectric surface such that the phosphor particles partially embed within such softened surface.

15. The process of claim **14** wherein the photosensitive material is a photopolymerizable monomer.

16. The process of claim **14** wherein the photosensitive material is a photocross-linking polymer.

17. The process of claim 14 wherein said heating step is carried out at atmospheric pressure.

18. The process of claim 14 wherein the photosensitive material is a vinyl cinnamate monomer or poly (vinyl cinnamate) polymer.

19. The process of claim 14 wherein the photosensitive material is ferric hydroxide, ferric chloride, benzoyl peroxide or benzophenone.

20. The process of claim 14 wherein the photosensitive material is a light-sensitive polymer containing recurring styryl ketone groups.

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