

Dec. 15, 1959

J. M. N. HANLET

2,917,442

METHOD OF MAKING ELECTROLUMINESCENT LAYERS

Filed Dec. 28, 1956

Fig. 1.

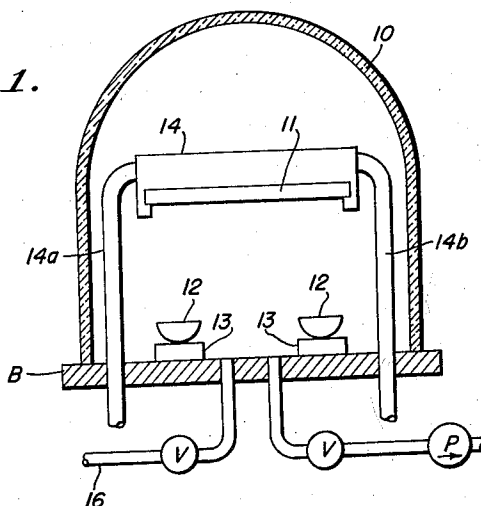


Fig. 2.

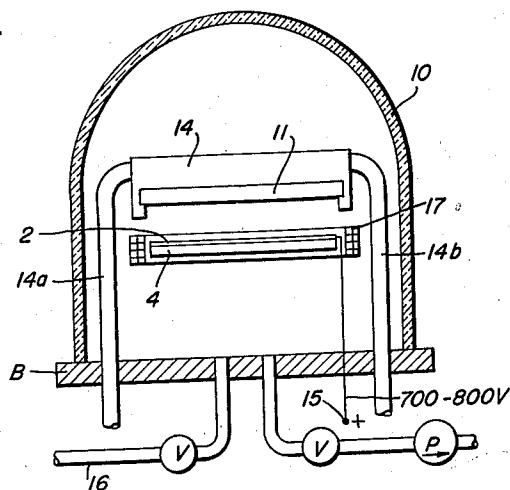
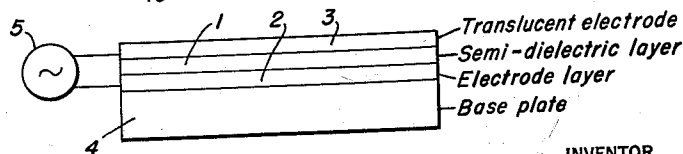


Fig. 3.



INVENTOR
JACQUES M.N. HANLET
BY *Ralph B. Stewart*
ATTORNEY

1

2,917,442

METHOD OF MAKING ELECTROLUMINESCENT LAYERS

Jacques Marie Noël Hanlet, Paris, France, assignor to Societe d'Electronique et d'Automatisme, Courbevoie, France

Application December 28, 1956, Serial No. 631,224

Claims priority, application France December 30, 1955

9 Claims. (Cl. 204—192)

The present invention relates to electroluminescent compositions for use in electro-optical converters and the like wherein they are included as semi-dielectric layers or films inserted between a pair of electrically conducting armatures, one of which at least is translucent and across which is applied an alternating electro-motive force. It is well-known that, in such compositions, two distinct materials at least are included, one of which emits electrons, when submitted to the said electric force, and thus acts as an activator for the other one of these materials which emits photons in response to the said emission of electrons from the first one.

It more particularly relates to such electroluminescent compositions which may be said to be of an all-oxide kind in that the one and the other of the said two materials, activated and activating, are constituted by oxides of metals and/or metalloids in a weight ratio not exceeding 1% of the activating material with respect to the activated material therein. Such compositions have been fully described in my copending application No. 631,226 wherein, further to a non limitative but preferred listing of the said oxides, viz. zinc, calcium, barium and cadmium oxides for the activated material and copper, lead, manganese, silver, thallium, selenium and germanium oxides for the activating material, it has been shown that an excess of free molecules of oxygen, not chemically combined with the said oxides, and introduced in the said compositions, was an important factor as concerns the efficiency thereof.

An object of the invention is to provide a new and improved method of making pellicular layers or films of such all-oxide electroluminescent compositions upon electrically conducting armatures or base plates therefor.

Another object of the invention is to provide a method such that the said layers or films are obtained as monocrystalline coatings of complexes of their component oxides.

A further object of the invention is to so provide this method so that the products resulting therefrom are totally independent of the raw materials from which they are made.

A further object of the invention is to so provide this method that the said layers or films are coated upon their armatures or base plates without any introduction of adhesive materials into the said compositions, thereby avoiding any introduction of dielectric losses in the finally obtained product other than those inhering in the composition itself.

According to the invention, a method of making an all-oxide electroluminescent coating upon an armature of an electro-optical converter comprises the steps of forming an alloy of the metals and/or metalloids of the said oxides upon an intermediary base plate, effecting a transfer of particles of the said alloy onto the said armature to form a layer thereupon, oxidizing the transferred particles and effecting the crystallisation of the oxide

2

layer resulting from the said transfer and the said oxidation.

According to the invention, further, such a method also includes a step for introducing an excess of non-metallic free molecules, e.g. oxygen molecules in the said crystalline layer.

Preferably but not necessarily, the steps of transferring part of the alloy to the said armature, oxidizing the transferred particles and effecting the crystallization of the formed coating are, partly at least, concomitant.

In the accompanying drawing Figure 1 shows apparatus for carrying out one step of the process; Figure 2 shows apparatus for carrying out another step; and Figure 3 shows the completed electroluminescent device.

The invention may be put into practice according to the following disclosure:

In a vessel 10 the atmosphere of which may be conditioned at will, for effecting the different steps leading to the final result sought herein, is first arranged a plate 11 of a material the required qualities of which will be hereinbelow determined, and for instance a plate of magnesium. The surface of this plate will be of dimensions which are substantially equal to those of the electroluminescent layer to be produced. Facing the said plate, which will later act as the intermediary alloy-supporting plate, several crucibles 12, for instance silica crucibles, are arranged in an "isotropic" pattern with respect to this plate, i.e. for instance, the said crucibles are placed at the corners of a square support facing the useful face of the said intermediary plate. The opening of each one of the said crucibles is so small with respect to the surface of the said plate that it may be considered as a point source of material. In the said crucibles are placed small loads of the metal or metalloid powders of which the oxides must be formed in the concerned electroluminescent composition to be obtained. The said crucibles may be heated by heaters 13 and the said intermediary base plate may be cooled, for instance by means of a circulation of a refrigerating fluid through a cooling jacket 14 applied to the rear face of plate 11 opposite to the face thereof exposed to the crucible openings. Jacket 14 and plate 11 are supported upon supply conduits 14a and 14b passing through base B of the jar 10.

The vessel 10 is evacuated by pump P up to a vacuum of the order of 10^{-4} and the crucibles are heated up to the temperature of thermal evaporation of the contents thereof. Obviously the evaporated products will condense upon the cool surface of the said intermediary base plate. As two distinct materials at least are placed within the crucibles, the coating which develops upon the cool surface will be an alloy of the evaporated materials. Due to the even distribution of the crucibles, this alloy coating will be of uniformly increasing thickness and in the said alloy the component materials will present a uniform distribution depending upon the opening surfaces of the crucibles wherein they are contained and/or their distribution amongst the said crucibles. The time interval during which the evaporation process is maintained obviously depends upon the required thickness of the alloy and the said thickness must be suitable for the further steps of preparation of the final electroluminescent layer.

In the said alloy coating, however, the weight proportions of the different components thereof will be controlled by the temperature of the crucibles. It is known that the weight or quantity of a metal or a metalloid which is evaporated under vacuo from a thermal process during a fixed time interval is fundamentally dependent upon the temperature applied to this material for such an evaporation. Illustratively, for instance, copper will

be evaporated at a rate of 10^{-5} gram per second per cm.² of surface of the copper "source," when copper is heated at 1000° C., but the rate of evaporation will be of 4×10^{-5} gram per second per square centimeter when the copper is heated up to 1100° C. The same will be true for any and all of the materials which have been listed hereinabove as possible components of electroluminescent compositions according to the present invention. It is consequently apparent that, for a single temperature of the crucibles, the proportions of the various component materials can be accurately controlled in the resulting alloy from a suitable provision of proportions of the relative opening surfaces of the crucibles wherein they are distributed. When, for instance, these component materials are copper and zinc, an alloy containing 0.8% of copper and the remaining percentage of zinc will be obtained when heating the crucibles at a temperature of 1100° C. The overall surface of the "Zn-source" is provided equal to one-half of the overall surface of the "Cu-source" since, at the said temperature, the rate of evaporation of the zinc is equal to 10 milligrams per second per square centimeter.

It must be noticed that, instead of putting into the crucibles, purified metallic powders, it will suffice to place into the said crucibles unpurified parcels of the said metals as the phenomenon of selective thermal evaporation will automatically eliminate any impurities in the said parcels.

The evaporation process useful for the formation of an electroluminescent film only lasts several seconds after the evaporation temperature has been reached, after which the vessel is cooled.

The material of the intermediary base plate upon which is formed the said alloy must obviously be such that it cannot enter in combination with any one of the component materials of the said alloy.

Once the vessel is cooled, there is introduced therein an armature plate 4 of suitable nature for receiving the electroluminescent coating thereon. This armature plate is supported in close proximity to the alloy coated plate and parallel thereto. A constitution of the said armature plate which is here estimated as being of special advantage is such that this plate is provided with a rhodium surface 2 prepared to present the so-called optical polish.

An atmosphere of pure oxygen is now admitted to vessel 10 through conduit 16 and is established within the vessel under a pressure which will be maintained at a constant value during the second part of the operative process. Thereafter a D.C. potential difference is applied between the alloy-bearing plate and the armature plate, with the positive pole 15 of the D.C. source to the said armature plate. The value of the said potential difference is such that the combination of said plates acts as an ionic discharge device wherein the ionic current will have a value from 70 to 100 milliamperes per square decimeter of the opposite surfaces. Such a density of the said ionic current is not critical but preferred as avoiding an overheating of the electrodes and consequently avoiding parasitic chemical reactions such as a diffusion of zinc or copper (when the said alloy consists of zinc and copper) within the material of the intermediary base plate. This material must then be so chosen as to avoid such a diffusion effect during this step of operation.

In this ionic discharge or cathodic projection process, the alloy coating acts as a cathode which emits electrons and the gaseous atmosphere ensures the formation of ions which are directed upon the said cathode and impact thereon, due to the acceleration of the gas molecules under the action of the electrostatic field established between the plates. For a suitable relative adjustment of the distance between these plates, the gas pressure within the

vessel and the value of the potential difference between the said plates the potential gradient in the neighborhood of the cathode is made very high and consequently the impacts of ions thereupon extract metal particles therefrom. These freed particles are attracted toward the anode plate and consequently the armature is progressively coated with a layer of a complex of oxides as the said particles are oxidized as soon as extracted from the alloy or even sooner due to the oxygen atmosphere established within the said vessel.

As a merely illustrative example, the spacing between the plates may be of 9 millimetres for a potential difference of the order from 700 to 800 volts D.C.

For the above example of a mixture of zinc and copper oxides, the percentage of components making up the metallic alloy on the intermediary base plate will not be changed in the thin layer resulting from the transfer and oxidation step since the zinc will be extracted from the alloy at a rate of 340 milligrams per ampere hour and the copper at a rate of 300 milligrams per amperehour. For other components, it shall be necessary to provide in the alloy a ratio of the components thereof different from the ratio required between the oxides in the finally obtained layer. Such a condition will be easily met as the values of the extraction coefficient, measured in electron-volts, are well-known for the various metals and metalloids concerned herein. When, for instance, silver is substituted for copper in the alloy, all the remaining conditions of operation remaining the same as herein above defined, the alloy which is formed on the intermediary base plate 11 during the first step will contain a quantity of silver equal to about one-half only of the corresponding quantity of copper since the rate of transfer of silver is of about 740 milligrams per ampere hour under the same conditions.

Obviously the material of the intermediary base plate must be of a rate of transfer substantially lower than the rates of transfer of the component materials in the alloy. In this respect also the use of magnesium for constituting the said base plate is quite justified, the rate of transfer of magnesium under the stated conditions being of the order of 9 milligrams per ampere hour.

The transfer operation is maintained as long as useful for the deposition upon the armature plate of the required thickness of the layer of oxides. It is for instance necessary to ensure the transfer of 0.4 milligram of the alloy consisting of zinc and copper per square centimeter of the armature plate for establishing a coating having a thickness of one micron. A suitable thickness of the electroluminescent layer will, for instance, be of the order of 10 microns. Consequently, and with a density of the current of 100 milliamperes, the transfer operation will last about seven minutes.

The advantage of making the plate armature with a rhodiated surface machined up to an optical polish may be explained as follows: the resistance to extraction of particles of this armature plate must be high; the melting temperature thereof must also be high; the optical polish of the surface is useful for a fair efficiency of the converter. Rhodium appears to be satisfactory for these three conditions, but nickel could also be used though its melting temperature and optical reflectivity coefficients are lower than those of rhodium.

The oxide coating must then be submitted to a thermal conditioning for the crystallisation thereof. This step may be operated through the means of a high frequency heater 17 surrounding the armature plate or that part of the vessel which surrounds the location of the said armature plate. Special advantage is obtained when the heat process for crystallization is made during the transfer and oxidizing operation proper, as in such a case the oxide layer will be obtained as a single crystal of a complex of oxides. A high frequency heating process does not present a substantial inertia and consequently there will be

no substantial risk of reaching a too high temperature of the armature plate.

As a specific embodiment of the above described process a magnesium base plate is placed in an evacuated bell jar. The bell jar rests on a suitable support plate. Placed on the plate support are four silica crucibles arranged one at each corner of said support plate with regard to the magnesium plate facing them. Each crucible contains an intimate mixture of powdered copper and zinc with the quantity of zinc equal to one half the quantity of copper. Each crucible is provided with a pin point opening to provide a point source of evaporated metal. The magnesium base plate is cooled by circulating a refrigerant fluid on the face opposite that exposed to the crucible openings. The crucibles are heated to 1100° C. to produce a layer of alloy containing 0.8% copper and 99.2% zinc on the base plate.

To carry out the next step of the process the bell jar is cooled and an armature plate is placed therein parallel to the base plate and 9 millimeters therefrom. The crucibles are removed. The armature plate possesses a rhodiated surface machined to an optical polish. An atmosphere of pure oxygen is maintained within the jar. A D.C. potential difference is applied between the alloy-bearing plate and the armature plate with the positive pole of the D.C. source running to said armature plate. A current density of 100 milliamperes is maintained for about seven minutes to deposit an electroluminescent mixed oxide layer of about 10 microns thickness on the armature plate by cathodic projection. To obtain crystallization of the oxide layer, the armature plate is heated by means of a high frequency heater surrounding the jar at the level of said armature plate. Heating is carried out during the entire seven minute transfer period, so as to impart a temperature to the rhodiated surface less than its melting point (about 1985° C.).

After the formation of the electroluminescent layer and the cooling of the armature plate, the other armature of the electro-optical electroluminescent converter may be made within the same vessel as used heretofore. A translucent armature of a metal such as silver or aluminum may, for instance, be formed over the electroluminescent oxide layer from an evaporation in vacuo of the said metal. This step however does not form part of the invention and the second armature of the converter can be made by any suitable process other than the above and applied elsewhere.

Referring back to the transfer operation proper, it may be stated that, when the particles of the alloy are extracted therefrom by the impacts of ions and are brought to the armature plate, the energies of the electrons of the internal orbits of the said molecules, viz. of the orbits which are the nearer to the nuclei of their atoms, are not changed at all whereas the energies of the electrons of the external orbits thereof, viz. the energies of the so-called valence electrons, are substantially modified. Under the influence of the intermolecular fields, the crystallized body behaves as a single homogeneous electronic system. The identical energy levels of the distinct molecules thereof are converted into as many levels of energy within the said body. For all the molecules therein, the quantic levels cannot comprise more than two electrons at most, and only the valence electrons act for the determination of the conductivity of the said body since only the said electrons will participate in the transfers of charges which will define the electric current through the said body. Otherwise said, in the monocrystalline layer and when an A.C. electromotive force is applied thereto, an electron can only pass from an energy level to another one when the latter presents at most a single electron; when this second energy level is previously occupied by two electrons, such a passage could not occur. Outside this normal zone which is more or less filled with electrons, there exists within the body another zone of conductivity which comprises as many quantic levels as

the said normal zone. The energy difference between these two zones is adequately small so that electrons are brought from the normal to the conductivity zone from the action of the driving field. Such a transfer of electrons would only necessitate a very small work and consequently the exchange of energy between the said zones would be quite small. It appears of advantage to provide an intermediate energy level between the said zones and this may be obtained by producing within the crystalline layer either an excess or a lack of non-metallic (or non-metalloid) atoms. When for instance an excess of atoms of oxygen is established within the copper oxide, the electrical conductivity of the said oxide will greatly increase: e.g. the introduction of 1% of oxygen in the copper oxide will multiply the conductivity thereof by a coefficient equal to 10^6 at a normal temperature. On the other hand, an excess of oxygen within the zinc oxide will appreciably reduce the conductivity thereof. A lack of oxygen atoms in the same oxides will produce corresponding opposite effects.

When the transfer and the oxidizing steps are simultaneously made, as described above, the transfer being then made within an atmosphere of pure oxygen, an excess of oxygen will be automatically obtained in the oxide layer, which is the wanted result. Of course it will be the adjustment of the pressure of the said oxygen atmosphere which will be the controlling factor of the oxygen percentage introduced into the oxide layer. But the heating process for the crystallisation of the said layer will also act upon the said introduction: the number of oxygen molecules trapped within the oxide layer will at first be quite important but, when the "baking" is made, a certain balance is established because the heat gives to the atoms of the one and/or the other of the component materials, e.g. zinc and copper, the possibility of balancing out part of these excedentary molecules from the crystal. The adjustment of the pressure of the atmosphere of oxygen and of the temperature of crystallisation of the oxides can be made such that a definite result is obtained as concerns the presence in the layer of a required percentage of free molecules of oxygen.

As said the crystallisation may be made after the oxide layer has been completely obtained. This does not change the final result of the above.

Further, the transfer operation need not be permanently made within an atmosphere of oxygen and this operation may be made with a filling of an inert gas such as argon or hydrogen. The oxidizing and crystallising steps would be postponed until after the transfer is completed.

Another manner of proceeding to the transfer operation is to introduce first an oxygen atmosphere within the vessel and apply the said D.C. potential difference across the intermediary and the armature plate; to ensure an oxidation of the surface of the alloy upon the transfer plate; and then to cut the admission of oxygen and substitute thereto an inert gas atmosphere of higher atomic weight such as argon for instance. The use of a high atomic weight gas may be considered as being of advantage for the transfer proper as it leads to a shorter time interval for the said operation because of the more efficient operation thereof in the extraction of oxide particles from the superficially oxidised alloy, but, of course, the processing or control is more elaborated due to the change of atmosphere during the formation of the oxide layer onto its supporting armature plate. The crystallisation may be made during such a transfer of particles of oxides or it may be postponed at will. In the first case, the crystal must thereafter be submitted to a diffusion process for the introduction therein of the said excess of molecules of oxygen. In the second case, the crystallisation and the introduction of the said excess of oxygen molecules into the oxide layer may be simultaneously made by heating the layer within an atmosphere of oxygen. In both cases, the pressure of the atmosphere of oxygen must be higher than the pressure adjusted for

the simultaneous operations of transfer, oxidation and crystallization which have been herein above described.

A plate of aluminum may be used, as a further substitute, as an intermediary base plate instead of magnesium.

The electroluminescent device produced according to the invention is shown in Figure 3, wherein the thin semi-dielectric layer is shown at 1, between two armatures 2 and 3. The armature 2 previously deposited on base plate 4 is formed of either rhodium or nickel, and translucent armature 3 is formed of either silver or aluminum. In operation, an alternating voltage is applied across armatures 2 and 3 from source 5.

Having thus described and ascertained my invention, I claim:

1. A method of making an electroluminescent coating of at least one activating oxide and one activated oxide upon an armature of an electro-optical converter which comprises, thermally evaporating within an evacuated vessel a mixture of materials selected from the class consisting of the metals and metalloids which are to make up said oxide coating, condensing the evaporated materials upon the surface of an intermediate base plate to form an alloy, transferring particles of said alloy to an armature by cathodic projection wherein the alloy serves as a cathode and the armature serves as an anode plate, oxidizing the transferred particles to produce an oxide coating, and heating said oxide coating to effect crystallization thereof, the quantity of activating oxide in the coating being maintained at not more than 1% of the weight of the activated oxide.

2. A method according to claim 1 wherein the quantity of activating oxide is maintained at not more than 1% of the weight of the activated oxide by proportioning the surface of evaporation of the materials with respect to their respective temperatures of evaporation.

3. A method according to claim 1 and wherein the proportioning of the component materials in the said

alloy are determined with respect to their cathodic projection rates for ensuring a predetermined composition of the transferred coating upon the said armature.

4. The process of claim 1 wherein excess uncombined oxygen is introduced into the oxide layer by conducting the ionic discharge transfer step in an atmosphere of pure oxygen.

5. The process of claim 1 wherein excess uncombined oxygen is introduced into the oxide layer by conducting the heating of the oxide coating within an atmosphere of oxygen.

6. The process of claim 1 wherein the components of the alloy are zinc and copper, and the intermediate base plate is of magnesium.

7. A method according to claim 1 wherein the cathodic projection is conducted in the absence of oxygen, and wherein the heating of the coating on the armature is conducted within an atmosphere of oxygen to produce a diffusion of free oxygen molecules into said coating.

8. A process according to claim 1 wherein said heating of the oxide coating is accomplished by high frequency heating of the armature.

9. A method according to claim 8 and wherein the armature is heated by a high frequency process during the concomitant operations of transfer and oxidation of the particles of the alloy onto the said armature.

References Cited in the file of this patent

UNITED STATES PATENTS

1,376,604	Case	May 3, 1921
1,624,071	Richardson	Apr. 12, 1927
1,982,774	Winkler et al.	Dec. 4, 1934
2,066,081	Ives	Dec. 29, 1936
2,112,975	Penning et al.	Apr. 5, 1938
2,151,457	Williams	Mar. 21, 1939
2,189,580	Hewlett	Feb. 6, 1940