Patented May 4, 1943

2,317,977

UNITED STATES PATENT OFFICE

2,317,977

LUMINESCENT COATING FOR ELECTRIC LAMPS

Ezio Thomas Casellini, Salem, Mass., assignor to Sylvania Electric Products Inc., a corporation of Massachusetts

No Drawing. Application November 24, 1939, Serial No. 305,939

1 Claim. (Cl. 117—97)

This invention relates to processes and compositions for coating the interior surfaces of hollow glass bodies, such as the envelopes of electric discharge lamps, with luminescent material.

Such material emits visible light when excited by invisible radiations, such as cathode rays or ultraviolet rays; and a coating of the proper material on the inner surface of the light-transmitting envelope of an electric discharge device enables the conversion into visible light of invisible radiations produced by the discharge. The luminescent material is generally an inorganic crystal, ground to a powder so that it may be applied to the tube; and in the finished coating the particles of the powder must not be covered by a binder which absorbs the desired exciting radiation. In practice, therefore, the coating is generally composed of the powder particles themselves, free from binder, and held to the envelope, which is generally of glass, by some peculiar adhesive action produced by the method of coating and the particle size. In a long, tubular envelope a coating uniform in arrangement of particles and in thickness from end to end of the envelope is difficult to produce, the difficulty increasing with the length of the tube and the smallness of its diameter; and yet long, tubular envelopes are necessary for certain types of discharge lamps.

An object of the present invention is a method by which such long, tubular envelopes can be uniformly coated. A further object is a method by which such a coating can be produced rapidly; and yet another object is a method by which a coating free from mottling, "comb-marks" and "taper" can be produced. A mottled coating is one composed of separate clusters of particles, rather than of uniformly-spaced, separate particles; comb-marks are longitudinal fissures in the coating which look as if a comb had been run through it; and a tapered coating is one thicker at one end than at the other, or one merely varying in thickness from point to point.

A feature of the invention is the suspension of fine, luminescent particles uniformly in a medium of low viscosity; and another feature is the application of such a suspension to the interior of the device to be coated, and drying the suspension at a controlled rate. A further feature is the use of a considerable quantity of low viscosity nitrocellulose in the suspending medium; and yet another is the use of a quick drying medium.

Other objects, advantages and features of the invention will be apparent from the following specification.

Perhaps the simplest method of coating the envelope of a discharge device with luminescent material is to suspend extremely fine particles of the material in a medium such as alcohol to apply it to the envelope, and to allow the coating to dry. For this method to be successful the particle size must be extremely small, practically of colloidal dimensions, say 0.01 micron. The grinding, or ball-milling, necessary to produce such small particles reduces their luminescent brilliancy markedly; and also produces an appreciable contamination of the powder by foreign particles worn down from the mill. Moreover, the particles tend to form separate aggregates, or clusters, and do not deposit out as separate single particles. This spoils the appearance and uniformity of the coating and reduces its brilliance, because the particles in the interior of the cluster are not excited and remain dark. The result is a mottled coating of separated clusters of particles.

I have found that the use of a suspending medium in which nitrocellulose has been dissolved eliminates the clustering of the particles, and enables a coating of spaced, separate particles to be produced, even with much larger particle sizes. I find, however, that even with nitrocellulose particle sizes larger than 20 microns or more should be particularly avoided. The particles will not generally be all of a single size, but will generally be of a number of sizes below a fixed size; I have found that a powder having an average size of 1 to 3 microns can be made free from particles of size greater than 7 microns. Powders of larger particle size will cause clumping which produces a mottled, or sandy appearance in the coating; and powders of less than 1 micron average particle size will in the case of many luminescent materials diminish greatly in brightness.

I suspend about 350 grams of the above powder, which may be, for example, a zinc silicate, manganese-activated for luminescence, in a medium of 350 cc. of acetone, 5.7 grams of one-half second viscosity nitrocellulose, and 7 cc. of dimethyl phthalate, the latter being added as a plasticizer to keep the dried nitrocellulose film from peeling off the wall of the glass tube when coated.

The greater the quantity of luminescent material in the binder, the greater will be the thickness of coating produced, other factors remaining the same. There will be an optimum thick-

ness of coating for which the light emission from the completed device will be greatest; too thin a coating or too thick a coating will give less light. If the tubing is to be bent after coating, a thickness slightly greater than the optimum will, however, be desirable, since the coating thickness may be reduced on bending. If a smaller particle size is used, the amount of powder required will be smaller. In that case, the amount of nitrocellulose required will be very much smaller; the reduction in its amount will be proportionately greater than the reduction in amount of powder.

Enough nitrocellulose must be added to the suspension to prevent aggregation or clustering of the particles. If too much is added, however, the coating will have longitudinal fissures, resembling marks made by passing a comb along the coating, in it. The amount of nitrocellulose added is thus critical; too little permits clustering, too much produces comb-marks; and the correct amount produces a smooth coating. This smoothness is much more important in a coating designed to luminesce than it is in one merely designed to reflect light. A heavier-coated spot may reflect light as well as a more lightly-coated spot, and be hardly noticeable by reflected light; but a heavier coated spot, such as a cluster of particles, in a luminescent coating would show up in marked contrast as a dark spot, since no light might be emitted from it.

The viscosity and body of the suspension should be low, to allow extremely quick draining; and yet enough nitrocellulose must be added to the mixture to reduce the interface charge of the particles enough to prevent clustering or aggregation of the particles. Accordingly, nitrocellulose of low viscosity should be used. The nitrocellulose apparently acts to change the interface charge on the suspended particles so that they will not tend to form aggregates; the viscosity of the nitrocellulose should be low enough to allow quick draining, but its exact viscosity is not as important as its quantity. That is, the number of grams of nitrocellulose may be the same, whether the half-second or quarter-second type is used.

In performing my process I place the tube to be coated vertically, and force the suspension up into the tube to the top of the latter, by providing a greater pressure on the coating liquid's surface outside the tube than inside. I may, for example, reduce the pressure in the tube, or increase the pressure on the liquid outside of the tube. When the column of coating suspension reaches the top of the tube, or the limit to which the coating is to extend, the column is allowed to drain out quickly. The main column of suspension will, of course, drain out almost instantly, due to the small viscosity; it will have wet the wall of the tubing, however, and have left a deposit of the suspension on the interior wall of the tube.

This thin layer of suspension on the wall of the tubing will drain off more slowly. Immediately after the main column of the suspension has drained out of the tube, there may be some irregularities in the coating, due to runs or turbulence. These will quickly smooth out leaving a uniform coating, but if the tube is allowed to dry before they have smoothed out, the coating will not have a uniform appearance, but may have "comb-marks" of various sizes, or other irregularities, in it. The drying must be delayed slightly until the flow of the coating has had time to smooth itself out. The drying cannot be delayed very much, however, because then a considerable portion of the liquid coating will have drained off the walls and the coating will be thinner, and may show runs due to excessive draining. For example, if the drying is delayed, by putting a cork in each end of the tube immediately after coating, the coating will eventually all run off, leaving the clear glass uncoated, and before all the coating has drained off, runs will occur in the coating; drops will form and run down.

For example, if a tube of one and one-half (1½) inches diameter and a foot or two long is coated with the suspension I have already specified, and allowed to dry by being simply left in fairly still room air at room temperature (about 20° C.) in a vertical position, the coating will have large numbers of irregularities in it, and the irregularities will vary with the distance from the top of the tube. If, however, the top of the tube is partly closed off by placing a baffle over it, the baffle having a hole of about one-quarter inch diameter, the drying will be slowed up enough to produce a uniform coating. If the tubing is completely closed off, the coating will show runs due to draining and will eventually drain off.

If the same suspension is used to coat so-called "neon sign" tubing of small diameters, say 10 to 15 mm., and about four feet long, the drying rate at room temperature in room air will be correct without closing off the top of the tube at all. The drying will start at the top of the tube, and proceed downward; and the entire length of tubing will be dry in three minutes.

The tubing is merely allowed to dry by itself, in a vertical position, without ventilation or forced draft; the acetone vapor produced by the drying will be heavier than air, and fall downward through the tube, producing an automatic gentle flow of air through the tube. Forced draft, in addition to drying the coating too fast, also tends to produce irregularities in the coating because of the turbulence due probably to non-lamellar flow. Forced draft, if used at all, must be gentle.

Accordingly, then, drying should be just slow enough to allow the coating to smooth itself out, which will generally take only a few seconds, and should not be slow enough to allow any appreciable part of the suspension, when once smoothed, to drain away. The drying will proceed gradually from top to bottom of the tubing, and must proceed rapidly enough so that the entire length of tubing, down to the bottom, has dried before any appreciable amount has drained off the surface.

For a piece of "neon-sign" tubing, 10 to 15 mm. in diameter and four feet long, complete drying takes about three minutes, with natural draft, and the suspension already described. If, however, the quick-drying acetone is replaced by the slow-drying amyl acetate, the drying will take about an hour and a half. In that case, the coating for the top inch or so of tubing, which dried first, will be fairly good, but the coating farther down will get thinner and thinner, and less regular, until we reach the bottom where there will be hardly any coating, it having drained off. Accordingly, it is seen that for small sizes of tubing, amyl acetate cannot be used, while acetone is about right.

For the larger sizes of tubing, say inch or inch and a half (25 or 40 mm.) diameter, as already pointed out, acetone is satisfactory if

the rate of drying is reduced below the natural rate in room air at room temperature (20° C.), for example, by placing a baffle with a small hole in it on top of the tube. Another way to retard the drying would be to dry the tube in an atmosphere partly saturated with acetone vapor.

A better way, however, is to use a somewhat slower drying medium, such as ethyl acetate.

The foregoing applies when the natural drying rate of the suspension used in the tube is employed. That will be the best rate generally, since it avoids any possible turbulence in the drying currents; but if a slightly forced draft is used, preferably by a slight suction at the bottom of the tube, the drying of slower-drying media, such as amyl acetate, can be speeded up so that their drying proceeds quickly enough to be finished before the tube has drained enough to alter its coating thickness. In any event, the drying should proceed at a rate slow enough so that the coating has time to flow sufficiently after the quick initial draining to smooth out any irregularities left by turbulent effects or the like, yet fast enough to dry the entire tube from top to bottom before the coating has drained enough to vary its thickness along the length of the tube.

It will be noted that if the tubes to be dried are placed vertically, the draining obviously occurs in the downward direction; and it is important that the drying also proceed in that direction. The solvent used should be one whose vapor is heavier than air, so that drying will occur downward and a stream of upwardly-directed air should never be present near the bottom of the tube, since that would dry the bottom of the tube before the coating there had drained.

A coating produced by my method will show no appreciable "taper" even on four foot long tubes, that is, the coating thickness will be substantially uniform from end to end of the tube. Some other methods will produce a "tapered" coating, thicker at one end of the bulb than the other. The use of such "tapered" coatings requires two coats of luminescent material, one coat in the reverse direction to have an opposite taper, so that the resultant of the two tapered coats will be a smaller taper in the finished tube. With my method, a single coat is sufficient: it will have no taper.

After the coating is dried, it is baked at a temperature sufficient to remove the nitrocellulose binder, by first decomposing it to a dark carbonaceous substance, and then oxidizing the latter away. A temperature of 450° may be used, for example.

There are, of course, a great number of luminescent materials of different colors. Some colors are, nonetheless, difficult to produce by the luminescent material alone, because the luminescent material may emit a wider band of colors than desired in a particular case. In that event a colored filter may, of course, be used to absorb the unwanted colors, transmitting only the colors desired. The color filter may be a layer of inorganic pigment placed between the glass envelope and the luminescent material, and may be produced by the same method used for coating with a luminescent material, the pigment replacing the latter. The envelope may first be coated with the colored layer, then with the luminescent layer. The pigment used in the filter layer is preferably of smaller particle size than that in the luminescent layer, so that the luminescent particles will not sink into the filter layer, where some of the existing light might be absorbed before reaching it. In order to insure that the pigment layer can be made sufficiently thick to at least completely cover the surface coated, and prevent non-uniformity, the pigment should be mixed with some neutral material like barium sulphate, which will not absorb ultraviolet light or the radiations used, and which will reflect any which penetrates the luminescent layer, back onto that layer, conserving the exciting radiations.

A yellow or gold lamp, for example, may be made by using a filter coating of cadmium sulphide as a pigment mixed with barium sulphate, and a layer of yellow-green luminescent material such as zinc beryllium silicate. The cadmium sulphide used should be a good grade, as some grades turn brown when heated, or on use in a lamp.

In some cases, where it is desired to excite the luminescent material by a particular type of radiation, on a particular wavelength, a filter layer may be used over the luminescent layer to absorb the unwanted portion of the exciting radiation.

What I claim is:

The method of coating with a luminescent material the interior of a long tubular discharge lamp envelope, said method comprising: placing said lamp envelope in a vertical position; flushing into said envelope a suspension of luminescent material in a vehicle comprising a quick-drying solvent and a quantity of low viscosity nitrocellulose; draining said suspention quickly from said tube; retarding the initial drying of the tube by placing a baffle over the top of the tube; and then drying the tube very quickly.

EZIO THOMAS CASELLINI.