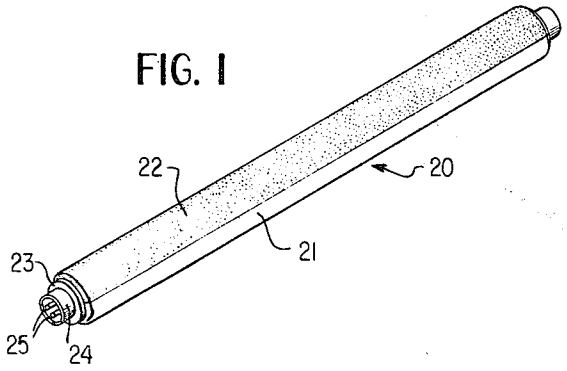
April 7, 1970 F. VERES 3,504,819

LAMP ENVELOPES

Filed Feb. 21, 1966 2 Sheets-Sheet 1

FIG. 1



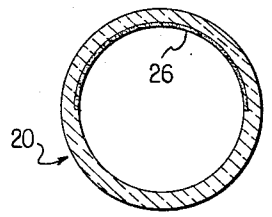


FIG. 2

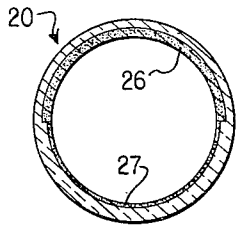


FIG. 3

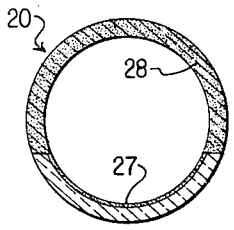


FIG. 4

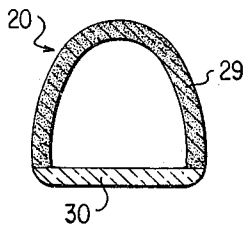


FIG. 5

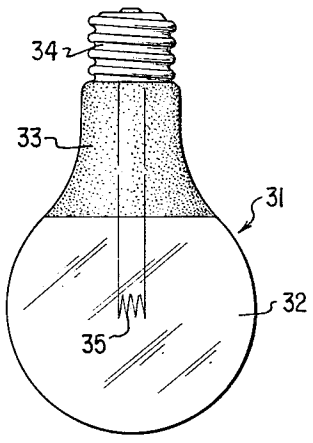


FIG. 7

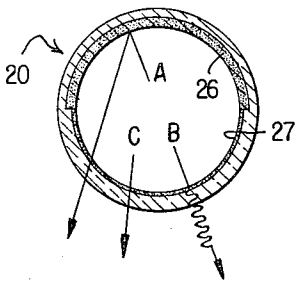


FIG. 6

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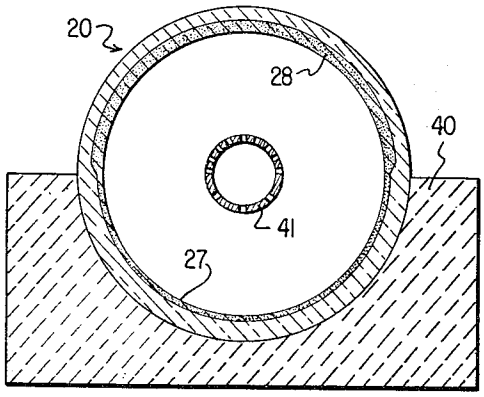

FIG. 8

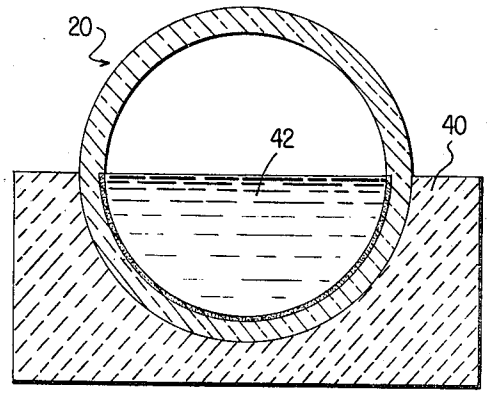

FIG. 10

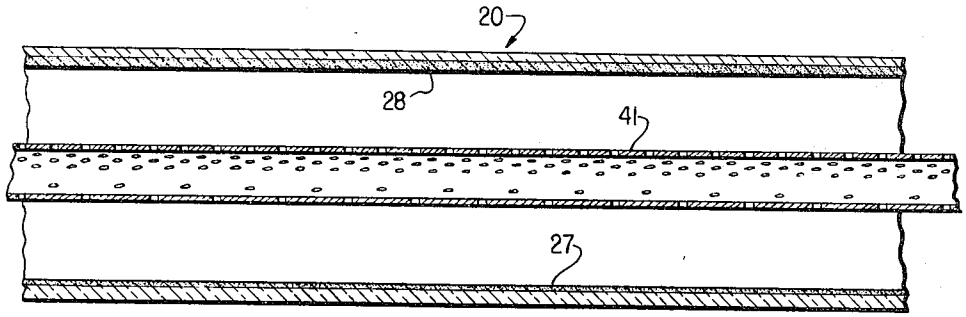

FIG. 9

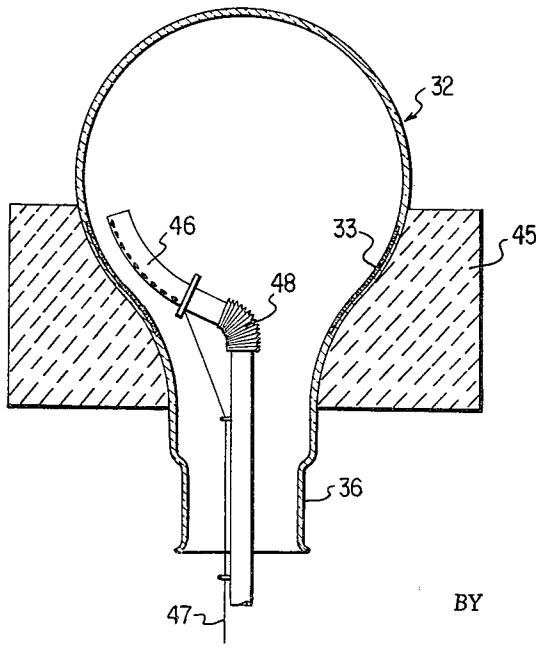

FIG. 11

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LAMP ENVELOPES

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Filed Feb. 21, 1966, Ser. No. 529,161
Int. Cl. H01k 1/28, 1/34
U.S. Cl. 220—2.1 22 Claims

ABSTRACT OF THE DISCLOSURE

Fluorescent lamp envelopes which are initially formed from thermally crystallizable glass and in which a portion of the interior surface of the envelope, such as the upper interior arcuate portion, is converted to a substantially completely reflecting thermally crystallized portion. This portion consists of finely divided crystals dispersed in a glassy matrix and reflects light. The remainder of the glass envelope, such as the lower section of the enevelope and opposite the reflecting surface, is transparent to the reflected light so that the reflected light will pass out through the walls of that portion of the enevelope which is transparent. The transparent section can be vitreous or partially crystallized.

This invention relates to improved lamp envelopes for fluorescent and incandescent lamps and, more particularly, to lamp envelopes having improved reflector means integral therewith.

The common fluorescent lamp in use today is a low pressure mercury vapor lamp having a tubular glass envelope with electrodes sealed to its ends. These electrodes include oxide coated tungsten wire cathodes which emit electrons when heated by an electric current. The envelope is filled with an ionizable noble gas, such as argon, which conducts electric current across the length of the envelope and causes mercury in the tube to vaporize. The vaporous mercury ions, also conducting electricity, emit ultraviolet radiation predominately of the wave length 2537 angstroms. In order to convert this ultraviolet radiation to visible light, the interior of the glass envelope is coated with layers of micron size phosphor particles. Generally, the interior of the glass envelope is uniformly coated so that light is emitted uniformly over the entire circumference of the envelope.

Fluorescent lamps of this type have been made into efficient sources of light in terms of total light emitted per watt input. However, efficiency measured in these terms can be misleading, especially where the light is uniformly emitted from the circumference of the envelope. To increase the useful light output, the glass envelope generally has a reflector positioned above it to downwardly direct the light emitted from the upper half of the envelope. As the reflector is positioned above the envelope the envelope itself provides an obstruction to this reflected light thereby decreasing the efficiency of the lamp. Additionally, the reflectors are usually provided with a series of openings, necessary for proper air circulation, which decrease the reflection of the light. Furthermore, in use, the upper portion of the envelope and the reflector become coated with dust which decreases the reflectivity. Periodic cleaning of the upper part of the envelope and reflector adds considerably to the expense of maintaining conventional systems of fluorescent lighting.

A recently developed type of fluorescent lamp has the appearance of being rectangular or square in shape. However, this type of fluorescent lamp, known as the labyrinth lamp, is merely a tubular glass chamber folded back and forth to give the outward appearance of a rectangle or square. The deficiencies inherent in the tubular type fluorescent lamp apply to the labyrinth lamp even to a greater extent. For example, the large cross-sectional areas of the lamp envelope is a great obstacle to light directed by the reflector positioned above the envelope.

One proposed solution to the above-discussed problems in the fluorescent lighting field is the aperture lamp which, rather than being uniformly coated with the phosphor material, has a portion of the envelope uncoated. These lamps can have a coating of a transparent reflective material positioned between the surface of the glass envelope and the phosphor coating. The purpose of the reflective coating is to aid in reflecting light from the phosphor coating back into the lamp and out through the aperture. Both the transparent high refractive index coating and the phosphor layer itself reflect light out through the aperture. The latter is most efficient; the high index reflective coating is merely an additional assist. As aperture lamps employ phosphor coatings, they are subject to the distadvantages inherent in more conventional lamps having these coatings. One of these disadvantages is the mechanical instability of phosphor coatings. A further disadvantage is that phosphor materials tend to agglomerate when applied to glass and non-uniform coatings are often formed. Still another disadvantage is a lower efficiency due to the fact that ultraviolet light photons impinging upon the uncoated, i.e., the aperture, section of the tube are converted into undesirable heat because the glass envelope per se is essentially non-photoluminescent. While the formation of heat is not serious, the loss in efficiency is significant.

In co-pending application, Ser. No. 176,412 filed Feb. 28, 1962 by Frank Veres now U.S. Patent No. 3,300,670 issued Jan. 24, 1967 to Owens-Illinois, Inc., the assignee of this application, there are described glass articles having intimately associated crystalline phosphor layers formed by the in situ crystallization of the glass surface. While articles of this type can be used to form numerous luminescent devices free from many of the disadvantages of the prior art, fluorescent lamps having envelopes described in this co-pending application still require cumbersome reflector means in order to efficiently utilize all of the light output. The reflective coatings employed in the aperture lamps described above cannot be utilized with this type of glass articles since a reflective coating cannot be positioned between the crystalline phosphor layer and the envelope wall.

Accordingly, it is an object of this invention to provide a lamp envelope free from the disadvantages inherent in presently available lamp envelopes, and in particular, to provide a lamp envelope not requiring the use of an external reflector in order to obtain maximum usage of the light output of the envelope.

Additionally, it is an object of this invention to provide a lamp envelope having an efficient reflector means integral therewith.

Furthermore, it is an object of this invention to provide an improved lamp envelope which does not require coating operations to form its reflective or phosphorescent layers.

It is a further object of the present invention to provide a lamp envelope the efficiency of which is not decreased by the accumulation of dust and dirt on its upper portion.

A still further object of this invention is to provide a method for making these improved lamp envelopes.

In attaining the objects of this invention, one feature resides in a glass lamp envelope having at least a portion of its inner surface intimately associated with a multiplicity of inorganic photoluminescent crystals. These crystals, which are formed by in situ crystallization of a portion of the glass, are of sufficient thickness and density to reflect light generated within the envelope.

Another feature of this invention resides in a glass envelope having a portion of its inner surface rendered reflective and photoluminescent by the formation of a multiplicity of inorganic crystals therein by the crystallizatioin of the glass and the remainder of its inner surface rendered photoluminescent by in situ surface crystallization of the glass to such a depth as not to seriously impair transparency.

A further feature of this invention resides in a glass lamp envelope having an arcuate upper portion and a relatively flat lower portion, the interior surface of the arcuate portion of the envelope having a multiplicity of inorganic crystals integral therewith. The presence of this multiplicity of inorganic crystals renders the arcuate portion of the envelope reflective.

Other objects, features, and advantages will be apparent from the following description of the invention and from the drawings, wherein:

FIG. 1 shows a three-quarter view of a fluorescent lamp envelope in accordance with this invention;

FIGS. 2–6 show cross-sectional views of fluorescent lamp envelopes in accordance with this invention;

FIG. 7 shows a side view of an incandescent lamp having an envelope in accordance with this invention;

FIG. 8 shows a cross-sectional view of a tubular lamp envelope being flame treated to effect surface crystallization;

FIG. 9 shows a side cross-sectional view of a tubular lamp envelope being flame treated to effect surface crystallization;

FIG. 10 shows a cross-sectional view of a tubular lamp envelope undergoing molten bath treatment to effect surface crystallization; and

FIG. 11 shows a cross-sectional view of a bulbous lamp envelope for an incandescent lamp undergoing flame treatment to effect surface crystallization.

In accordance with this invention, a lamp envelope, made of a glass which crystallizes to form photoluminescent phosphors, has a portion of its inner surface integral with a multiplicity of inorganic crystals formed by the in situ crystallization of the glass. This multiplicity of crystals reflects light generated within the envelope back into the envelope and out through the remainder of the surface which is transparent and preferably photoluminescent.

As illustrated in FIG. 1, a lamp envelope **20** has a portion **22** of its surface reflective and the remainder **21** of its surface transparent. As is conventional with fluorescent lamp envelopes, the envelope **20** is fitted at each end with an insulating plastic base **23** and a boss **24** housing contacts **25**. The surface portion **22** of lamp envelope **20** is rendered reflective by thermally in situ crystallizing the glass adjacent the inner surface to form a phosphorescent reflective crystalline layer **26** integral with the inner surface of envelope **20**, as shown in FIG. 2. These crystals are dispersed in the glassy matrix which consists essentially of the uncrystallized portion of the glass. The remaining portion of the inner surface of envelope **20** can be free of crystalline growth as shown in FIG. 2 or can have a transparent crystalline layer **27** integral therewith as shown in FIG. 3. Naturally, reflective crystalline layer **26** is substantially thicker than transparent crystalline layer **27**. Generally transparent crystalline layer **27** will have a thickness of the order of 20–100 microns while reflective crystalline layer **26** has a thickness of at least 400 microns. Additionally, as shown in FIG. 4, the major portion of the lamp envelope can be thermally in situ crystallized throughout to form reflective crystalline portion **28**.

Thus, lamp envelopes in acordance with this invention have an internal reflector which downwardly directs light generated within the envelope. As the upper half of the envelope emits little or no light, the accumulation of dust particles on it does not significantly decrease the light output. Bulky reflectors above the lamp and the attendant shortcomings of this external reflector are eliminated. In particular, air circulation above the lamp is unimpeded by the external reflector and the lamp may operate at a lower temperature and consequently at a higher efficiency. Furthermore, as the photoluminescent material is formed by in situ crystallization, the shortcomings inherent in coating photoluminescent materials onto glass envelopes are eliminated.

As illustrated in FIGS. 1–4, glass envelope **20** can be circular in cross-section. However, in the embodiment of the invention illustrated in FIG. 5, lamp envelope **20** is in the shape of a paraboloid with a relatively flat base. Thus, envelope **20** has an arcuate upper portion **29** and a relatively flat lower portion **30**. Upper portion **29**, which comprises a major portion of envelope **20**, can be thermally in situ crystallized throughout to form the reflective crystalline portion of the envelope as illustrated in FIG. 5. Alternatively, a surface layer of a multiplicity of inorganic crystals can be formed on the interior surface of arcuate portion **29** of envelope **20**. While FIG. 5 illustrates relatively flat surface **30** as being free of crystalline growth, a thin transparent crystalline layer can be formed on the interior surface of flat portion **30** to form a lamp envelope similar to that illustrated in FIGS. 3 and 4.

The transparent phosphors formed by in situ crystallization of the glass envelope are lower in luminescent efficiency than the opaque phosphors. Therefore, it is desirable to increase the area of the light reflecting opaque luminescent upper part of the envelope and to decrease the transparent luminescent area in the lower part of the envelope. The lamp envelope illustrated in FIG. 5 accomplishes this and constitutes a preferred embodiment of this invention.

As is conventional in the fluorescent lamp art lamp envelope **20** is provided with an anode and cathode and contains an ionizable inert gas, such as argon, and mercury vapor. Electrons colliding with mercury atoms in the lamp produce resonance radiation of 2537 angstroms wave lengths as at A or B in FIG. 6. The 2537 A. wave length photons incident upon the upper half of the envelope as at A are converted to visible light of 4000 to 7000 angstroms wave lengths by the luminescent crystals constituting reflective layer **26**. As layer **26** reflects visible light, the wave lengths of visible light are reflected back into envelope **20** and emerge from the envelope through transparent portion **27** thereof. The 253 A. wave length photons incident upon transparent crystalline layer **27** converted to longer wave length photons and, if directed outward, pass through the envelope. If directed inwardly, these photons will strike reflective layer **26** and be redirected back into envelope **20** to emerge from the envelope through transparent portion **27**. The small amount of longer wavelengths of light generated within envelope **20** as at C will pass through transparent portion **27** if incident thereon. Of course, these longer wavelengths will be reflected back into the envelope by layer **26** if they should strike it.

As explained above, the lamp envelopes of this invention are particularly useful in fluorescent lamps where external reflectors were previously required. However, the invention is not limited to envelopes for fluorescent lamps

and is applicable to envelopes for incandescent lamps. FIG. 7 illustrates an incandescent lamp **31** having a glass envelope **32**, a metal base **34**, and a filament **35**. A portion of the upper surface of glass envelope **32** has been thermally in situ crystallized to form a layer **33** of inorganic crystals integral with the inner surface thereof. Crystalline layer **33**, which is of sufficient thickness to be reflective, reflects the visible light radiated by filament **35**. Additionally, short wave lengths of light radiated by filament **35**, which are useless for illumination, are converted to useful longer wave lengths of light by crystalline layer **33**, which has luminescent properties.

The envelopes of this invention are formed of a glass which is thermally in situ crystallizable to form a crystalline layer which will reflect visible light. Particularly preferred glasses are those which are thermally in situ crystallizable to form phosphor crystals which when subjected to short wave lengths of radiation, such as ultraviolet radiation, emit visible light. Suitable glasses are disclosed in the above identified co-pending application and in co-pending applications Ser. Nos. 216,319 filed Aug. 13, 1962 and 216,289 filed Aug. 13, 1962, all assigned to the assignee of this application. The disclosures of these applications are relied upon and incorporated herein by reference.

One of the many types of glasses suitable for this invention is a glass broadly characterized as a zinc silicate glass. Such a glass can have a wide variation in composition as shown in Table I.

TABLE I

Constituent:	Percent by weight
SiO_2	38.1–68.5
ZnO	21.4–49.9
MnO	.1–1.9
Na_2O	0–11.7
NaF	0–5.0
Al_2O_3	0–4.8
B_2O_3	0–6.7
SnO_2	0–4.5
Li_2O	0–5.0
BeO	0–6.5
SrO	0–7.1
CaO	0–8.0
PbO	0–8.5
TiO_2	0–3.0

The zinc silicate glasses after being surface crystallized become highly luminescent and compare very favorably with commercial zinc silicate phosphores. By proper control of the thermal crystallization or heat treatment methods, it is possible to regulate the depth of the crystalline surface formations to such an extent that high luminescence is obtained with crystalline or micro-crystalline surface layers so thin that they are visibly transparent. Furthermore, by prolonging the heat treatment, crystalline surface layers of sufficient thickness to reflect visible light can be formed.

A particular advantage of the zinc silicate glasses is that very little light scattering is caused by thin crystalline zinc silicate layers. Light scattering is a function of the difference in the refractive indices of the crystals and the medium in optical contact with the crystals. With the surface crystallized glasses of this invention, an amorphous, transparent, inorganic glass is in optical contact with large areas of the in situ grown luminescent crystals. As the zinc silicate glass has a refractive index of 1.6 while the crystals have a refractive index of 1.7, only an insignificant amount of light scattering results and most of the visible light passes through the relatively thin zinc silicate crystalline layer on the bottom interior surface of the envelope. In conventionally formed phosphor layers, the individual phosphor particles are in optical contact over the greater part of the surface area of the particles with a gaseous atmosphere having a refractive index of only 1.0. The advantage described above for zinc silicate glasses may also apply to other types of surface crystallized glasses.

Notwithstanding the transparency of thin crystal layers as described above, reflectance measurements show that thicker crystal layers so formed have excellent reflectivity with respect to incident visible radiation.

By heating zinc silicate glasses in air at a temperature of 1450° F, the crystal growth achieved will luminesce yellow upon excitation with 2537 angstrom radiation. When the glass is treated at a temperature above 1450° F, the crystal growth is predominately green luminescing willemite crystals. The green luminescing willemite crystals can be formed at lower temperatures, on the order of 900° F. when the glass is heated in steam.

It is within the scope of the invention to heat treat the upper portions of the envelopes to opaque, light-reflecting, green luminescing crystals and to heat treat the lower portion to relatively transparent yellow luminescent crystals, thereby achieving a composite light output ranging from a cool to a warm white depending upon the areas luminescing green versus the area luminescing yellow.

Forming a very light coating of a commercial, particulate, red-emitting, photoluminescent phosphor on the green luminescing crystallized glass surfaces will also give a composite white light ranging from cool white to warm white depending upon the amount of red phosphor that is used.

Another glass particularly suitable for use in the lamp envelopes of this invention is a lead barium silicate glass having the composition set forth in Table II.

TABLE II

Constituent:	Percent by weight
SiO_2	23.6–43.0
PbO	23.2–43.3
BaO	19.8–39.6
MnO	0–0.25
Li_2O	0–1.6
Al_2O_3	0–4.9
Sb_2O_3	0–12.9
Au	0–0.027

The lead barium silicate glasses emit luminescent light of a character extending throughout the visible spectrum. As such, these glasses are highly desirable for use in lamp envelopes for fluorescent lamps.

Calcium tungstate glasses are also suitable for use in forming the lamp envelopes of this invention. As calcium tungstate glasses cannot be drawn into tubing, lamp envelopes of this composition are formed by pressing or casting the glass. The relative amounts of metal oxides in the calcium tungstate compositions can vary over wide ranges as shown by Table III.

TABLE III

Constituent:	Percent by weight
SiO_2	43.7–57.3
Al_2O_3	2.0–4.3
CaO	24.3–35.0
PbO	1.1–5.6
MgO	0–2.7
Na_2O	0–8.0
MnO	0–1.06
Li_2O	0–5.7
WO_3	10.6–15.5

The surface crystallized glasses having the composition of Table III, when energized with ultra-violet rays, produce a bluish white luminescence characterized by relatively rapid rate of decay following termination of excitation. In this respect, the surface crystallized glasses are very similar in properties to commercial calcium tungstate phosphors.

Zinc borate glasses are typical of another class of glasses with which the present invention may be practiced with good results. As zinc borate glasses cannot be

drawn into tubing, the lamp envelopes formed from zinc borate glasses are pressed or cast into shape. Permissible variations in the zinc borate compositions are set forth in Table IV.

TABLE IV

Constituent:	Percent by weight
SiO_2	0–7.9
B_2O_3	27.4–42.7
ZnO	49.5–64.2
MnO	0.3–1.6
Al_2O_3	0–13.0
PbO	0–2.0
Na_2O	0–1.7
F_2	0–7.1
SnO_2	0–2.6

In the preceding compositions, the percent by weight of the various constituents is calculated from the materials used to make the respective batches, that is, the calculated metal and metal oxide content in each case actually refers to the metal or metal oxide content of the raw batch constituents and assumes that associated impurities in volatile constituents such as water and carbon dioxide are eliminated. The foregoing glasses may accordingly be fabricated by mixing carbonates, borates, etc. of the various components which will decompose to the corresponding oxides during melting. For example, the calcium oxide content may be calculated from such raw mixed constituents as calcium carbonate.

While the above described glasses form crystalline layers which are light reflective and photoluminescent, it is not necessary that the glass be crystallizable to form photoluminescent phosphors. Thus, any of the well-known glass compositions which are thermally in situ crystallizable to form light reflective layers having no photoluminescent properties can be employed. Exemplary of these compositions are the glasses disclosed in U.S. Patent No. 3,117,881. Naturally, when these glasses are used, a layer of photoluminsecent material must be coated onto the interior surface of the envelope, if it is to be used in a fluorescent lamp. The coatings and techniques known to the art can be used for this purpose.

Glasses which are crystallizable to a light reflective luminescent state constitute a preferred embodiment of this invention. In addition to not requiring use of a coated phospho layer, these glasses have better reflectivity in the visible spectrum than do the non-luminescent crystallized glasses. This is because the relatively invisible wavelengths of light below 4200 angstroms incident on the crystallized luminescent surface are converted to relatively bright wavelengths of 5400 angstroms by the process of luminescence. This conversion results in a higher average light reflectivity in the visible spectrum from 4,000 to 7,000 angstroms for the crystallized luminescent materials as opposed to the non-luminescent compositions.

In general, the lamp envelopes of this invention are first shaped and then a portion of the inner surface of the envelope is heated to thermally in situ crystallize the glass adjacent the inner surface of the envelope and form a layer of photoluminescent crystals of sufficient thickness to reflect visible light. The remainder of the envelope surface is uncrystallized so as to remain transparent or crystallized to form a thin substantially transparent layer of photoluminescent crystals. Alternatively, the envelope can be formed in sections and one section thermally in situ crystallized to a reflective state prior to joining the sections to form the envelope. In an additional embodiment, the entire envelope can be thermally in situ crystallized to a reflective state and then one portion of the envelope heated to a temperature above the liquids point of the glass to render the glass amorphous and transparent.

Any of the methods disclosed in the above-identified copending application can be used to thermally in situ crystallize the glass envelope.

One method of accomplishing surface crystallization of the lamp envelope is by direct flame heat treatment of the interior surface of the envelope. Such flame treatment can be carried out by directing a gas-air, gas-oxygen or acetylene-oxygen flame onto the surface of the glass. A preferred method of flame surface crystallization is illustrated in FIGS. 8 and 9, wherein tubular glass lamp envelope **20** is supported in refractory block **40** with an elongated gas-air or gas-oxygen burner **41** disposed in the interior of envelope **20**. Differential heat input necessary to crystallize the upper half of envelope **20** to a sufficient depth to render it reflective while forming either no crystals or only a thin inner surface layer of crystals on the lower half of envelope is obtained by having a greater number of burner ports opposite portion **28** of envelope **20** than are opposite portion **27**. It is preferred that either burner **41** or envelope **20** be moved during the heat treatment so that uniformity of crystallization is obtained. Brighter photominescence is obtained if a neutral or slightly reducing flame is employed.

A further method of accomplishing crystallization of the glass surface involves the treatment of the surface of the glass lamp envelope with a molten salt or metal bath. A preferred salt bath is a mixture of calcium chloride and lithium chloride and lithium chloride, for example, 60 parts of calcium chloride and 40 parts of lithium chloride. Tin baths are also very useful. As illustrated in FIG. 10, lamp envelope **20** is supported in refractory block **40** with its interior partially filled with molten bath **42**. In order to maintain the temperature of the molten bath **42** at the desired level, induction heating coils (not shown) can be located about envelope **20**.

The particular temperature of the molten salt bath and the length of heat treatment will vary with the particular glass composition and degrees of crystallization required. It is therefore not possible to set forth a definite range of heat treatment time and temperature. When the glass has the composition SiO_2 59.5%, Na_2O 5%, NaF 5%, ZnO 26.5%, Al_2O_3 3–4% and MnO 0.25%, it has been found that a thin transparent crystalline layer can be formed on the glass surface by maintaining it in contact with molten bath having a temperature of between 1800° F. and 2000° F. for a period of 2 to 5 minutes. By maintaining this bath in contact with the lamp envelope for about 20 minutes, the interior surface of the envelope can be crystallized to a sufficient depth to render it reflective. It is preferred to maintain an inert gas atmosphere over the molten bath during the heat treatment.

Those skilled in the art will readily appreicate that the "Flame" and "Molten Bath" treatment, described above, are not limited in applicability to the treatment of tubular lamp blanks, but can be used to treat bulbous lamp blanks. For example, as illustrated in FIG. 11, an incandescent lamp blank **32** can have a portion of its interior surface **33** crystallized to a light reflective state by supporting lamp blank **32** in refractory block **45** and inserting a natural gas burner **46** through the neck portion **36** of the blank. By means of wire **47** and bellows **48**, the distance between blank **32** and burner **46** can be regulated. By rotating either burner **46** or blank **32** during the heat treatment, the entire surface portion **33** of blank **32** can be thermally in situ crystallized to a highly reflective state.

As discussed previously, the portion of the lamp envellope which is not rendered reflective can have a thin transparent layer of crystals on its inner surface. Preferably, this crystalline layer is formed by a relatively low temperature heat treatment which does not cause deformation of the glass. One method of accomplishing this is by autoclaving the envelope at an elevated temperature and a steam partial pressure above 15 p.s.i. Steam partial pressures of from 1000 to 5500 p.s.i. give good results with temperatures of at least 500° F. and no higher than 50° F. below the fiber softening point of the glass. Treatment times of from 5 minutes to 6 hours are typical. Autoclaving is followed by either flame or molten bath treatment to

form the relatively thick light reflective crystalline layer.

The following examples will point out, by way of illustration only, certain embodiments of this invention.

EXAMPLE 1

A glass having the composition SiO_2 59.5, Na_2O 5.0, NaF 5.0, ZnO 26.5, Al_2O_3 4.0, and MnO 0.25, calculated in parts by weight from the raw batch, was melted in a platinum crucible for 7 hours at 2850° F. and stirred at 60 r.p.m. with a platinum propeller during 5 of the 7 hours. The melt chamber was maintained under an atmosphere containing 1.7% uncombined oxygen. The glass melt was cooled to a temperature of 1850° F., causing its viscosity to increase and tubing was drawn.

Following this, a thin, uniform, transparent surface layer of crystals was formed on the glass tubing by autoclaving the tubing at a temperature of 900° F. and a pressure of 4000 p.s.i. for 1 hour. This layer of crystals was approximately 90 microns thick and luminesced green when excited with ultraviolet radiation.

The glass tubing was then placed in a refractory block and a gas-air burner inserted into its interior in the manner shown in FIGS. 8 and 9. The upper portion of the tubing was heated by the gas flame to a temperature of 1300° F. and maintained at this temperature for 1 hour. Heating in this manner crystallized the upper portion of the tubing throughout and rendered it reflective to visible light.

EXAMPLE 2

Glass tubing prepared in a manner identical to that of Example 1 was placed in a refractory cradle and its interior was filled about half-way with molten tin. The molten tin, which was at a temperature of 1900° F. was maintained in contact with the tubing for 20 minutes. After removal of the molten tin, it was found that a relatively thick layer of crystals had been formed on the interior surface of the glass tubing which was in contact with the tin bath. This crystalline layer reflects visible light.

EXAMPLE 3

A lamp envelope for a labyrinth fluorescent lamp was made by melting a glass composition whose theoretical oxide composition in parts by weight calculated from the raw batch was ZnO 40.18, SrO 6.98, SiO_2 44.50, Al_2O_3 3.97, Li_2O 1.50, B_2O_3 1.98 and MnO 0.64. This composition was mixed with 1% by weight of sea coal and melted at a temperature of 2400° F. for 5 hours in a melting chamber having an atmosphere containing less than 3% uncombined oxygen.

The glass was then cast on a metal slab to form a glass sheet 150 mils in thickness. This glass sheet, which is to form the upper portion of the lamp envelope, was placed over a corrugated mold, heated at a temperature of 1500° F. and caused to sag and conform to the shape of the mold. Following this, the glass sheet, still supported by the mold, was placed in an oven and heated at a temperature of 1775° F. for 2⅓ hours under an atmosphere of carbon monoxide. After the shaped glass sheet was removed from the oven and the mold removed, it was found by X-ray diffraction that the glass had crystallized throughout to willemite i.e., alpha zinc orthosilicate. The reflectivity of the crystallized glass averages in excess of 90% throughout the visible spectrum. Analysis of the luminescent emission spectrum showed symmetrical distribution of light output on either side of the peak wave lengths of emitted light which was 5250 angstroms. With a Pritchard photometer, it was determined that the luminescent brightness of the crystallized glass was equal to or slightly greater than that of a commercial phosphor plaque of willemite crystals of equivalent thickness.

Another sample of the molten glass was formed to a glass sheet 50 mils in thickness. This glass sheet was placed in a furnace which was at a temperature of 1440° F., heated at this temperature for 20 minutes and quenched in room temperature air to form substantially transparent layer of beta zinc orthosilicate about 40 microns thick on its surface. This glass sheet, which is to form the lower half of the labyrinth lamp envelope, was joined to the previously formed upper half of the envelope by placing their surfaces in contact and heating until fusion. The upper half of the envelope, which is crystallized throughout, will reflect visible light generated within the envelope back into the envelope and out through the transparent lower portion of the envelope.

EXAMPLE 4

A glass was made from a batch having the following equivalent oxide composition in parts by weight: BaO 36.4, PbO 35.2 and SiO_2 28.4. The glass batch was melted in a platinum crucible for 1 hour at 2500° F. under an ambient atmosphere. Glass tubes made from this composition were heated with a gas flame, in the manner illustrated in FIGS. 8 and 9, at a temperature of 1500° F. for 3 hours to form a relatively thick crystalline layer on one portion of the glass surface. This crystalline layer reflects visible light and converts ultra-violet light having a wave length of 2537 angstroms to visible light.

Thus, the present invention provides lamp envelopes having a layer of inorganic crystals integral with a portion of the inner surface of the envelope. This crystalline layer is of sufficient thickness to reflect visible light generated within the envelope and can also have the property of converting ultra-violet radiation to visible light. The visible light will be directed outwardly through another portion of the envelope which is transparent to visible light.

What is claimed is:

1. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass, a substantial portion of the inner surface of the envelope having a multiplicity of inorganic crystals integral therewith, said crystals formed by in situ crystallization of said portion of said glass and being of a sufficient thickness so that said portion reflects visible light, the remainder of the inner surface of the envelope being transparent to visible light.

2. The lamp envelope of claim 1 wherein said inorganic crystals are photoluminescent.

3. The lamp envelope of claim 2 wherein the remainder of the inner surface of the envelope has a multiplicity of inorganic photoluminescent crystals integral therewith, said crystals formed by in situ crystallization of a surface portion of said glass and having the characteristic of transmitting light generated within the envelope.

4. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass and having a multiplicity of inorganic crystals integral with the inner surface thereof, said crystals formed by in situ crystallization of a portion of said glass envelope and being dispersed in a glassy matrix which consists essentially of the uncrystallized portion of said glass, the thickness of said multiplicity of crystals being relatively greater in a major portion of said envelope so as to reflect the incident visible light generated within the envelope, the remaining minor portion of said surface inside said glass envelope being transparent to visible light and luminescent to ultraviolet radiation.

5. The lamp envelope of claim 4 wherein the major portion of the envelope is arcuate and the minor portion is substantially flat.

6. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass and having a multiplicity of inorganic crystals on a major portion of the inner surface thereof and dispersed throughout the glassy matrix adjacent said inner surface, said crystals formed by in situ crystallization of the surface portion and the glass matrix of any said surface, the thickness of said multiplicity of inorganic crystals on said major portion being sufficient so that visible light generated within said envelope is reflected back into the envelope and emerges from the remaining minor portion of the envelope which is transparent to visible light.

7. The lamp envelope of claim 6 wherein the major portion of the envelope is arcuate and the minor portion is substantially flat.

8. The lamp envelope of claim 6 wherein the glass is of the following composition.

Constituent:	Percent by weight
SiO_2	38.1–68.5
ZnO	21.4–49.9
MnO	.1–1.9
Na_2O	0–11.7
NaF	0–5.0
Al_2O_3	0–4.8
B_2O_3	0–6.7
SnO_2	0–4.5
Li_2O	0–5.0
BeO	0–6.5
SrO	0–7.1
CaO	0–8.0
PbO	0–8.5
TiO_2	0–3.0

9. The lamp envelope of claim 6 wherein the glass is of the following composition:

Constituent:	Percent by weight
SiO_2	23.6–43.0
PbO	23.2–43.3
BaO	19.8–39.6
MnO	0–0.25
Li_2O	0–1.6
Al_2O_3	0–4.9
Sb_2O_3	0–12.9
Au	0–0.027

10. The lamp envelope of claim 6 wherein the glass is of the following composition.

Constituent:	Percent by weight
SiO_2	43.7–57.3
Al_2O_3	2.0–4.3
CaO	24.3–35.0
PbO	1.1–5.6
MgO	0–2.7
Na_2O	0–8.0
MnO	0–1.06
Li_2O	0–5.7
WO_3	10.6–15.5

11. The lamp envelope of claim 6 wherein the glass is of the following composition:

Constituent:	Percent by weight
SiO_2	0–7.9
B_2O_3	27.4–42.7
ZnO	49.5–64.2
MnO	0.3–1.6
Al_2O_3	0–13.0
PbO	0–2.0
Na_2O	0–1.7
F_2	0–7.1
SnO_2	0–2.6

12. The lamp envelope as defined in claim 6 wherein the remaining portion of the envelope has a multiplicity of inorganic photoluminescent crystals integral with the inner surface thereof which are transparent to visible light.

13. In a fluorescent lamp including an envelope intimately associated with a phosphorescent material and containing mercury vapor, the improvement comprising material and containing mercury vapor, the improvement comprising a glass envelope formed from a thermally crystallizable glass, said envelope having a multiplicity of inorganic crystals dispersed through a glassy matrix adjacent a major portion of the inner surface of the envelope, said crystals formed by in situ crystallization of the surface portion of the glass matric beneath said surface in sufficient thickness to reflect visible light incident thereon back into said envelope, a remaining portion of the envelope being transparent to visible light so as to permit the reflected incident light to engage through the remaining portion of the envelope.

14. The fluorescent lamp as defined in claim 13 wherein the ramaining portion of the envelope has a multiplicity of inorganic photoluminescent crystals integral with the inner surface thereof.

15. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass, a substantial portion of the inner surface of the envelope having a multiplicity of inorganic crystals integral therewith, said crystals having been formed by in situ crystallization of the entire thickness of said glass envelope in said portion of said glass, so that said portion reflects visible light, the remainder of the inner surface of the glass envelope being transparent to visible light.

16. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass and having a multiplicity of inorganic crystals integral with a major portion of the inner surface thereof, said crystals having been formed by in situ thermal crystallization of said glass envelope in said major portion of said glass envelope, said crystals being dispersed in a glassy matrix which remains after the crystallization, said crystallization being throughout the thickness of said major portion of said glass envelope so as to reflect the incident visible light generated within the envelope, the remaining minor portion of said inner surface of the glass envelope being transparent to visible light and luminescent to ultraviolet radiation.

17. A lamp envelope comprising a glass envelope formed of a thermally crystallizable glass and having a multiplicity of inorganic crystals on a major portion of the inner surface thereof dispersed throughout the glassy matrix adjacent said inner surface, said crystals being formed by thermal in situ crystallization of the glass envelope, said crystallization being throughout the thickness of said portion of said glass envelope so that visible light generated within said envelope is reflected back into the envelope and emerges from the remaining minor portion of the envelope which is transparent to visible light.

18. In a fluorescent lamp including an envelope intimately associated with a phosphorescent material and containing mercury vapor, the improvement comprising a glass envelope formed from a thermally crystallizable glass, said envelope having a multiplicity of inorganic crystals dispersed through a glassy matrix adjacent a major portion of the inner surface of the envelope, said crystals formed by in situ thermal crystallization of the entire thickness of said portion of said glass envelope so as to reflect visible light incident thereon back into said envelope, the remaining portion of the envelope being transparent to visible light so as to permit the reflected incident light to emerge through the remaining portion of the envelope.

19. A method of making a glass lamp envelope which has an efficient reflector means integral therewith, a portion of the inner surface of said lamp envelope formed from a multiplicity of inorganic photoluminescent crystals by in situ crystallization of a portion of a glass which comprises shaping a glass melt to form a hollow glass body of the desired shape, said glass being thermally crystallizable and heating a substantial portion of the inner surfaces of the glass body to thermally in situ crystallize said glass throughout its entire thickness in said portion and form a multiplicity of inorganic crystals throughout its thickness in said portion so as to reflect light generated within the body, the remaining portion of said body being transparent to visible light.

20. A method of making a glass lamp envelope which has an efficient reflector means integral therewith, a portion of the inner surface of said lamp envelope formed of a multiplicity of inorganic photoluminescent crystals by in situ crystallization of a portion of the glass in a

sufficient thickness and density to reflect the light generated within the envelope, which comprises shaping a glass melt to form a hollow glass body of the desired shape, said glass being a thermally crystallizable glass and heating a substantial portion of the interior surfaces of said glass body to thermally in situ crystallize said glass and form a multiplicity of inorganic crystals integral with the surface portion in a sufficient thickness to reflect light generated within the body, the remaining portion of the interior surface of said glass body being transparent to visible light.

21. The method as defined in claim **20** wherein said surface portion is thermally in situ crystallized throughout.

22. The method as defined in claim **20** wherein the remainder of the interior surface of said glass body is heated to thermally in situ crystallize the glass adjacent the said portion and form a thin transparent layer of inorganic photoluminescent crystals integral therewith.

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