Sept. 6, 1960 N. C. BEESE 2,951,767

PHOSPHOR AND METHOD

Filed Oct. 29, 1958

FIG. 1.

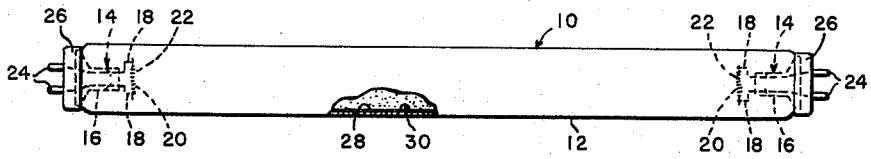


FIG. 2.

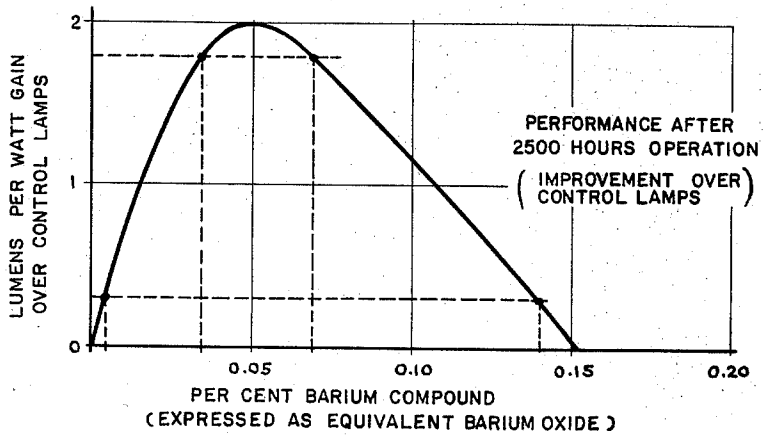
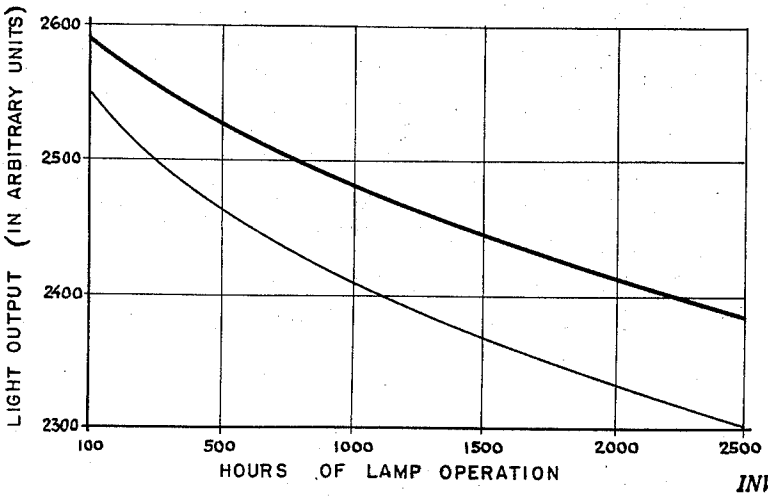


FIG. 3.



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PHOSPHOR AND METHOD

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This invention relates to fluorescent lamps and, more particularly, to phosphor material for fluorescent lamps and to methods for improving the fluorescent response of both phosphor material and fluorescent lamps.

The maintenance of the light output of fluorescent lamps (called lumen maintenance) is an important factor in measuring the performance of such lamps. In actual practice, the lumen output of a fluorescent lamp is measured at 100-hours operation, since the output during the first 100 hours is apt to vary somewhat from lamp to lamp. In the usual fluorescent lamp, the light output decreases something in the order of 4% to 5% during the first 100 hours of operation and after 500 hours of operation, the light output of an average lamp will have dropped approximately 7% to 8% from the zero-hour output. Thereafter the light output drops off more slowly.

It is the general object of this invention to avoid and overcome the foregoing and other difficulties of and objections to prior-art practices by the provision of a method for improving the lumen maintenance of fluorescent lamps.

It is another object to provide a method for stabilizing the lumen output of finely-divided phosphor material for use in fluorescent lamps.

It is a further object to provide phosphor material for use in fluorescent lamps which phosphor, when incorporated into such lamps, will display improved lumen output.

It is an additional object to provide permissible and preferred ranges for specific phosphor additive material which will improve the performance of fluorescent lamps.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by depositing onto finely-divided phosphor material selected amounts of selected barium compound. There is also provided the improved phosphor material having selected barium compound added thereto as well as a method for processing a fluorescent lamp incorporating such phosphor material.

For a better understanding of the invention reference should be had to the accompanying drawing wherein:

Fig. 1 is an elevational view, partly in section, of a fluorescent lamp having an envelope coated with phosphor in accordance with the present invention;

Fig. 2 is a graph of lamp performance wherein lumens per watt gain is plotted versus percent of barium compound (expressed as equivalent barium oxide) deposited on the phosphor of the lamp;

Fig. 3 is a graph of lamp light output versus hours of lamp operation, further illustrating the improved performance which is obtained through the use of the present invention.

With specific reference to the form of the invention illustrated in the drawing, the numeral **10** in Fig. 1 illustrates generally a 40 w. T12-type fluorescent lamp comprising a tubular vitreous envelope **12**, which is normally

fabricated of the usual soda-lime-silica glass, having mounts **14** sealed into either end thereof as is customary. Each mount comprises a vitreous portion **16** sealed to the end of the envelope **12** with lead conductors **18** sealed therethrough and supporting at their inwardly-extending extremities refractory metal coils **20**, which are fabricated of tungsten for example. These coils are normally of a coiled-coil construction or of a triple-coil construction, such constructions being well known, and contained within the turns of the inner coil or coils is a filling of electron-emitting material **22**. Such electron-emitting materials are well known and normally comprise a mixture of alkaline-earth oxides which may have other materials such as zirconia added thereto. As a specific example, the electron-emitting material comprises a mixture of 60% by weight barium oxide, 30% by weight strontium oxide and 10% by weight calcium oxide and the electron-emitting material may have an additive such as 0.9% by weight of zirconia if desired. This specific electron-emitting material is given only by way of example and many other mixtures of alkaline-earth materials or even single alkaline-earth materials can be used if desired, as is well known. Electrical connection for the lead conductors **18** is normally effected by contact pins **24** which project from the supporting base caps **26** at either end of the lamp envelope **12**.

The envelope **12** has coated on its interior surface a phosphor material **28**, which previously has had selected amounts of selected barium compound substantially evenly deposited thereon, as will be explained in detail hereinafter. The envelope also contains a small filling of argon or other inert, ionizable gas at a pressure of 4 mm., for example, in order to facilitate starting, although other starting gas fill pressures can be used, as is well known. Also contained within the envelope is a small charge of mercury **30**, as is customary. In the operation of such a lamp, the phosphor responds to the 2537 A.U. resonant radiation of the mercury discharge to produce longer wavelength radiations, as is well known.

The phosphor material can comprise any of the usual phosphors as used with a fluorescent lamp, the most-commonly used being categorized as a halophosphate phosphor. Halophosphate phosphor materials are described in U.S. Patent No. 2,488,733, dated November 22, 1949, are generally analogous to the natural mineral apatite and will display substantially the same X-ray diffraction pattern as this mineral. These halophosphate phosphor materials can be represented by the matrix $3M_3(PO_4)_2 \cdot 1M'L_2$ where L represents a halogen or mixture of halogens and M and M' represent either different or identical bivalent metals or mixtures of such metals. In practice, the primary constituent for most halophosphate phosphors is calcium orthophosphate although strontium orthophosphate is used in some limited cases. The halide constituent normally comprises calcium chloride or fluoride or strontium chloride or fluoride or mixtures of both and the activator materials are normally antimony or antimony plus manganese.

The details for preparing halophosphate phosphors are generally well known and the raw-mix constituents comprising the phosphor are normally thoroughly mixed or blended and then fired, preferably in covered crucibles, at temperatures which can vary from about 1100° C. to about 1260° C. for example, with the maximum firing temperature being determined by the hardness of the resulting fired batch. As a first specific example, 583 grams of calcium oxide are admixed with 538 grams of phosphorus pentoxide, 10.17 grams manganous carbonate, 31 grams antimony trioxide, 48 grams strontium chloride and 77.3 grams calcium fluoride. This admixture is fired at a temperature of about 1185° C. for a period

of three hours to produce what is known as a 4500° K. halophosphate phosphor. As a second example, 63.6 grams calcium oxide, 54.4 grams phosphorus pentoxide, 1.48 grams antimony trioxide and 8.92 grams calcium fluoride are admixed and fired in a covered crucible at a temperature of about 1180° C., for example, to produce a blue halophosphate phosphor. As a third example, 569 grams calcium oxide, 538 grams phosphorus pentoxide, 21.5 grams manganous carbonate, 31 grams antimony trioxide, 48 grams strontium chloride and 77.3 grams calcium fluoride are admixed and fired at a temperature of about 1190° C. for about two and one-half hours to produce what is known as a warm-white halophosphate phosphor. As a fourth example, 569 grams calcium oxide, 538 grams phosphorus pentoxide, 16.25 grams manganous carbonate, 31 grams antimony trioxide, 48 strontium chloride and 77.3 grams calcium fluoride are admixed and fired at about 1130° C. for about three hours to produce what is known in the art as a 3500° K. halophosphate. To complete the processing for the foregoing examples, the phosphors are all lightly ground after final firing to reduce them to a finely-divided status suitable for coating. The state of division of the phosphor is not critical and as an example, the finely-divided phosphor has an average particle diameter of 7 microns. Any of these specific examples or any other halophosphate-type phosphor can be first prepared and then processed in accordance with the present invention, as explained in detail hereinafter. Phosphors other than the so-called halophosphate phosphors such as zinc silicate activated by manganese can also be first prepared and then processed later as per the present invention.

In accordance with the present invention, selected amounts of selected barium compound are substantially evenly deposited on the finely-divided phosphor material after it is completely processed, desirably before the phosphor is coated onto the lamp envelope 12. These barium compounds desirably are quite soluble in liquid medium in order to facilitate their being deposited on the finely-divided phosphor in a substantially even fashion. The barium compounds found to be suitable are barium chloride, barium acetate, barium azide, barium hydroxide and barium trimethyl acetate. The latter four of these specified barium compounds are all readily convertible to barium carbonate when heated to a temperature of from 300° C. to 675° C. in the presence of carbon dioxide and moisture. It has been found that the permissible amounts of the specified barium compound which can be added, with the barium content therein expressed as equivalent barium oxide, constitutes from 0.005% to 0.14% by weight of the phosphor. The preferred amount of the specified barium compound which is added to the phosphor, with the barium content therein expressed as equivalent barium oxide, constitutes from 0.035% to 0.07% by weight of the phosphor.

As a specific example, 100 cc. of a 1.33 molar percent solution of barium acetate can be added to 400 grams of finely-divided 4500° K. halophosphate phosphor as specified hereinbefore. This mixture is stirred into a phosphor slurry which is then evaporated to dryness to produce on the finely-divided phosphor a substantially even deposit of barium acetate, wherein the barium content of the acetate, when expressed in terms of equivalent barium oxide, constitutes approximately 0.05% by weight of the phosphor. To facilitate drying, the liquid vehicle used in forming the slurry can comprise 97 cc. of ethanol and 3 cc. of water, with the barium acetate content remaining the same. Any of the other specified barium compounds can be substituted for the barium acetate in the foregoing specific example in such amount as will provide the equivalent amount of barium compound, when expressed as barium oxide. Alternatively, any of the foregoing barium compounds can be mixed in any proportions, such as equal parts by weight of barium hydroxide and barium chloride, to provide such equivalent barium oxide content as falls within the foregoing permissible or preferred ranges.

The equivalent barium compound can also be added in dry-powder form, but it is difficult from a production standpoint to obtain a substantially even deposition of the compound on the finely-divided phosphor when using such a dry-additive technique. From a production standpoint, it is desirable to add the specified barium compound in the form of a rinse, thereby eliminating the necessity for drying a substantial amount of liquid vehicle from the phosphor. With such a technique, sufficient residual barium compound can be deposited in solution form onto the finely-divided phosphor particles to provide for adequate residual barium compound after the phosphor is completely dried.

After the phosphor material has the specified barium compound deposited thereon, it is coated onto the vitreous lamp envelope in accordance with the usual techniques. To form a coating paint, any of the foregoing phosphor materials having the specified barium compound deposited thereon can be mixed with a vehicle such as butyl acetate and a small amount of binder material such as nitrocellulose. As a specific example, 200 kilograms of a 4500° K. halophosphate phosphor material having the specified barium compound deposited thereon are admixed with 75 liters of butyl acetate and 25 liters of butyl acetate having included therewith 2% by weight of nitrocellulose, with the 25 liters of butyl acetate and nitrocellulose having a number 7 Parlin cup viscosity of 65–75 seconds. This phosphor-vehicle admixture is pebble-milled to form a homogeneous suspension which constitutes the so-called paint and this paint can be further thinned if desired. The paint is then flushed over the inside of a fluorescent lamp envelope to coat same, after which the nitrocellulose binder is volatilized by lehring the coated envelope at a temperature of about 665° C. for a period of 2 or 3 minutes, for example. The lehring temperature is limited by the tendency of the vitreous envelope to deform and for the usual soda-lime-silica glass, the maximum lehring temperature should not exceed 675° C. The primary purpose of the lehring operation is to volatilize the binder material from the phosphor. During the foregoing lehring operation, the deposited nitrocellulose binder material, which amounts to about 0.05 grams for a four foot T12 lamp envelope, breaks down to form carbon dioxide and moisture and other products of decomposition and under such conditions, any of the foregoing specified barium compounds, other than barium chloride, will readily convert in the presence of such moisture and carbon dioxide to barium carbonate. The usual 40 w. T12-type fluorescent lamp will have approximately 4 to 5 grams of phosphor coated therein and the additive barium compound will be deposited in a substantially even manner on the finely-divided phosphor material.

To complete the lamp fabrication, the mounts are sealed into the ends of the vitreous envelope and the cathodes are treated by passing an electric current through the cathode coils in order to convert the alkaline-earth carbonates to oxides, as is usual. Simultaneously during cathode treating, the envelope is baked to a temperature of at least 300° C. and preferably about 450° C. in order to remove any residual traces of moisture which inherently are present. Thereafter the proper mercury charge is introduced along with the starting gas fill, the envelope is sealed off and the base caps affixed to the ends of the envelope.

As outlined hereinbefore, the specified barium compound which is added in the specified amount comprises barium chloride or barium compound which is convertible to barium carbonate at temperatures of from 300° C. to 675° C. in the presence of carbon dioxide and moisture. The carbon dioxide will always be present in small amounts, both from decomposition of the nitrocellulose binder and breakdown of the alkaline-earth carbonates to

form the electron-emissive material. Small amounts of moisture are also present at all times, because of the breakdown of the nitrocellulose binder and because of the absorption of such moisture on the surface of the phosphor, which moisture is substantially driven off during lamp baking just before the envelope is sealed. The amounts of carbon dioxide and moisture which are required to cause the very small amounts of the specified barium compound to convert to barium carbonate are in no way critical and even when lehring out the binder material, an excess of carbon dioxide and moisture will always be present over that required to effect such a conversion. These barium compounds will convert to the carbonate at temperatures considerably less than 300° C., but the lamps are required to be baked at least at this temperature to remove residual moisture and the lehring or baking temperatures cannot normally exceed 675° C. because of the tendency for deformation of the lamp envelope.

In Fig. 2 are illustrated performance characteristics after 2500 hours operation for lamps which have deposited onto the phosphor the specified barium compound such as the acetate in the specified amount. The ordinate values in the graph shown in Fig. 2 are expressed in lumens per watt gain over the control lamps which had no barium compound added thereto, but which were otherwise processed in an identical fashion. The abscissa values represent the percent of barium compound which is substantially evenly deposited onto the finely-divided phosphor material, with the percent by weight of specified barium compound expressed as a percent by weight of the phosphor in terms of equivalent barium oxide. As shown in the curve in Fig. 2, in order to have any appreciable improvement over the control lamps, the amount of additive barium compound, with the barium therein expressed as equivalent barium oxide, should constitute from 0.005% to 0.14% by weight of the phosphor. In order to obtain best output, the amount of specified additive barium compound, with the barium expressed as barium oxide, constitutes from 0.035% to 0.07% by weight of the phosphor.

In Fig. 3 is shown a graph which represents the actual performance characteristics for fluorescent lamps having added thereto the specified barium compound versus control lamps which did not incorporate the barium compound, but which were otherwise processed in an identical fashion. The improved lamps have their performance plotted as the heavy curve. The ordinate values are expressed in terms of light output in arbitrary units and the abscissa values represent hours of lamp operation. After 100-hours operation, the lamps having the specified barium compound added thereto have an increased output of approximately 1 lumen per watt. After 500 hours, the output increase is approximately 1.8 lumens per watt and after 2500 hours, the increase in output is approximately 2 lumens per watt and this latter increase continues through the life of the lamps.

The reason for the improvement which is realized through the addition of the barium compound as specified is not clearly understood. As one possible explanation, however, very thin layers of barium oxide are known to be transmissive to 2537 A.U. radiations while simultaneously acting as a filter for 1850 A.U. radiations. The phosphor materials which are used with fluorescent lamps respond primarily to 2537 A.U. radiations to generate visible light and the 1850 A.U. radiations which are generated by the mercury discharge are known to be detrimental to the phosphor. The amount of barium compound which is deposited onto the phosphor is extremely small and is sufficient to form on the phosphor a film or layer of a thickness in the order of about five angstrom units. While the specified barium compounds, other than barium chloride, are readily converted to barium carbonate during lamp processing, the energy contained in the radiations generated by the mercury discharge is sufficient to convert barium carbonate to barium oxide. Such a conversion has been proved experimentally. This theoretical explanation is substantiated by the experimental observations that only extremely limited amounts of barium compound can be utilized. The action of barium chloride, however, is not clearly understood and it is not known whether barium chloride acts as a filter for 1850 A.U. radiations or whether the very thin deposit of barium chloride is converted to barium carbonate under the conditions of lamp processing.

As another possible explanation, the barium compound may react with any sodium sulphate present in order to form barium sulfate. While sodium sulfate is detrimental to lamp performance, barium sulfate is a stable compound and will probably not react with the mercury present within the lamp, as in the case of sodium sulfate. While such a theoretical explanation encompasses all of the additive barium compounds, it does not explain why only limited amounts of barium compounds are required in order to realize the present benefits and why, if the specified limited amounts are exceeded, no increase in output is obtained. Whatever the mechanism involved, the improvements to be obtained from the specified amounts of the specified deposited barium compounds are appreciable.

In the preferred method for processing the fluorescent lamps, the specified barium compound has been deposited on the phosphor before it is coated onto the lamp envelope. This procedure is preferred from a production standpoint. It is possible, however, to deposit the barium compound on the phosphor after the phosphor has been coated onto the lamp envelope and this is readily achieved by pouring a water solution, for example, of the specified barium compound through the phosphor after it has been coated onto the lamp envelope.

It will be recognized that the objects of the invention have been achieved by providing a method for improving the lumen maintenance of fluorescent lamps and a method for stabilizing the lumen output of finely-divided phosphor material for use in fluorescent lamps. In addition, there has been provided a phosphor which will have a stabilized output as well as permissible and preferred ranges for specific phosphor additive materials which improve the performance of fluorescent lamps.

As a possible alternative embodiment any of the specified barium compounds can have admixed therewith any light-transmitting inert material such as equal parts by weight of silica, in order to disperse such barium compound in a more uniform manner. The amount of added silica is not critical. Also, while numerous examples of suitable barium compounds have been given, other barium compounds which will convert to barium carbonate under the specified conditions of temperature and atmosphere can be substituted for those barium compounds specified.

While best-known embodiments have been illustrated and described in detail, it is to be particularly understood that the invention is not limited thereto or thereby.

I claim:

1. The method of stabilizing the lumen output of finely-divided phosphor material for use in fluorescent lamps: comprising substantially evenly depositing on the phosphor material substance of at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture; and the amount of said substance deposited on the said phosphor, with the barium therein expressed as barium oxide, constituting from 0.005% to 0.14% by weight of said phosphor.

2. The method of stabilizing the lumen output of finely-divided halophoshate phosphor material for use in fluorescent lamps: comprising substantially evenly depositing on the phosphor material substance of at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temper-

atures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture; and the amount of said substance deposited on the said phosphor, with the barium therein expressed as barium oxide, constituting from 0.035% to 0.07% by weight of said phosphor.

3. The method of stabilizing the lumen output of finely-divided halophosphate phosphor material for use in fluorescent lamps, comprising substantially evenly depositing barium chloride on the phosphor material in such amount that the barium-content thereof when expressed as equivalent barium oxide constitutes from 0.005% to 0.14% by weight of said phosphor.

4. The method of stabilizing the lumen output of finely-divided halophosphate phosphor material for use in fluorescent lamps, comprising substantially evenly depositing barium acetate on the phosphor material in such amount that the barium-content thereof when expressed as equivalent barium oxide constitutes from 0.005% to 0.14% by weight of said phosphor.

5. The method of stabilizing the lumen output of finely-divided halophosphate phosphor material for use in fluorescent lamps, comprising substantially evenly depositing barium azide on the phosphor material in such amount that the barium-content thereof when expressed as equivalent barium oxide constitutes from 0.005% to 0.14% by weight of said phosphor.

6. The method of stabilizing the lumen output of finely-divided halophosphate phosphor material for use in fluorescent lamps, comprising substantially evenly depositing barium hydroxide on the phosphor material in such amount that the barium-content thereof when expressed as equivalent barium oxide constitutes from 0.005% to 0.14% by weight of said phosphor.

7. The method of stabilizing the lumen output of finely-divided halophosphate phosphor material for use in fluorescent lamps, comprising substantially evenly depositing barium trimethyl acetate on the phosphor material in such amount that the barium-content thereof when expressed as equivalent barium oxide constitutes from 0.005% to 0.14% by weight of said phosphor.

8. A phosphor material for use in fluorescent lamps, a substance substantially evenly deposited on said phosphor material, said substance selected from at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture, and the amount of said deposited substance expressed in terms of equivalent barium oxide constituting from 0.005% to 0.14% by weight of said phosphor.

9. A halophosphate phosphor material for use in fluorescent lamps, a substance deposited on said phosphor material, said substance selected from at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture, and the amount of said deposited substance expressed in terms of equivalent barium oxide constituting from 0.035% to 0.07% by weight of said phosphor.

10. The method of improving the fluorescent response of fluorescent lamps, which method comprises: substantially evenly depositing on phosphor material before incorporation into fluorescent lamps, substance comprising at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture, with the barium content of the substance in said group expressed in terms of equivalent barium oxide constituting from 0.005% to 0.14% by weight of said phosphor; coating said deposit-carrying phosphor material onto the interior surface of a fluorescent lamp vitreous envelope; and heating said phosphor-coated envelope to a temperature of from 300° C. up to the deformation temperature of said vitreous envelope in an atmosphere containing carbon dioxide and moisture while simultaneously removing any products of decomposition from the interior of said envelope.

11. The method of improving the fluorescent response of fluorescent lamps, which method comprises: substantially evenly depositing on halophosphate phosphor material before incorporation into fluorescent lamps, substance comprising at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture, with the barium content of the substance in said group expressed in terms of equivalent barium oxide constituting from 0.005% to 0.14% by weight of said phosphor; coating said deposit-carrying phosphor material onto the interior surface of a fluorescent lamp vitreous envelope; and heating said phosphor-coated envelope to a temperature of from 300° C. to 675° C. in an atmosphere containing carbon dioxide and moisture while simultaneously removing any products of decomposition from the interior of said envelope.

12. The method of improving the fluorescent response of fluorescent lamps, which method comprises: substantially evenly-depositing on halophosphate phosphor material before incorporation into fluorescent lamps, substance comprising at least one of the group consisting of barium chloride and barium compound convertible to barium carbonate at temperatures of from 300° C. to 675° C. and in the presence of carbon dioxide and moisture, with the barium content of the substance in said group expressed in terms of equivalent barium oxide constituting from 0.035% to 0.07% by weight of said phosphor; coating said deposit-carrying phosphor material onto the interior surface of a fluorescent lamp vitreous envelope; and heating said phosphor-coated envelope to a temperature of from 300° C. up to the deformation temperature of said vitreous envelope in an atmosphere containing carbon dioxide and moisture while simultaneously removing any products of decomposition from the interior of said envelope.

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