Feb. 25, 1941. T. E. FOULKE 2,232,780

LIGHT SOURCE AND METHOD OF PRODUCING THE SAME

Filed June 22, 1937

Fig. 1

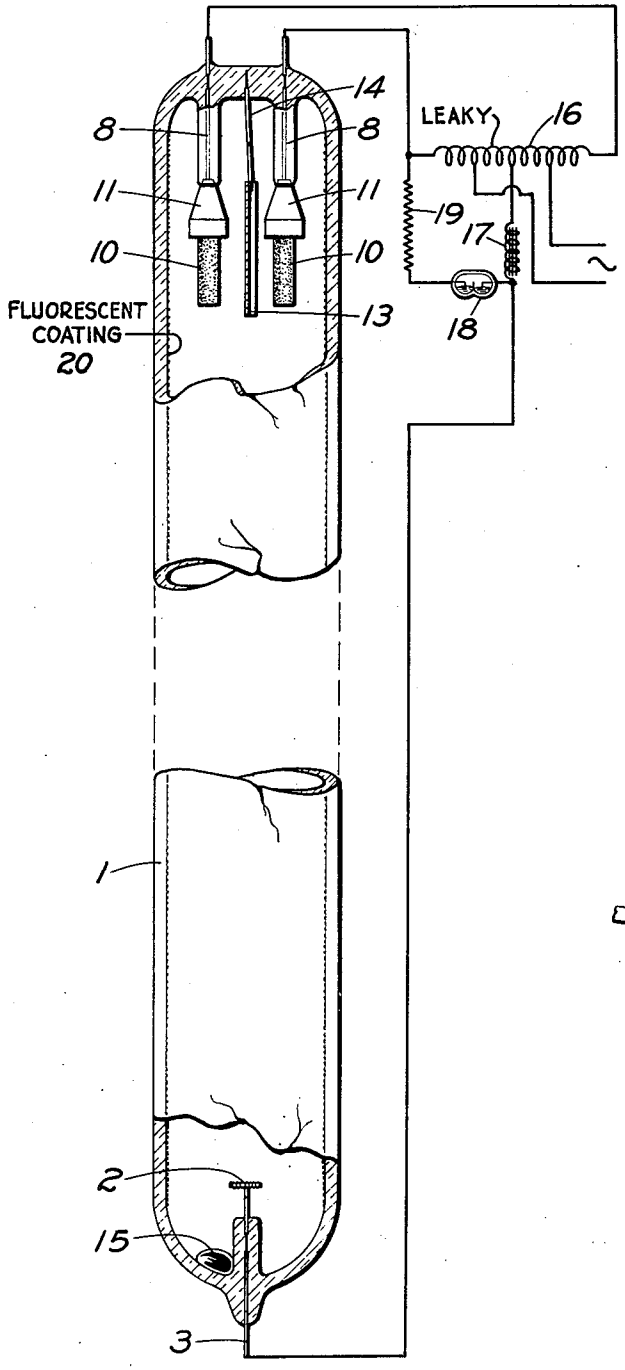


Fig. 2

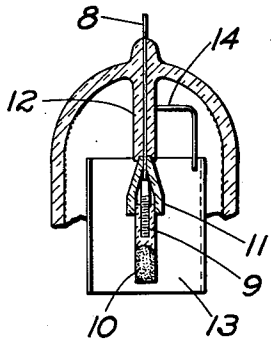


Fig. 3

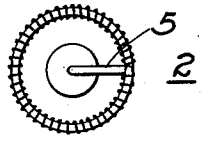
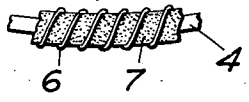


Fig. 4



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LIGHT SOURCE AND METHOD OF PRODUCING THE SAME

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3 Claims. (Cl. 176—122)

The present invention relates to electric gaseous discharge devices generally and in particular to devices producing light at least in part by luminescence.

A particular object of the invention is to provide a lamp of the electric gaseous discharge type having an extremely high efficiency. A further object is to provide a gaseous discharge device having an internal coating of a novel fluorescent material producing light which complements or modifies the light emitted by the discharge. Another object of my invention is to provide a lamp which will retain its high efficiency throughout a long useful life. Still another object of my invention is to provide novel electrodes which will function efficiently without impairing the fluorescent coating. Another object of my invention is to provide a novel and inexpensive method of producing the fluorescent material employed in my novel lamp. Still other objects and advantages of my invention will appear from the following detailed specification or from an inspection of the accompanying drawing.

The invention consists in the novel gaseous discharge device and in the new and novel composition of matter and in the novel steps of the method of producing the same, as hereinafter set forth and claimed.

In an effort to improve the luminous efficiency of electric gaseous discharge devices various suggestions have been offered from time to time for the use of fluorescent coatings within these devices. Difficulties have been encountered, however, in putting these suggestions into effect, one of the most important of these difficulties being the rapid depreciation of these fluorescent coatings when exposed to a gaseous electric discharge. I have now discovered that magnesium tungstate is extremely effective and longlived when used within a gaseous discharge device to produce fluorescent light. Thus when used within the envelope of a mercury vapor lamp, for example, this magnesium tungstate has been found to depreciate in brilliancy at an extremely low rate so that a lamp having such a coating has a useful life of many thousands of hours. The light from such a lamp is moreover extremely desirable, since it closely approximates daylight. I have further found that the efficiency of such a coating is greatly increased if additional magnesium oxide is combined therewith. Thus the best results are obtained by heating together 2.9 parts by weight of tungsten oxide (WO_3) and 1 part of magnesium oxide (MgO), this being substantially the proportions indicated by the formula Mg_2WO_5 or $2MgO.WO_3$. With either increase or decrease of this ratio of WO_3 to MgO the brilliancy of the material under a given ultra violet excitation is reduced. Thus either an increase in this ratio to 4.0 or a reduction to 2.5 reduces the brilliancy of the coating under identical excitation by substantially 25%.

I have also found that the efficiency of my novel fluorescent coating is markedly affected by the impurities present therein. Thus even small amounts (less than 0.1% of the MgO component of my novel material) of manganese, chromium, arsenic, iron, molybdenum or of most of the rare earths have been found to very materially reduce the fluorescence of this material, and hence I have found it essential to eliminate any traces of these metals therefrom. Certain other metals, however, have been found to increase the fluorescence, and particularly the response to radiations shorter than 2537 Å., and also to add other desirable characteristics to the material. Cadmium, lead, bismuth, thorium and cerium have all been found to have this favorable effect, and hence my invention further contemplates the addition of one or more of these metals in effective amounts, of the order of .05 to .5% of the MgO content of the fluorescent material.

The preparation of this fluorescent material is important if the maximum fluorescence is to be obtained therefrom, and hence the novel steps in the method of preparation thereof form a part of my invention. In this preparation I first take the purest tungstic oxide (WO_3) and magnesia (MgO) which are obtainable and then further purify them either by heating separately to a high temperature, of the order of 1200–1400° C., or by the preferred method of washing them separately in distilled water until all soluble alkalis have been removed, after which they are dried. This purification step is important, since thereupon depends the attainment of the greatest fluorescence from the resulting product, the alkali metals being particularly objectionable in my novel fluorescent material, since they limit the temperature at which the mass can be fired without hard sintering, with attendant loss of fluorescent efficiency, and also tend to produce a more crystalline powder, with still further loss in efficiency upon pulverization. The tungstic oxide and the magnesia are then mixed, preferably in the proportion of 2.9 parts by weight of WO_3 to 1 part of MgO, this being substantially in the proportion of one molecule of WO_3 to two molecules of MgO, as indicated by the formula Mg_2WO_5. Care is taken during this mixing to

produce an intimate mixture without contaminating the mixture with particles from the container. Thus in particular any hard grinding with mortar and pestle is especially avoided. When thoroughly mixed a little distilled water is added to form a paste, and the desired impurities, such as cadmium, bismuth, lead, thorium and cerium, are also added at this time, preferably as nitrates or other easily decomposed compound. These additions are made in such proportions that the metal component thereof is from .05 to .5% of the MgO, or from .013 to .13% of the Mg_2WO_5, since these proportions have been found to give an exceptionally high fluorescent efficiency in the resulting product, the cadmium and bismuth being especially effective in this respect. The addition of any of these impurities has been further found to have another effect on the resulting product, in that they produce a soft flocculent powder which has many advantages over the coarser structure otherwise obtained by oven treatment. Thus first of all this powder is so soft that the usual loss in fluorescent efficiency which is well known to accompany ball-milling is entirely avoided. Furthermore the covering power of this powder is exceptionally high, since due to the flocculent nature thereof it provides a tenacious even film with about one eighth of the material that is required to produce a satisfactory coating with coarse crystalline material. The depreciation of this coating when exposed to a gaseous discharge has furthermore been found to be less than that obtained with a more crystalline coating. It may be noted that the production of this soft powder is further facilitated by the initial choice of tungstic oxide of a low density or bulky type which is available on the market.

The pasty mixture thus produced is then dried at a temperature of the order of 150° C., a reaction thereupon occurring which changes the color of the mixture from yellow to white, this heating being continued until the reaction appears complete, as denoted by the change in color. At this stage the resulting mixture has no fluorescence.

The mixture is then placed in a furnace when it is slowly raised over a half-hour period to a temperature of approximately 850 to 900° C., and then maintained at this temperature for about a half hour, whereupon the material becomes highly fluorescent. The temperature attained in this heating is not highly critical, the essential feature being to keep it well below 1000° C., since at this temperature undesired changes occur which materially reduce the fluorescent efficiency of the resulting product, unless there has been an exceptionally perfect intermixture of the component parts beyond that usually attained. After this heating the mixture is allowed to cool and is then powdered, this requiring little pressure due to the softness of the material, so that there is virtually no loss in fluorescence.

In some cases, where it is desired to eliminate the addition of the impurities mentioned hereinbefore the MgO and the WO_3 are mixed with distilled water and boiled together until the reaction is complete, as denoted by the loss of the original yellow color. The mixture thus produced is also flocculent and has been found to have many of the characteristics of that prepared in the preferred way described hereinbefore.

The mixture produced in either of the foregoing ways is then put in a furnace and the temperature slowly increased for about an hour to approximately 1250° C., and then slowly cooled over a period of a half hour to approximately 1000° C. The powder is then removed from the furnace and is ready for use without further treatment.

Due to the extreme fineness of my novel material it is easily made into a paint which is flowed over the surface which it is desired to coat. Thus I prefer to mix 30 grams of the foregoing fluorescent material with 100 c. c. of amyl acetate, 50 c. c. of butyl acetate and 2 grams of relatively high viscosity nitrocellulose. his mixture is then ball milled, using glass marbles, for about 16 hours in order to produce a suspension of the fluorescent material in the vehicle. A surface is then coated with this paint and checked for light transmission against a desired standard, after which it is usually diluted further by similar relative proportions of the amyl acetate, butyl acetate and nitrocellulose until a desired density of coating is produced. In practice I find that a good coating is obtained with a dilution of the order of .2 gm. to .16 gm. of the magnesium tungstate per c. c. of the mixture.

The use of a mixture of butyl acetate and amyl acetate, as described above, has been found to be exceptionally desirable, since this mixture gives a uniformly smooth coating when flowed through a relatively long tube, for example, which firmly adheres to the glass wall thereof in the subsequent treatment thereof, as described hereinafter, a result which is not attainable with the use of either of these solvents separately.

The foregoing mixture is flowed over the surface which it is desired to coat, dried and baked. In the case of tubes for gaseous discharge lamps and the like this is easily accomplished by filling the tube with the mixture, draining thoroughly, and then allowing the adherent coating which remains to dry in air at room temperature, after which the tubing is baked at approximately 500° C. for say twenty minutes, air preferably being allowed to pass through the tubes during this baking period. The preliminary drying period allows the acetates to vaporize, of course, while the subsequent baking decomposes the nitrocellulose and drives it off as volatile gases, leaving only a thin film of the fluorescent material on the inner surface of the glass tube. This film, due to the flocculence and fineness of the material, is extremely adherent, despite the removal of the binder and successfully withstands all shocks which the tube may sustain in handling and shipment, although it may be removed where desired by abrasion.

While in the foregoing reference has been made only to the production of a magnesium tungstate fluorescent material, I have also discovered that zinc tungstate is likewise increased in fluorescent brilliancy if treated in the same manner. In this case, of course, the proportionate weights of the ZnO and the WO_3 are different, but the molecular proportions are the same as described for the MgO and WO_3, that is, for the most efficient coating these elements of the coating are mixed in substantially the proportion of two molecules of ZnO to one molecule of WO_3. The preferred treatment of this mixture is identical with that described hereinbefore for the magnesium coating.

I have further found that with these fluorescent coatings the internal diameter of the arc tube is critical for maximum efficiency. This is due to the fact that a magnesium tungstate coat-

ing, especially when prepared in my novel manner, differs sharply from most other fluorescent compounds in its response to radiations of wavelengths shorter than 2537 Å. U. Thus whereas most of these compounds are excited most efficiently by radiations of 2537 Å. U. with little response to shorter wavelengths my novel magnesium tungstate coating is very efficiently excited by radiations of the order of 1200–3100 Å. U., especially when the described impurities are used. I have found that as a result of this different characteristic these fluorescent materials are most efficient when used in an arc tube of larger diameter than is desirable with the fluorescent materials which have heretofore been used. Thus I have discovered that with arc tubes of varying diameter internally coated with my novel magnesium tungstate, the efficiency varies markedly with the diameter. For example, with a one ampere discharge in mercury vapor flowing therethrough, this efficiency increases rapidly as the tube diameter is increased from less than 25 to more than 66 lumens per watt and then with further increase in diameter rapidly decreases to the order of 49, the peak occurring with an internal tube diameter of approximately 1.1 inches. With lower currents the maximum efficiency is increased, reaching more than 74 lumens per watt at .2 ampere, but the peak occurs at substantially the same tube diameter. Either an increase or a decrease of .10 inch in this diameter produces a very substantial lessening in the luminous efficiency of the device. As a further result of this different absorption characteristic of my novel fluorescent material I have found that I can operate a mercury vapor lamp coated therewith with considerably higher currents than has heretofore been possible without serious impairment of the luminous efficiency. Even with currents four or five times as large as those which could be efficiently used with the luminescent materials heretofore used the shift in energy from the 2537 Å. U. line to longer wavelengths, which is typical with such an increase in current in a mercury vapor arc, does not produce any marked reduction in the luminous efficiency of my novel device, this efficiency remaining at an extremely high level.

The cathodes which are used in my novel lamp have also been found to be of paramount importance. Thus most of the thermionic cathodes which have been tried have been found to produce considerable blackening of the arc tube. While this is a disadvantage in any device, the situation is particularly aggravated with my novel fluorescent coatings for several reasons. The most important of these is the fact that the black deposits produced by these cathodes on the arc tube are far more opaque to the ultraviolet radiations which excite the fluorescent coating than they are to visible radiations, so that a deposit which would cause only a slight depreciation in the luminous efficiency of an ordinary gaseous discharge device causes a serious decrease in the light emitted by the fluorescent coating in my novel discharge device. Furthermore these deposits are far more noticeable on my fluorescent coating, and produce a decidedly objectionable appearance. I have now found that this difficulty is entirely elminated by use of a novel cathode of my invention. This novel cathode, which comprises a tungsten loop on which there is loosely mounted a tungsten helix with a sintered mixture of alkaline earth compounds filling the interstices therebetween has been found to give good starting, long life and exceptional freedom from tube discoloration. I have found that by making the tungsten helix of very fine wire, of the order of 3 mils, and by spacing the turns by three or four wire diameters this new electrode will allow an arc to be initiated and maintained at a very low current. This makes this cathode especially desirable in my novel lamp, where the arc currents are preferably maintained at an ampere or less in order to obtain an efficient response of the fluorescent material. The nature and the proportions of the alkaline earth compounds employed in this cathode have also been found to be extremely important, affecting both the blackening of the arc tube and the rate of deactivation of the cathode. I have now found that a mixture of substantially 2.1 parts of barium oxide with 1.0 part by weight of calcium oxide produces a highly active surface which has a long useful life. I have further found that the binder used to retain this active material on the electrode is highly important, since this binder affects both the life of the cathode and the amount of tube blackening produced thereby. Thus I have found that the addition of a small quantity of barium silicate, say .53 part by weight of the calcium oxide to the foregoing mixture sinters the mass together upon heating and produces a cathode which not only has an extremely long life but which also virtually eliminates the migratory blackening throughout the tube which is characteristic with other binders which have been tried. In some cases a partial substitution of calcium silicate for the barium silicate has been found to produce very desirable results, although a complete substitution is undesirable, since extensive tube blackening of a migratory nature then results.

The anode structure in those lamps which are intended for use in a self-rectifying alternating current circuit, is also highly important. Thus when the anodes were placed near each other at one end of the arc tube serious short circuit arcing occurred between the anodes which soon destroyed the lamp. I have now found that this difficulty is eliminated by so designing the anodes that every portion thereof which is exposed to the gaseous atmosphere is also exposed to direct radiations from the discharge. According to my invention these anodes have the back thereof carefully shielded with insulating material, and they are also in some cases made with a slight taper away from the path of the discharge, whereby it is made more certain that radiations from the discharge will impinge upon every exposed point on said anodes. A baffle of metal or the like is also preferably positioned between said anodes since this has been found to materially decrease the blackening produced in the vicinity of the anodes.

For the purpose of illustrating my invention I have shown a preferred embodiment thereof in the accompanying drawing, in which

Fig. 1 is an elevational view in part section of my novel lamp, together with a schematic diagram of the operating circuit therefor,

Fig. 2 is a sectional view through one of the anodes of Fig. 1,

Fig. 3 is an enlarged plan view of the cathode shown in Fig. 1, and

Fig. 4 is a greatly enlarged view of a part of the cathode of Fig. 3.

As shown in this drawing, my novel gaseous electric discharge device has a tubular sealed envelope 1 of glass or the like of any suitable length,

usually of the order of forty to fifty inches. A cathode 2 is supported on an inlead 3 which is sealed into one end of said tube through a conventional pinch seal.

As best shown in Figs. 3 and 4 this cathode consists of a tungsten core 4 which is bent into a loop and welded to form a short circuited turn, with the end 5 thereof extending inwardly and down to a welded connection with the inlead 3. Said core 4 is preferably made of tungsten wire of the order of 12 mils in diameter and in practice is formed into one or more loops approximately one-fourth inch in diameter. Around this core there is a helix 6 of tungsten wire of the order of 3 mils in diameter and preferably wound with of the order of 60 turns per inch, so that there is approximately four wire diameters between each turn. In addition this helix 6 is preformed on a mandrel 25 mils in diameter, so that there is approximately two wire diameters of the helix 6 between the turns thereof and said core. The space between said core 4 and helix 6 is filled with a coating 7 comprising a mixture of alkaline earth compounds.

The particular compounds employed for this coating and the relative proportions thereof have been found to be quite critical, if good starting and long life are to be attained without tube blackening, especially of the migrating type which moves from point to point within the tube during operation. I have found that the best results are obtained by mixing together 60 parts by weight of barium carbonate, 40 parts of calcium carbonate, and 12 parts of barium silicate. Enough water is added to this mixture to form a paste which is applied to the cathode in such a fashion as to fill the interstices between the core 4 and the helix 6, as described hereinbefore. This cathode coating is then dried in air and the assembly sealed into the lamp envelope 1.

At the opposite end of the envelope 1 there are sealed in a pair of inleads 8 through a suitable seal, to the inner end of each of which there is welded a threaded member 9. On each of these members 9 there is screwed an anode 10 of graphite or other suitable material. These anodes as shown are cylindrical with a diameter of the order of $\frac{3}{32}$ inch and a length of about $\frac{5}{8}$", but in some cases these anodes are made slightly tapered with the larger end toward the seal whereby no shadow will be cast on any part of this anode by another portion thereof if it chances to be slightly tilted on its lead during the sealing-in process. The end of each anode which is away from the discharge is enclosed within a refractory body 11 of lavite or the like having a socket which closely fits the anode for a short distance from the end thereof, and which also encloses the exposed end of the threaded member 9, the inlead 8 passing through a suitable opening in the end of said refractory body 11. In sealing in the inleads 8 they are carefully beaded with glass or other insulating material 12 from the seal to the refractory body 11, said bead preferably being fused to the end of said refractory body, as shown. A baffle 13 of sheet nickel or the like which extends between the anodes 10 is supported by a wire 14 which is fused into the same pinch seal as the inleads 8.

The tube 1 is coated internally with the fluorescent material 20 which has been described hereinbefore. This consists of MgO and WO_3 in substantially the proportions required by the formula Mg_2WO_5, preferably with the addition of the oxide of cadmium, bismuth, lead, thorium, or cerium in such proportion that the metal content of this oxide constitutes from .05 to .5% of the MgO present. This coating, which is applied in the manner described hereinbefore, appears white and offers little obstruction to the visible radiations emitted by the discharge within the tube 1. This coating is strongly adherent to the walls of the tube 1, so that it will not separate therefrom under ordinary conditions of shipment or use, but is readily scraped therefrom at the points where vitreous fusion is necessary in the fabrication of the lamp, so that it does not interfere with the perfect fusion of the inleads and the like. This coating transforms the ultraviolet radiations emitted by the discharge into visible radiations which supplement the visible radiations from the discharge to produce a close simulation of white light.

In the case illustrated the tube 1 is preferably approximately 1.1 inches in internal diameter, and is substantially 50 inches long between electrodes.

The lamp thus fabricated is then connected to an exhaust system and heated to 430° C. The oven temperature is then increased to 530° C. in order to drive water vapor out of the walls of the tubing, carefully dried air or other inert gas being admitted to the tube during this final heating to prevent collapse of the walls. This step is highly important, since where water vapor is left in the tube wall or coating which can be released during operation of the discharge a peculiar whirling of the discharge about the arc tube occurs, and the mercury vapor also varies in density along the arc tube after continued operation, due to the well known phenomenon of "pumping," giving a considerable diminution in the light emitted toward the anode end of the arc tube. Both of these difficulties are eliminated by the foregoing step of heating the lamp to 530° C. The lamp is then allowed to cool to 430° C., and is then again evacuated, the lamp being maintained at a temperature of from 420–430° C. until the pressure within the lamp is finally reduced to the order of a few microns. This entire pumping and heating procedure ordinarily requires from 20 to 30 minutes.

The anodes are then heated up in a high frequency field to degas them, after which the cathode is heated in a similar manner, first to a temperature of the order of 1200–1300° C., at which temperature the carbonates decompose to the oxide with the evolution of gas, then further to a temperature of approximately 1700° C., whereupon the silicate fuses, followed by a final heating to a temperature of the order of 1800–2000° C. to complete the sintering of the cathode activating materials.

A small quantity 15 of mercury, equal to or slightly in excess of that which will be vaporized under the designed operating conditions, is then distilled into the tube and argon at a pressure of the order of 1–3 mm. of mercury admitted, and the lamp sealed off. The lamp is thereupon operated at designed current for about 5 minutes, and then with about 4 times the normal operating current for about 10 minutes in order to activate the cathode. In some cases this so-called "arcing" of the cathode is done before the lamp is sealed off from the system, in which case the argon content may be removed if desired, and a fresh supply admitted after the arcing is complete.

A preferred operating circuit for this lamp, which closely parallels the usual Cooper-Hewitt

circuit, is shown schematically in Fig. 1, the inleads 8 being connected to the ends of a leaky auto-transformer 16, while the inlead 3 is connected to the midpoint thereof through an inductance 17. A conventional shifter 18 is connected in series with resistance 19 between one end of said auto-transformer and the end of said inductance which is connected to the cathode inlead 3. A suitable connection to an alternating current source is, of course, provided for said auto-transformer. With this arrangement, using a 50 inch arc tube, the voltage across the anodes 10 before a discharge is started is about 400, this voltage dropping to about 260 as soon as the discharge has stabilized at equilibrium condition, the direct current voltage between the anodes 10 and the cathode 2 then being about 90 volts with a rectified direct current of approximately .9 ampere flowing from the anodes to the cathode. Under these conditions the input to the auto-transformer 16 is substantially 100 watts with an overall efficiency of better than 50 lumens per watt.

While I have illustrated my invention by reference to a particular lamp, it is to be understood that it is not limited thereto, but may also be used with gaseous discharge lamps of any type, for use on either A. C. or D. C., and that various omissions, substitutions and changes, within the scope of the appended claims, may be made therein without departing from the spirit of my invention.

I claim as my invention:

1. An electric gaseous discharge lamp comprising a sealed envelope containing a plurality of electrodes, a gaseous atmosphere therein which is capable of emitting ultraviolet radiations when excited, and an internal coating of a fluorescent material on said envelope, said coating comprising MgO and WO_3 in substantially the proportions indicated by the formula Mg_2WO_5, said tubing having an internal diameter of substantially 1.1 inches.

2. An electric gaseous discharge device comprising a sealed envelope containing a plurality of electrodes, at least one of which is an activated thermionic cathode comprising a core of refractory metal loosely overlaid with a helix of refractory metal wire and having the interstices therebetween filled with a sintered mixture of substantially 2.1 parts by weight of barium oxide, 1.0 part of calcium oxide and .53 part of barium silicate.

3. An electric gaseous discharge device comprising a sealed tubular envelope containing a gaseous atmosphere and having a cathode at one end thereof and a plurality of anodes at the other end thereof, each of said anodes having every portion thereof from which a straight line cannot be drawn to a point on the discharge path between either of said anodes and said cathode without passing through said anode covered with an insulating material, and a baffle between said anodes.

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