Jan. 16, 1968 L. V. McCARTY 3,364,375

METAL VAPOR LAMP THORIUM COATED ELECTRODE

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FIG. 1

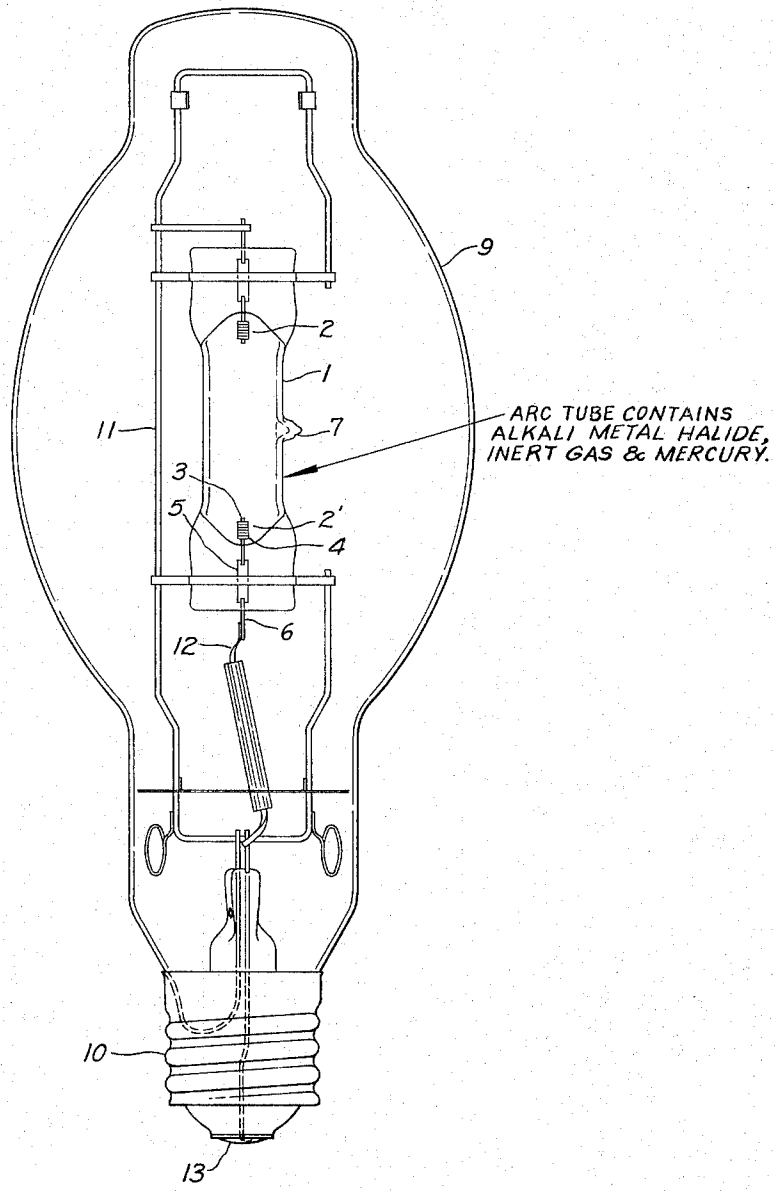
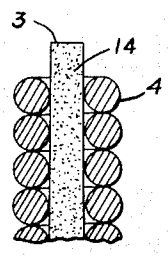


FIG. 2



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METAL VAPOR LAMP THORIUM COATED ELECTRODE

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This invention relates to metallic vapor lamps using an arc discharge in mercury and metal halide vapors to produce visible light, and is more particularly concerned with the electrodes.

The mercury arc lamp has a long life and reasonably good efficiency but relatively poor color rendition due to the bluish-green quality of its light. A radical improvement in both color rendition and efficiency may be achieved by adding to the mercury one or more vaporizable metal halides under proper control of loading, temperature and pressure, the preferred metal halide additive being sodium iodide, optionally with thallium iodide. Such improved lamps are described and claimed in Letters Patent 3,234,421 issued to Gilbert H. Reiling, on Feb. 8, 1966, entitled Metallic Halide Discharge Lamps and assigned to the same assignee as the present invention. For convenience, such lamps will henceforth be referred to herein as mercury metal halide lamps.

In its general construction and appearance, the mercury metal halide lamp may resemble the conventional high pressure mercury vapor lamp comprising a quartz arc tube mounted within a glass outer jacket having a screw base at one end. Thermionic main electrodes are provided at the ends of the arc tube which contains a quantity of mercury and metal halide along with an inert gas for starting purposes. Thus, by way of example, one may add sodium iodide either alone or combined with a lesser quantity of thallous iodide to the mercury to achieve a luminous efficiency of as much as 80 lumens per watt as against the 50 to 60 lumens per watt range of the ordinary mercury lamp, with the further advantage of an improved spectral distribution more pleasing to the eye.

Two types of cathodes have been widely used with the mercury vapor lamp. Up until a few years ago, the thorium insert type was more common; it consists of a tungsten rod with a tightly wound tungsten coil thereover and a slender piece or sliver of thorium metal inserted under the coil. More recently, the oxide type cathode has been widely used wherein the tungsten coil is coated with a mixture of an alkaline earth oxide and a refractory oxide such as barium oxide and thorium oxide. Neither type of cathode is entirely satisfactory for use in mercury alkali metal halide lamps such as the mercury sodium iodide lamp. With the thorium insert type, a dark generally olive-brown spot appears near the end of the tube, in line with the electrode tip, early in life. As lamp life progresses, this spot may develop devitrification which penetrates the sides until finally a leak develops and life is ended. In life tests of a substantial group of such lamps, a high rate of failure from this cause was observed, in excess of 50% during the first 2,000 hours. With the emissive oxide type, darkening and spot devitrification is not a problem but, after a few cycles of operation, the lamps become hard starters and require excessively high voltages to start them. It appears that the halide vapor reacts with the metal oxides of the emission mix and destroys their effectiveness.

The object of the invention is to provide a cathode suitable for use in a mercury metal halide lamp, particularly a mercury sodium iodide arc lamp.

Study of the dark spot which forms in mercury sodium iodide lamps with thorium insert electrodes shows that it contains a high percentage of thorium. On the basis

of these studies and of theoretical considerations, I have concluded that thorium enters into a reaction with sodium iodide and that this reaction is favored by the presence of the silica (quartz) which constitutes the envelope wall. The usual construction of the thorium insert electrode comprising a thorium sliver within the tungsten slip-over coil contains a great excess of thorium over the theoretical requirement for satisfactory electron emission. In accordance with the invention, a tungsten cathode for a mercury metal halide arc lamp is provided with a minute amount of thorium metal which is applied over the tungsten base metal as a thin film ranging in thickness from 3 A. to 2000 A. In general, a quantity of thorium in the range of 0.16 to 100 micrograms per cathode is suitable for the cathode of a mercury alkali metal halide lamp. The quantity of thorium is sufficient for successful use as an electron emitter but so small that it does not react appreciably with the metal iodide such as sodium iodide. As a result, dark spotting of the wall and localized quartz attack previously experienced are eliminated.

For further objects and advantages and for a better appreciation of the invention, attention is now directed to the following detailed description of a preferred embodiment. The features of the invention believed to be novel will be more particularly pointed out in the appended claims.

In the drawing: FIG. 1 shows in side view a mercury sodium iodide arc lamp in which the invention is embodied; FIG. 2 is an enlarged fragmentary cross section of one of the electrodes.

Referring to the drawing, the illustrated mercury sodium iodide vapor lamp comprises an inner arc tube **1** formed of a generally tubular quartz envelope having electrode **2, 2'** on inleads pinch-sealed into opposite ends. The electrode proper comprises a tungsten shank **3** having wound thereover a tungsten coil **4**. The inlead comprises a thin molybdenum foil **5** to one end of which is welded the tungsten shank **3**, and to the other end a molybdenum outer lead **6**. The molybdenum foils **5** are hermetically sealed into the envelope through full diameter pinch seals. The envelope is exhausted and the ionizable filling introduced into it through a lateral exhaust tube which is subsequently tipped-off at **7**. The filling consists of a quantity of mercury which is entirely vaporized during operation of the lamp which at such time exerts a pressure in the range of 1 to 15 atmospheres. A quantity of sodium iodide is provided in excess of that vaporized at the operating temperature which should be not less than 500° C. at any place. If desired, a lesser quantity of thallous iodide may also be provided. An inert gas, suitably argon, is provided at a low pressure, for instance 25 millimeters of mercury, to facilitate starting and warm-up.

In a practical lamp as illustrated, the arc tube is supported within an outer glass jacket **9** provided with a screw base **10** at one end in the same fashion as in a conventional high pressure mercury vapor lamp. The arc tube is supported within the outer jacket by means of a frame or harp **11** which serves also as a conductor between electrode **2** and the base shell; conductor **12** connects the other electrode **2'** to the center contact **13**. The interenvelope space is preferably evacuated as a heat conservation measure to permit the arc tube to operate within the desired temperature range under practical conditions of loading.

Thermodynamic free energy data and experimental studies of the reactions of thorium and sodium iodide in the presence of silica (quartz) at high temperatures (in excess of 800° C.) indicate that dark spot formation and quartz devitrification are related to the formation of various thorium iodides at the electrodes. The reaction is

favored by the fact that the envelope is quartz because this gives the sodium vapor, which forms when sodium iodide and thorium react, free access to react with the quartz: this effectively lowers the equilibrium vapor pressure of sodium, permitting more sodium iodide to react. Dark colored products are produced only when there is an excess of thorium with respect to the formation of thorium tetraiodide. Two kinds are found: a dark blue-gray material which has been identified as thorium dioxide, and a brown material which is thought to be "silicon monoxide." Since these occur only when thorium is present in stoichiometric excess with respect to thorium tetraiodide, it seems likely that a thorium diiodide or triiodide is one of the molecular species causing transfer to the quartz, but not necessarily the only thorium iodide present.

The below-noted reaction scheme appears plausible at the temperatures existing in the lamp. The parenthetical subscripts have the indicated significance:

c=crystal standard state;
l=liquid std. state;
g=gas at 1 atm. std. state;
gl=glassy state.

$$Th_{(c)}+2NaI_{(g)}\rightleftarrows ThI_{2(g)}+2Na_{(g)} \quad (1)$$

$$ThI_{2(g)}+2SiO_{2(gl)}\rightarrow ThO_{2(c)}+2SiO_{(g)}+I_{2(g)} \quad (2)$$

$$2SiO_{(g)}\rightleftarrows SiO_{2(gl)}+Si_{(c)} \quad (3)$$

$$2Na_{(g)}+SiO_{2(gl)}\rightarrow Na_{2(soln.\ in\ quartz)}+SiO_{(g)} \quad (4)$$

$$Th_{(c)}+I_{2(g)}\rightarrow ThI_{2(g)} \quad (5)$$

$$Th_{(c)}+4NaI_{(g)}\rightleftarrows ThI_{4(g)}+4Na_{(g)} \quad (6)$$

One may consider Reactions 1 and 2 as the initial reactions between thorium, sodium iodide, and quartz. Silicon monoxide results but it is only stable in the gas phase at high temperatures and forms silica and solid silicon upon condensing, as per Reaction 3. More silicon monoxide can form when either sodium vapor or thorium diiodide react with quartz, as per Reactions 2 and 4. Thermodynamic considerations indicate that the iodine formed in Reaction 2 can react much more completely with thorium than sodium iodide, and this probably explains why so little sodium iodide is used up in Reaction 1. As soon as a small amount of free iodine is formed, it promotes Reaction 5 almost exclusively to produce thorium diiodide which in turn reacts by Equation 2 to regenerate the iodine so that a cycling of iodine results. It will be noted that the end product of Reactions 1 and 6 is to produce sodium which reacts with the quartz as indicated in Reaction 4 and dissolves in it; the latter reaction is believed to be responsible for the devitrification which takes place. Reaction 2 produces thorium dioxide which is believed to have a dark blue-gray color due to occluded impurities; Reactions 2 and 4 produces silicon monoxide which disproportionates according to Reaction 3 to give a brown material; these are believed to be responsible for the dark spotting.

The foregoing has suggested to me that a cure to the dark spotting and devitrification which occurs with the thorium insert type electrode may be found in limiting the amount of thorium as nearly as possible to the minimum practically required to achieve the desired electron emission. This has been confirmed experimentally. The thorium should be distributed as a thin film over the area of the tungsten electrode rather than concentrated in a sliver as was the case in the prior thorium insert type electrode. The film should be at least one atomic layer in thickness; this means that the minimum thickness should be approximately 3 A. inasmuch as a monatomic layer of thorium is theoretically 3.26 A. thick. Some depletion of the thorium layer inevitably occurs during life and therefore more than the minimum is ordinarily desirable. A suitable thickness will generally be found in the range of 3 A. to 2000 A. At the lower limit of the range, depletion of thorium will give rise to hard starting early in life.

At the upper limit, there is a tendency to dark spotting and devitrification. Therefore the quantity of thorium to be used must be decided on the basis of a practical compromise between optimum performance and long life.

In a thermionic electrode comprising a tungsten base body and suitable for mercury alkali metal halide lamps, a thorium film thickness in the range of 3 A. to 2000 A. corresponds approximately to a quantity of thorium in the range of 0.16 to 100 micrograms per cathode. For use in mercury sodium iodide lamps operating with arc currents in the range of 1 to 15 amperes, a preferred range of thorium film thickness is from 150 A. to 500 A., corresponding approximately to a range of weight from 8 to 25 micrograms per cathode. By comparison, the thorium sliver in prior thorium insert type cathodes commonly used in high pressure mercury vapor lamps weighed 1 milligram. Therefore my invention calls for at least a ten-fold reduction in the quantity of thorium, and preferably at least a forty-fold reduction.

By way of example, in a mercury sodium iodide high pressure lamp such as illustrated in the drawing rated for 400 watts input, the electrodes comprise tungsten shanks 3 about 14 millimeters long by 40 mils in diameter and weighing about 215 milligrams. These are provided with a uniformly distributed thorium coating as shown at 14 in FIG. 2, to a weight of 13.6 micrograms per cathode corresponding to a thickness of 260 A. or 80 atomic layers. The tungsten slip-over coils 4 are then placed on the shanks and serve to protect the underlying thorium layer during operation of the lamp. Lamps using these electrodes are substantially free of localized dark spotting and quartz devitrification; the inside walls remained clear to about the same extent as in a conventional mercury vapor lamp during a life test extending up to 5000 hours. Over this life, starting voltage and operating voltage did not increase appreciably, indicating that the exceedingly thin layer of thorium is adequate for electron emissivity at the same time as it avoids the undesirable thorium-sodium-quartz cycle previously discussed.

A preferred method for providing the thin thorium layer on the tungsten electrodes is disclosed and claimed in copending application Ser. No. 318,985, filed of even date herewith, of Clarence G. Cook, entitled "Metal Vapor Lamp Electrode Processing," and assigned to the same assignee as the present invention. In that process, the thin film of thorium is vapor deposited at high temperature in a hard vacuum. This method achieves degassing and cleaning of the tungsten electrode at the same time as it provides the thin layer of thorium in a state of high purity. However, alternative methods are available such as flashing a thorium filament onto the tungsten electrode in a vacuum, or electrolytic deposition of thorium onto the tungsten from a fused salt bath, or by chemical deposition.

The preferred embodiment of the invention which has been illustrated and described is intended by way of example and not in order to limit the invention thereto. The scope of the invention is to be determined by the appended claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A high pressure arc discharge lamp comprising a quartz envelope containing a filling of mercury, an alkali metal halide, and an inert gas, said envelope having electrodes sealed into the ends thereof, at least one of said electrodes being a thermionic cathode comprising a tungsten base body having thereon a coating of thorium having a thickness in the range of 3 A. to 2000 A., there being no other thorium metal in said envelope.

2. A high pressure arc discharge lamp comprising a quartz envelope containing a filling of mercury, an alkali metal halide, and an inert gas, said envelope having thermionic electrodes sealed into the ends thereof, the electrodes comprising a tungsten shank activated by a quantity

of thorium in the range of 0.16 to 100 micrograms, the thorium being substantially uniformly distributed as a thin film over the tungsten shank, there being no other thorium metal in said envelope.

3. A high pressure arc discharge lamp comprising a quartz envelope containing a filling of mercury, sodium iodide, and an inert gas, said envelope having thermionic electrodes sealed into the ends thereof, the electrodes comprising a tungsten base body having thereon a coating of thorium having a thickness in the range of 150 A. to 500 A., there being no other thorium metal in said envelope.

4. A high pressure arc discharge lamp comprising a quartz envelope containing a filling of mercury, sodium iodide, and an inert gas, said envelope having thermionic electrodes sealed into the ends thereof, the electrodes comprising a tungsten shank activated by a quantity of thorium in the range of 8 to 25 micrograms, the thorium being substantially uniformly distributed as a thin film

over the tungsten shank, and a close-wound coil of tungsten wire fitted on said shank.

5. A high pressure arc discharge lamp comprising a quartz envelope containing a filling of mercury, sodium iodide, and an inert gas, said envelope having thermionic electrodes sealed into the ends thereof, each electrode comprising a tungsten shank coated with a layer of thorium approximately 260 A. thick and having a coil of tungsten wire close wound thereon.

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