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METHOD OF ACTIVATING CATHODES

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This invention relates to exhausting discharge devices and activating their electrodes, whether cathodes or (in some cases) activated anodes. When suitably carried out, my novel method or technique results in a superior cathode, characterized by a very low cathode drop, and allows of effecting the exhaust and activation expeditiously and with ordinary commercial equipment, such as is commonly used for evacuating discharge lamps. This application is a continuation-in-part of my application Serial No. 470,119, filed December 26, 1942, assigned to the assignee of this application.

To reduce the work function of cathodes of electric discharge devices and increase their emission relative to the "cathode drop" or fall in voltage, "activating" alkaline-earth-metal-oxides are very commonly used, either in the form of surface coatings on the metal cathodes, or in the form of inclusions or impregations in the metal. The oxides in question include those of barium, strontium, and calcium, mixtures of several or of all of these being generally preferred, though barium and strontium oxides are considered specially desirable. Because of the great susceptibility of barium and strontium oxides to contaminating reaction with moisture and with carbon dioxide in the atmosphere, however, the activating substances actually applied to metal cathodes in ordinary practice are not the oxides themselves but other alkaline-earth-metal compounds, which can afterward be decomposed to yield the oxides by heating in a suitable protective environment, very commonly, in the discharge envelope of the lamp or other device, after the cathodes have been sealed into this envelope. By such heating, furthermore, the activating alkaline-earth-metal oxide material used (whether the oxide itself with atmospheric contamination that is practically unavoidable, or some other compound that is decomposible to oxide by heat) is activated and rendered copiously electron-emissive.

Preferred alkaline-earth-metal compounds for purposes of activation include carbonates, formates, and oxalates. Other compounds such as nitrates, sulphates, or hydroxides may be used; but they generally result in corrosion of the carrier metal of the cathode, or are themselves difficult to decompose. Of the preferred compounds here mentioned, carbonates give the highest percentage yields of oxides, while formates and oxalates decompose to oxides at somewhat lower temperatures than do carbonates.

In practice, the heating of the cathode(s) to activate the alkaline-earth-metal oxide material becomes an incident or sequel of the exhaust processing of a discharge device, which includes evacuation of air from the device, "degassing" the internal walls and parts of occluded or adsorbed air, gas, or moisture, and charging the device with any desired working atmosphere or substance(s)—such as inert rare gas like argon, neon, xenon, etc., or mercury or other vaporizable and ionizable metal, or both. The evacuation and degassing are effected by connecting the device to a pumping or exhaust system and heating it to expel occluded gases and vapors, which are drawn out by the pumps; and so likewise are the gases or vapors that are liberated from the alkaline-earth-metal oxide material in activating the cathode(s). The heating of the discharge envelope and the internal parts for these purposes is usually partly external and partly internal: i. e., it is effected partly by having the discharge device in a suitably heated oven while being evacuated, and partly by passing current through the electrodes of the device, when these electrodes are of filament type. Other types of electrodes may be heated by high-frequency methods.

Now while the general method of exhaust-processing and activation just outlined produces discharge devices which start and operate satisfactorily in many cases, difficulty is sometimes encountered in producing devices that are always satisfactory for their rated voltage, especially when this is a relatively low voltage. The trouble in such cases is that a great many of the lamps turned out prove to be inoperable on their rated voltage, though perhaps capable of operation on somewhat higher voltages. Such high shrinkage in output of satisfactory lamps can, indeed, be ameliorated by greatly extending the time spent in the exhaustion, or by laboratory expedients such as the use of liquid air or dry ice traps in the exhaust system, or even by the use of getters to clean up gas in the devices; but these remedies are objectionable and impracticable for commercial production of lamps—even though getters can be and are widely used in the manufacture of vacuum or radio tubes. This is because such getters usually form obscuring deposits on the light-transmitting lamp envelope, which seriously reduce the desired radiant output.

I have found that such difficulties in the production of discharge devices that will operate on the desired voltage can be overcome by modification of the technique outlined above, without necessity for resorting to any of the disadvantageous remedial measures that have been

suggested. The modification consists, essentially, in performing the outgassing and the real activation of the cathodes as distinct operations, and under somewhat diverse conditions. This rests upon a realization that two theoretically distinct operations are involved in the heating of the cathodes in exhaust processing: an initial decomposition of the alkaline-earth-metal oxide material (in whole or in part) to yield oxide(s), and a further decomposition or transformation of oxide(s) (in whole or part) to yield other highly emissive matter, which may either be some lower oxide or suboxide, or the alkaline-earth-metal as such. For alkaline-earth-metal carbonates (which I rather prefer to other materials above mentioned), initial decomposition is satisfactorily effected by heating at temperatures of the order of 1100° C. or somewhat lower; and the ultimate activation is satisfactorily effected at temperatures of the order of 1200° C. to 1300° C., with a preference for the higher temperature limit of this range.

As already mentioned, the decomposition of the alkaline-earth-metal compound employed or present on the cathode(s) results in a considerable liberation of gas or vapor, which is mainly carbon dioxide when alkaline-earth-metal carbonate is used. Hence it is desirable to initially heat and outgas the cathode(s), at some 1100° C., while the discharge device is connected to the exhaust system as above mentioned. But when this outgasing is done thoroughly, the subsequent higher heating to activate the oxide results in very little evolution of gas or vapor. After the evacuation and degassing of the discharge envelope and the outgassing of the cathode(s), the envelope is charged with argon or other starting gas of similar character, or with mercury or the like, or both, and is sealed off from the exhaust system; and the cathode(s) are heated to a higher temperature, preferably of the order of 1300° C., more or less, which results in a high degree of activation and a low starting and operating voltage for the discharge device. Apparently such small amount of gas as is liberated from the cathodes during the higher heating—which is presumably oxygen—reacts with the mercury or other metal vapor in the device, or with the electrodes or other heated metal inside the discharge envelope, since it does not remain detectable in the discharge atmosphere. The decomposition of oxide during activation may be a reduction effected by carbon of the nitrocellulose or other carbonaceous binder that is used to coat the alkaline-earth-metal oxide material on the cathode(s), or it may be a mere thermal dissociation, probably favored by the relatively low pressure in the discharge envelope when it occurs.

The success of the technique described in producing superior activation and voltage characteristics of the cathode(s) would seem to be due to the circumstance that in this technique the small amount of alkaline-earth-metal or its lower oxide to which activation is due is not liberated, presumably, until the discharge envelope is sealed or tipped off from the exhaust system, and hence is not exposed to react with the water-vapor present in the whole exhaust system, but only with the much smaller amount of water vapor present in the sealed-off discharge envelope itself. In other words, it is to be supposed that little or no active material is formed by heating up to 1100° C., but a good deal (relatively speaking) by the heating around 1300° C. This seems confirmed by the fact that if the temperature of heating of the cathode(s) before the device is sealed off is much above 1100° C.—say 1200° C.—only an occasional very low-voltage lamp operable on its rated voltage will be obtained.

The practical application of my invention may be illustrated by describing its use in exhaust-processing the low-voltage fluorescent discharge lamps described in my U. S. application Serial No. 470,119, filed December 26, 1942, these lamps being known commercially by the designation "3W RP–12," and being capable of readily starting and operating on a 12 volt D. C. circuit. A feature of these lamps is an arrangement of fixed cathode and anode electrodes so that while they are closely spaced for easy starting, their discharge gap in operation (i. e., the distance from the anode to the point of the cathode where the cathode spot forms) is substantially longer than this spacing that is effective in starting, whereby a good light output is secured. The arc voltage of such a lamp may be as low as 6¼ to 8½ volts, and it may contain argon at a pressure ranging from ½ to 8 mm., preferably 3½ to 4½ mm., as well as an amount of mercury such that not all of it is vaporized during operation. The lamp cathode may consist of triple coils of tungsten wire such as disclosed in U. S. Patent 2,306,925 to John O. Aicher, granted December 29, 1942, coated with an activating mixture of barium and strontium oxides, and mounted in an RP–12–A2 bulb.

In coating the filamentary cathode coil of such a lamp, a mixture of carbonates of the desired alkaline-earth-metals is suspended in a nitrocellulose binder and thus applied to the coil and dried on, etc., in the usual way. After the electrodes have been mounted in the lamp bulb, the lamp undergoes an exhaust schedule on the pumps wherein the cathode is outgassed at a temperature above that at which the carbonates decompose but not exceeding 1100° C. at the maximum, so that the cathode is not activated during the exhaust. The preferred temperature for the outgassing is about 1050° C. While an oven is preferably used to degas the lamp envelope, the heating of the filamentary cathode for outgassing is effected by connecting the cathode across a suitable source of current, and is continued until no more carbon dioxide (CO_2) comes off, which may take some 3 to 5 minutes, more or less. After sealing off from the exhaust system, the lamp undergoes a seasoning schedule in which current is passed through the filamentary cathode to heat it to about 1300° C. for some two to six minutes, thus fully activating the cathode and bringing the arc and starting (or break-down) voltages of the lamp within the proper limits—a maximum D. C. arc voltage of 9, and a D. C. starting voltage of 12, say.

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

1. An improvement in exhaust and activation-processing an electric discharge device having cathode means comprising activating alkaline-earth-metal oxide material, and yielding gas when heated; which improvement comprises heating and degassing the discharge device and its said cathode means, while concurrently withdrawing the liberated gas from the device into an exhaust system in communication with said device, all at temperatures too low for effecting activating transformation of alkaline-earth-metal oxide; sealing off said device from

said exhaust system; and thereafter heating its said cathode means to higher temperature, resulting in activating transformation of alkaline-earth-metal oxide in said cathode.

2. An improvement in exhaust and activation-processing an electric discharge device having cathode means comprising alkaline-earth-metal compound that is initially decomposed by heat to yield alkaline-earth-metal oxide, which is in turn further decomposed and activated by higher heat; which improvement comprises heating and degassing the discharge device, and initially decomposing said alkaline-earth-metal compound as aforesaid, while concurrently withdrawing the liberated gas from the device into an exhaust system in communication with said device, all at temperatures too low for effecting the further decomposition aforesaid; and thereafter sealing off said device from said exhaust system and heating its said cathode means to higher temperature, resulting in the aforesaid further decomposition and activation.

3. An improvement in exhaust and activation-processing an electric discharge device having cathode means comprising alkaline-earth-metal carbonate; which improvement comprises heating and degassing the discharge device, and decomposing said carbonate to alkaline-earth-metal oxide, while concurrently withdrawing the liberated gas from the device into an exhaust system in communication with said device, all at temperatures not exceeding substantially 1100° C.; and thereafter sealing off said device from said exhaust system and heating its said cathode means to a higher temperature, of the order of 1200° C. to 1300° C.

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