

UNITED STATES PATENT OFFICE

2,547,869

FLUORESCENT LAMP ELECTRODE

Gerald W. Keilholtz, Lynn, and Charles W. Jerome, Marblehead, Mass., assignors to Sylvia Electric Products Inc., Salem, Mass., a corporation of Massachusetts

No Drawing. Application October 31, 1947,
Serial No. 783,436

2 Claims. (Cl. 117—33.25)

1

This invention relates to electric gaseous discharge device electrodes and more particularly to the composition of the electron-emissive coating with which they are provided.

An object of our invention is to provide an improved coating composition for electric gaseous discharge device electrodes, particularly those of the filamentary or "hot cathode" type.

Another object is to provide an improved coating composition for fluorescent lamp electrodes.

Further objects, advantages and features will be apparent to those skilled in the art from the following description.

In the case of fluorescent lamp electrodes, of the type shown in U. S. Patent 2,258,158, for example, the electron-emissive material with which the electrodes are provided usually consists of an oxide of one or more of the alkaline earth metals.

In the manufacture of fluorescent lamps the electrodes thereof are usually coated with a mixture of barium, strontium and calcium carbonates which are broken down during lamp processing to the oxides. We have found that a superior coating composition may be obtained if the several ingredients thereof are present in certain definite proportions. We have found that the best results are obtained within the following range: calcium—20 to 40 mole percent; barium—40 to 60 mole percent; and strontium—10 to 20 mole percent.

Our preferred coating composition has been developed from a realization that an excessive amount of any one of the ingredients has a deleterious effect on the lamp, particularly insofar as discoloration thereof is concerned. For example, calcium helps to reduce "end bands" but it also tends to cause the formation of "cathode spots." We have found 40 mole percent to be the practical upper limit. Strontium, when added to the barium, increases the emission but also tends to cause an increase in "end-band" discoloration. We have found that when about 10 mole percent is added increased emission is obtained without any perceptible increase in "end band" discoloration. Barium is an active ingredient in electrode coatings but it requires the presence of some strontium and calcium for best results. When used alone or with small amounts of calcium, the glass-like coating which is formed is a poor emitter and makes the lamps hard to start.

2

The terms used herein in describing certain types of lamp discoloration are cathode spots, end bands and multiples. Cathode spots are dark gray or black spots which appear on the inner wall of the lamp near the ends thereof, and are usually found opposite the electrodes. End bands are rings of discoloration, usually light yellow, brownish or black, which usually extend completely around the periphery of the inner wall of the lamp. End bands are usually defined by a sharp edge on the side near the electrode and a diffused edge on the side near the longitudinal center of the lamp. End bands are usually found forward of the electrodes with the sharp edge located opposite the end of the positive column discharge. Multiples are narrow crescents of discoloration, usually light yellow, brownish, or black, which appear near the ends of the lamp on both sides of the electrodes, i. e., on the base-side of the electrode as well as the side near the longitudinal center of the lamp.

The triple carbonates (carbonates of barium, strontium, and calcium) tested were coprecipitated by ammonium carbonate from the nitrates of barium and strontium and the formate of calcium. The formate of calcium was used because the nitrate is so hygroscopic that it makes precise weighing extremely difficult. The proper weights of the nitrates and formates to form one mole of the end product desired were dissolved in approximately one liter of distilled water and the solution heated to $85^{\circ}\text{C} \pm 3^{\circ}$. One mole of ammonium carbonate, plus a slight excess, was dissolved in another liter of water and heated to $35^{\circ}\text{C} \pm 3^{\circ}$. The latter solution was then poured slowly into the former with rapid stirring.

The precipitate was allowed to settle for about thirty minutes and the supernatant liquid drawn off. Warm water, approximately $70^{\circ}\text{C}.$, was added and the precipitate stirred. This slurry was then transferred to two 1-liter graduates to be used as settling columns. In these columns the carbonate was agitated by bubbling dry air for about 10 minutes. The carbonate was then allowed to settle for about 30 minutes and the supernatant liquid drawn off. This was repeated several times.

After the several washes, water was added and the slurry transferred to a suction filter. The filtrate was washed twice on the filter and allowed

to dry under a heat lamp. The powder was then transferred to an evaporating dish and dried at least 5 hours at about 110° C. and finally for about 4 hours at 325° C.-350° C.

The electrode coating was prepared in one pint ball mills according to the following schedule. About 45 grams of the triple carbonate was milled with about 60 cc. of amyl acetate for about one hour. Then about 15 grams of the triple carbonate was added and milled for about an hour, after which two separate additions of about 15 grams each of the triple carbonate was made, and after each addition, the mixture was milled for about two hours. Then about 10 grams of the triple carbonate and about 5 grams of a lacquer such as nitrocellulose and amyl acetate was added and the mixture milled for from 18 to 24 hours. The milled coating was then adjusted to the desired viscosity by the addition of amyl acetate and/or amyl acetate and nitrocellulose. In our work we used a viscosity of about 15 centipoises.

The filamentary electrode coils were hand coated with this coating composition, keeping the coating weight between 5 and 6 milligrams. Coils were also coated in a similar manner with a conventional triple carbonate coating composition which consists of about 12 mole percent calcium, about 39 mole percent barium and about 49 mole percent strontium. Lamps were made with both types of electrode coatings, the lamps with the conventional coating composition serving as the controls.

The data in the following tables clearly indicate the effect which an excess or a deficiency of either barium, strontium or calcium in the electrode coating composition has on lamp discoloration. Table I shows the effect on discoloration caused by increasing the calcium content. Table II shows the effect which increases in the barium content has on lamp discoloration. Table III shows the effect of increased strontium content. These effects are illustrated on the basis of a factor of demerit. Each result is expressed as a fraction, the numerator of which is the figure of demerit of the test sample, and the denominator is the corresponding figure of demerit of the control. The results tabulated were taken at 500 hours of lamp life. After this period of time any discoloration is usually well developed and shows the gradations necessary for an accurate evaluation thereof.

TABLE I

Effect of increasing calcium content

	Coating Composition, in Percent			F. D. Sample/F. D. Control at 500 Hours		
	Ba	Ca	Sr	Cathode Spots	End Bands	Multiples
<i>Series A</i>						
Test 1.....	50	—	50	0/0.4	12.0/3.3	15.0/9.2
Test 2.....	45	10	45	0.8/0.4	10.0/3.3	20.0/9.2
Test 3.....	40	20	40	3.3/0.4	1.7/3.3	12.5/9.2
Test 4.....	30	40	30	5.0/0.4	0/3.3	3.3/9.2
<i>Series B</i>						
Test 1.....	70	0	30	0/1.3	38.0/17.5	0/0
Test 2.....	60	20	20	7/1.3	8/17.5	1.0/0

The data in series A and B in Table I show that by increasing the calcium content the cath-

ode spot discoloration is increased. It might also be deduced that as the calcium content is increased the end bands and multiples decrease. However, it is possible that this effect may be due to the decrease in the contents of barium and strontium rather than to the increase of calcium.

TABLE II

Effect of increasing barium content

	Coating Composition, in Percent			F. D. Sample/F. D. Control at 500 Hours		
	Ba	Ca	Sr	Cathode Spots	End Bands	Multiples
<i>Series A</i>						
Test 1.....	—	50	50	All lamps failed at 100 hours.		
Test 2.....	30	40	30	5.0/0.4	0/3.3	3.3/9.2
Test 3.....	50	30	20	2.0/1.3	12.0/17.5	0/0
Test 4.....	70	20	10	0/1.3	36.0/17.5	5.0/0
Test 5.....	84	10	6	3.5/1.3	64.0/17.5	0/0
<i>Series B</i>						
Test 1.....	35	30	35	0/0.4	0/0	0/0
Test 2.....	60	20	20	7.0/1.3	8.0/17.5	1.0/0
Test 3.....	70	10	20	0/1.3	50.0/17.5	4.0/0

The data in series A and B in Table II show the effects on discoloration with increasing amounts of barium and decreasing amounts of calcium. The end band discoloration increases appreciably as this variation is made.

TABLE III

Effect of increasing strontium content

	Coating Composition, in Percent			F. D. Sample/F. D. Control at 500 Hours		
	Ba	Ca	Sr	Cathode Spots	End Bands	Multiples
<i>Series A</i>						
Test 1.....	60	30	10	0/5.0	0/0	0/0
Test 2.....	40	40	20	5.5/5.0	0/0	0/0
Test 3.....	40	20	40	3.3/0.4	1.7/3.3	12.5/9.2
Test 4.....	30	10	60	2.5/5.0	17.5/0	0/0

The results of increasing amounts of strontium as listed in Table III indicate a tendency towards end bands and suggest that the strontium content should be kept in the neighborhood of about 10 mole percent.

A review of the data in the three tables above indicates that test 3 in series B of Table I and test 1 in series A of Table III gave the best results. In the former test the coating composition of 50 mole percent of barium, 40 mole percent of calcium, and 10 mole percent of strontium; in the latter test the coating composition consisted of 60 mole percent of barium, 30 mole percent of calcium and 10 mole percent of strontium.

What we claim is:

1. A fluorescent lamp electrode having a coating of electron-emissive material comprising a mixture of the oxides of calcium, barium and strontium in the following proportions: between about 20 to 40 mole percent of calcium, about 40 to 60 mole percent of barium and about 10 to 20 mole percent of strontium.

5

2. A fluorescent lamp electrode having a coating of electron-emissive material comprising a mixture of the oxides of barium, calcium and strontium in the following proportions: about 60 mole percent of barium, about 30 mole percent of calcium and about 10 mole percent of strontium.

GERALD W. KEILHOLTZ.
CHARLES W. JEROME.

6**REFERENCES CITED**

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,939,075	McCulloch -----	Dec. 12, 1933
2,238,595	McNall -----	Apr. 15, 1941