United States Patent Office

2,984.534 Patented May 16, 1961

2,984,534

METHOD OF MANUFACTURING VACUUM TUBES

Herbert Kallweit and Karl M. Veith, Ulm (Danube), Germany, assignors to Telefunken G.m.b.H., Berlin, Germany

No Drawing. Filed Dec. 18, 1957, Ser. No. 703,479

6 Claims. (Cl. 316-8)

The present invention relates to the manufacture of 15 electronic discharge or vacuum tubes of the type having a cathode coated with an oxide of an alkaline-earth metal. More particularly, this invention is concerned with the feature of scavenging the vacuum tube with an extraneous gas during the evacuation stage of the manu- 20 facture.

Since the emissive oxide coating, for example barium oxide, is not air-resistant, but tends to readily absorb gases, such as water vapor and carbon dioxide, it is conventional in the manufacture of the emission layer to 25 apply first an air-resistant starting material to the cathode carrier and then to decompose this starting material thermally during the evacuation step in order to obtain the oxide of the emission layer.

To carry out this decomposition operation, the cath- 30 ode is usually heated to a temperature which lies above the normal cathode temperature. In case of the abovementioned emission substance, the starting material is barium carbonate (BaCO₃) which is decomposed to barium oxide (BaO) and carbon dioxide (CO_2). This decomposition step takes place during the evacuation and the carbon dioxide (CO2) formed thereby should be simultaneously sucked off, as it is extremely detrimental to the cathode. How good a vacuum can be obtained during this step depends upon the type of vacuum pump used. After the tube has been removed from the source of suction and after it has been sealed in a conventional manner, the vaccum may be further improved by the agency of a conventional "getter."

conditioning operation comprising several steps. First, the emission layer has to be activated because the oxide layer thus obtained on the cathode carrier, for example, a nickel sleeve, is not yet capable of emitting. This activation takes place by means of an activator which 50 may be added to the material of the cathode carrier. In case of the above-mentioned barium oxide cathode, magnesium may be used. This activator diffuses into the oxide layer and sets free elemental barium when the cathode is heated to slightly higher temperature. 55

In the second part of the conditioning process, gas residues still present on the surface of the individual electrodes, for example, the grid and the anode, are removed by an electron stream and are consumed as far as possible by the getter. For this purpose, voltages 60 are applied to the tube electrodes, first, by employing lower voltages which are gradually increased. The above described and conventional conditioning operation generally takes about one to three hours; in difficult cases, a longer period is necessary. Such a slow conditioning 65 operation has been necessary according to the present state of the art, because it has been discovered that the sudden release of large quantities of gas produces a very detrimental effect on the emission surface of the cathode and, under certain circumstances, may make emission by 70 the cathode impossible.

Tests have shown that the above described difficulties

2

are due to the gas residues remaining in the tube as a result of the thermal disintegration described in the foregoing. During the first part of the conditioning operation, when elemental barium is freed from the emission layer, particles of this elemental barium are discharged from the surface of the emission layer and, thereby, take along gas particles still remaining in the tube envelop which has been evacuated and subjected to the operation of the getter. These barium particles together with gas 10 particles are then deposited on the electrodes, such as the grids and the anode. If voltages are now applied to these electrodes, the impinging electrons remove the barium with the gas particles from the surfaces of the electrodes so as to form positively charged ions. These positive ions will then impinge on the cathode surfaces where they will react with elemental barium particles present in the emission layer. As a result of this, these gas particles impair the semi-conductive character of the emission layer, i.e., they partially contaminate the emission layer of the cathode. Due to this contamination action, it has, heretofore, been considered necessary to design the cathode or its emission layer sufficiently large in order to insure the obtaining of useful cathodes under any circumstances.

It is an object of the present invention to avoid these difficulties by shortening the conditioning operation on the tube and/or improve the cathode by diluting the gas formed during the reaction with another gas which is non-reactive with the emission layer. This dilution will assure a more thorough removal of the first-mentioned gas. Such non-reactive gas, which may comprise several substances, may either be introduced into the vacuum tube or be produced therein.

It is another object of this invention to shorten considerably the time required for the conditioning operation while, simultaneously, avoiding the above-mentioned contamination of the cathode. Whereas, heretofore, conditioning periods of about one to three hours have been required, the conditioning step of a tube now can be reduced to approximately three to ten minutes by employing the method of the present invention. Thus, the voltages applied to the individual electrodes can be much higher at the outset, since the gases in the tube are considerably less harmful with respect to the cathode. In The tubes thus treated are now subjected to a final 45 view of the fact that the added gases do not react with the elemental emission substance at the operating temperaure of the cathode, a contamination of the emission layer of this cathode will not take place.

In addition to the shortening of the conditioning step, an improvement of the cathode itself is obtained by the invention, because the amount of detrimental gases present in the resulting end product, i.e., the vacuum tube, is considerably reduced. Thus, the life of such cathodes is increased accordingly.

The method of the present invention can be carried out in two different ways. The gases present in the tube envelop after the decomposition step may be diluted by scavenging the tube envelop during the evacuation step once or several times with other gases. Thus, fewer gas particles of the gas detrimental to the cathode will remain in the tube envelop.

It is also possible to introduce into the vacuum tube one or more compounds which can be split under heat, so that these compounds, upon heating to a suitable temperature, will give up the desired gas or gases. As such compounds, for example, hydrides or nitrides may be used. Ziroconium hydride has proven particularly suitable, because, upon splitting of this compound by applying heat, zirconium remains in the tube envelop so as to serve simultaneously as a getter.

The added gases are suitably introduced prior to the

5

sealing of the tube, but at least prior to the setting off of the getter.

As indicated above, if carbonates are used as the starting material for the emission substances, the carbon dioxide formed as a result of the decomposition step may tend to have a detrimental effect on the cathode. If nitrates are used as starting material, the nitric oxides formed are likewise detrimental. If carbonates are employed, nitrogen or hydrogen may be used as the scavengof nitrates.

As already mentioned in the introduction, the contamination of the electrodes by the gases released during the decomposition step was observed during tests carried out to gain knowledge concerning the phenomena in- 15 volved. During these tests, a radioactive component was added to the starting material for the emission substance so as to be contained in the forming gas after the heat decomposition. Thus, in case of the preparation of a cathode of barium oxide, a radioactive carbon 20 component (C14) was included in the starting material, i.e., barium carbonate. After freeing the elemental barium from the barium oxide layer during the first part of the forming operation, radioactivity was observed in the anode of the tube thus treated. Therefore, it was concluded that the radioactive component of the carbon had deposited on the anode. However, after application of the scavenging step, the corresponding radioactivity was no longer noticeable. Thus, the forming step could be made much simpler.

This novel method can be used in accordance with a further development of this invention to supervise the steps in the manufacture of the tubes. For this purpose, it is merely necessary to add a radioactive compound to the emission starting material of about each 100th tube, which element or compound, upon thermal decomposition of the starting material, remains in the forming gas. By testing one or several electrodes of these pilot tubes with respect to radioactivity, it can be ascertained whether or not the dilution of the detrimental gas is carried out 40 maximum evacuation has been reached. to a sufficient degree so as to prevent contamination of the emission layer of the cathode.

While in the foregoing the method according to the invention is described as being applied to the manufacture of barium oxide cathodes, the new method can also 45 be employed in the manufacture of oxide cathodes with other starting materials fulfilling the described conditions. For example, the oxides of other alkaline-earth metals, such as barium or strontium, may be used.

The novel principles of this invention are broader than the specific embodiments recited above and rather than unduly extend this disclosure by attempting to list all the numerous modifications which have been conceived and reduced to practice during the course of this development, these novel features are defined in the following claims.

We claim:

1. In the method of manufacturing a vacuum tube ing gas, but only hydrogen should be used in the case 10 having a cathode with a metallic oxide coating wherein said oxide coating is formed by decomposing a metallic compound to said oxide and a gas by heating during the evacuation of said tube, said gas tending to produce a detrimental effect upon the emissive properties of said oxide, the step which comprises diluting said gas with another gas which is non-reactive with respect to said oxide coating, continuously evacuating the tube both during and after said diluting step, and sealing the tube after maximum evacuation has been obtained.

2. Method according to claim 1, characterized in that the vacuum tube is flushed with the additional gas at least once.

3. Method according to claim 1, characterized in that a compound selected from the group consisting of hy-25 drides and nitrides is introduced into the vacuum tube, and heated to give up the desired gas.

4. Method according to claim 1, characterized in that, in case of use of carbonate as starting material for the emission substance, nitrogen is used as the diluting gas.

5. Method according to claim 1, characterized in that, 30 in case of use of carbonate as starting material for the emission substance, hydrogen is used as the diluting gas.

6. Method for the supervision of the manufacturing process according to claim 1, including the step of introducing a radioactive component into the metallic compound such that said component will be present in the detrimental gas after thermal decomposition of the starting material, and testing at least one of several tube electrodes to determine the presence of radioactivity after

References Cited in the file of this patent

UNITED STATES PATENTS

		Foulke				
;	2,572,881	Rothstein	Oct.	30,	1951	
	2,747,121	Silver	May	22,	1956	
		Lehrer				