

March 4, 1941.

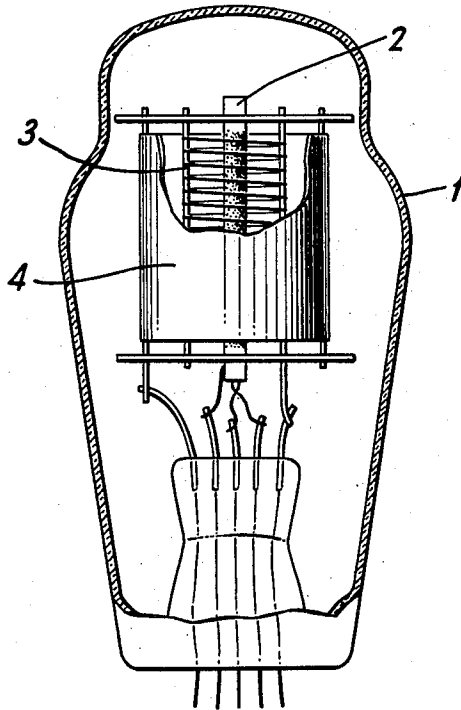
J. H. DE BOER ET AL

2,233,917

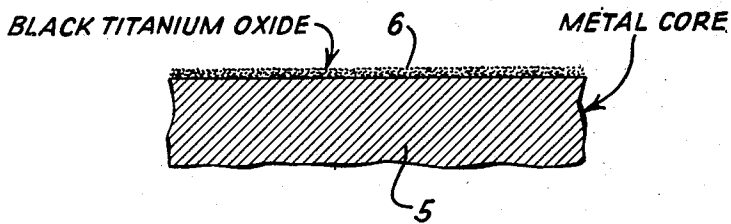
BLACK COATING FOR ELECTRON DISCHARGE DEVICES

Filed Dec. 17, 1938

*Fig. 1*



*Fig. 2*



JAN HENDRIK DE BOER,  
HAJO BRUINING AND  
LEONARDUS THEODORUS SCHEERMAN  
INVENTORS

BY

*Charles M. Clair*  
ATTORNEY.

## UNITED STATES PATENT OFFICE

2,233,917

BLACK COATING FOR ELECTRON  
DISCHARGE DEVICES

Jan Hendrik de Boer, Hajo Bruining, and Leonardus Theodorus Scheerman, Eindhoven, Netherlands, assignors, by mesne assignments, to Radio Corporation of America, New York, N. Y., a corporation of Delaware

Application December 17, 1938, Serial No. 246,284  
In Germany March 25, 1938

5 Claims. (Cl. 250—177)

The invention relates to electron discharge devices and to methods of manufacturing them.

Different materials have been proposed to reduce secondary emission during operation of tubes and to improve the radiation of heat from the electrodes and envelope walls. It is known to provide the electrodes of discharge tubes, such as grids and anodes, with cooling members and also to blacken these electrodes, either entirely or partly, with a coating material such as carbon or chromium oxide, or with a coating material which has low secondary emission such as chromium oxide, silver oxide, zirconium or zirconium oxide. A coating which has good black body characteristics and low secondary emission, however, is usually difficult to apply to the electrodes in a smooth adherent layer.

According to the present invention, a coating material is used which reduces secondary emission, improves the radiation of heat and adheres well to the electrodes. According to the invention one or more electrodes or other parts are coated with black titanium oxide. Use may be made of black titanium oxide which may readily be produced by partial reduction of titanium dioxide. This material has a very low secondary emission and because of its good radiation properties it materially reduces the temperature of the bodies on which it is coated.

The characteristic features of the invention are defined with particularity in the appended claims and preferred embodiments are described in the following specification and shown in the accompanying drawing in which Figure 1 shows an electron discharge device embodying the invention, and Figure 2 is a detailed sectional view of a portion of an electrode coated with black titanium oxide according to the invention.

A conventional electron discharge device with an envelope 1 enclosing a cathode 2, grid 3 and anode 4 may be constructed in the usual manner with the cold or non-emitting electrodes coated with a layer of black titanium oxide. The metal core 5 of an electrode such as the grid or plate, is coated with a layer 6 of titanium dioxide which when reduced to black titanium oxide leaves the surface of the core velvety black. The coating is adherent, is not electron emissive and because of its good heat radiating properties keeps the coated electrodes relatively cool.

According to one particular embodiment of the invention, an electron discharge tube comprises a grid, the operative portion of the wires of which are coated with black titanium oxide.

According to a further embodiment, an anode is coated, at least on part of its surface, with black titanium oxide. It may be desirable in this case to provide this material both on that side of the anode which is directed towards the cathode, in order to reduce the secondary emission, and on the outside of the anode, in order to improve the thermal radiation.

An advantage of the above described material is that it can be applied very easily to a support. Titanium dioxide may be first coated on the electrodes and then partially reduced. Titanium dioxide is of advantage compared to zirconium oxide since titanium dioxide can be reduced more easily.

The core or base to which the improved coating material is applied should be a metal which favors the reduction of the titanium dioxide. For this purpose use is preferably made of a metal such as tungsten or molybdenum or ferrous metals such as iron or nickel. If these metals are used for the core the titanium dioxide coating is easily reduced by heating in vacuum to a temperature of about 1500° C. The use of further reducing agents may not be necessary in this case. If other metals are used for the core or support, the titanium dioxide is reduced by heating, for example, in the presence of hydrogen or of mixtures of hydrogen and nitrogen.

The titanium dioxide may be applied to the support in different ways. Very satisfactory results are obtained by cataphoretically depositing the dioxide. Alternatively, powdered titanium dioxide may be suspended in a nitrocellulose lacquer and sprayed or painted on the cores and then heated in a reducing atmosphere such as hydrogen to reduce the coating to black titanium oxide. When applied to nickel and fired at 1350° C. the white titanium dioxide may readily be reduced to a black adherent coating that can not be rubbed off in handling. Apparently the particles of the coating move into intimate contact with the core as the higher oxide is heated and reduced to the monoxide.

Rutile,  $TiO_2$ , is less expensive in manufacture and insures good adhesion of the titanium dioxide when wet and of the black titanium oxide when subsequently produced.

We claim:

1. An electron discharge device comprising an envelope, a non-emitting electrode in said envelope, said electrode being coated with black titanium oxide, and a cathode within said envelope.

2. An electrode for an electron discharge device said electrode being of a metal included in the group consisting of iron and nickel, and a black titanium oxide coating on said electrodes.
- 5 3. An anode comprising a metal core and a coating consisting of a substantially black oxide of titanium.
4. An electrode for an electron discharge device comprising a metal core, a non-emitting adherent coating of a black compound of titanium and oxygen on said core.
- 10
5. A method of manufacturing an electrode for an electron discharge tube comprising applying a coating of titanium dioxide to said electrode and then reducing said titanium dioxide to an adherent black coating of an oxide of titanium. 5

**JAN HENDRIK DE BOER.**

**HAJO BRUINING.**

**LEONARDUS THEODORUS SCHEERMAN.**