May 5, 1959

B. J. GREEN

2,885,334

THERMIONIC CATHODE HEATERS

Filed Dec. 28, 1954

FIG. 1.

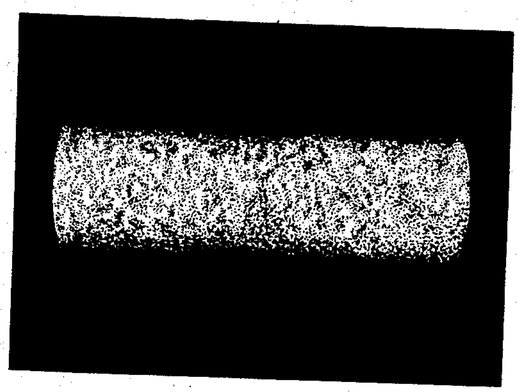
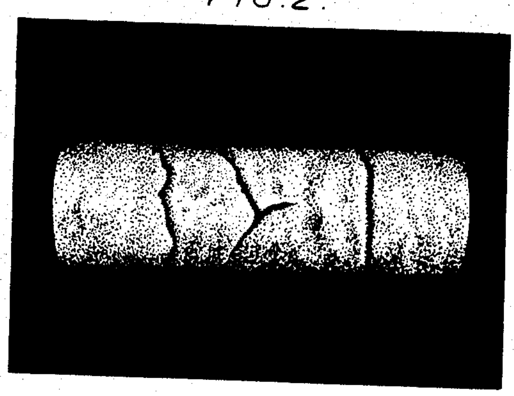


FIG. 2.



INVENTOR
B. J. GREEN
BY Philip M. Bolton
ATTORNEY

United States Patent Office

2,885,334
Patented May 5, 1959

1

2,885,334

THERMIONIC CATHODE HEATERS

Bernard Jeffrey Green, London, England, assignor to International Standard Electric Corporation, New York, N.Y., a corporation of Delaware

Application December 28, 1954, Serial No. 478,028

Claims priority, application Great Britain January 1, 1954

3 Claims. (Cl. 204—181)

The present invention relates to heaters for thermionic cathodes.

Heaters for thermionic cathodes are normally coated with alumina to ensure adequate cathode-heater insulation. In the past it has been commonly accepted that a desirable heating coating should be smooth and certainly free from any cracks. We have found, however, that, particularly with fine heater wire, in order to avoid brittleness of the heaters, a smooth and dense coating should be avoided, it being preferred that the coating should, on the contrary, be intentionally made so as, in use, to have a surface crazed with small fissures.

According to the present invention, therefore, there is provided a thermionic cathode having a heater coated with alumina, the surface of the alumina being intentionally crazed with small fissures.

Cathode heaters of the coil type are usually coated either by spraying or electrophoretically. Straight or faggot type heaters are usually dipped or "dragged." Although, over a very long time, electrophoretic methods of coating have been tried out, for various reasons they have not been entirely successful, and, in consequence, for coiled heaters spraying is more popular, in spite of the great waste of coating material involved. The main fault with electrophoretic coating up to the present time has been its extreme embrittling effect on tungsten. If this effect could be eliminated, or at least minimised, the electrophoretic method of coating has great advantages, viz:

(1) It gives a coating which provides a consistent value of cathode-heater insulation.

(2) The thickness of the coating can be accurately controlled within finer limits than is possible with spraying.

(3) The coating process is very simple, little skill being required to produce good heaters.

(4) The economy of material is very great compared with spraying, in which some 99% of the coating is wasted in the spray booth, air ducts etc.

Alumina exists in three main forms: α-alumina, which has a specific gravity of 3.8 and is characterised by a triagonal crystal structure; β-alumina with a specific gravity of 3.3 and a hexagonal crystal structure; and γ-alumina having a cubic structure and a specific gravity of 2.8.

In the past electrophoretic coatings were based on a suspension consisting mainly of α-alumina in a suitable liquid, the suspension containing little or no binder. The coated wire, in the case of continuously coated heaters passed direct into drying and sintering ovens. In the case of unit heaters such as double helical coils which were dipped into the electrophoretic bath, an external nitro-cellulose binder was applied, usually after drying, but sometimes the binder was included in the coating suspension. This binder supported the coating until sintering was completed.

In both cases a very smooth closely packed coating of hig density alumina was obtained with a hard porcelain-

2

like character. This coating became even harder during processing and life of the valve, due to the coalescing of the particles aided by a certain amount of recrystallisation of the alumina. The result was a coating which became a solid rod of high mechanical strength. In the case of fine tungsten wires the coating was actually strong enough to fracture the tungsten by leverage across the already enlarged crystal boundaries. This "brittleness" became progressively less with increasing core diameter.

The three forms of alumina mentioned above are related in that, on heat treatment γ-alumina can be converted into β- and on further heating the β- into α-alumina. With a view to overcoming the brittleness of heaters coated with α-alumina we use a less dense alumina as part of the coating, which coating shrinks on processing, producing a network of fine cracks. This allows for free expansion and contraction of the heater core without affecting the electrical properties of the insulator.

Accordingly, the present invention further provides the method of manufacture of a heater for a thermionic cathode in which the heater is electrophoretically coated with alumina containing eight parts by weight of γ-alumina for every eight to twelve parts of α-alumina, resulting in the fully processed cathode having a heater with an insulated coating which is crazed with small fissures. The preferred proportion of γ to α alumina is such as to result in the mean specific gravity of the mixed alumina being 3.5.

The invention will be further described with reference to the accompanying drawings in which:

Fig. 1 is a drawing taken from a photomicrograph of a portion of a heater according to the present invention after electrophoretic coating and before processing and

Fig. 2 is a drawing taken from a photomicrograph of a portion of heater manufactured according to the present invention after removal from a valve which has been fully processed.

The γ-alumina for use in coatings of the present invention is first treated with hydrochloric acid, as known in the art, to condition the charge carrying properties of the particles.

The preparation of the electrophoretic suspension is preferably carried out in the following manner:

900 millilitres of N-butyl alcohol, 600 millilitres of a 5% solution of nitrocellulose in butyl acetate, together with 120 millilitres of N-butyl acetate and 9 millilitres of N-butyl phthalate are introduced into a ball-mill and then 1000 grams of α-alumina, as normally supplied in the trade for coating radio valve heaters, and 800 grams of γ-alumina, treated as above, are added. Finally, a sufficient amount (of the order of 40 millilitres) of a 25% solution of aluminum nitrate in butyl alcohol is added to the mix to provide, in the final suspension, a pH value of between 2.5 and 3.0. The mix is then ball-milled for 24 hours, after which it is kept under constant operation until required for use, agitation being maintained in the electrophoretic bath.

In general I have adopted the method of the present invention for the coating of pre-formed helical heaters of shapes which are not convenient for coating by a "drag" process and also for very fine wire heaters which would not stand up to spraying, even if this were otherwise desirable. The heaters are suitably supported in the coating bath and after coating they are immediately washed in methylated spirits. The spirit removes the suspension dragged out from the coating bath but does not attack the electrophoretically deposited layer. The heaters are then dried in a warm air blast and sintered.

The appearance of the heater wire after coating but before sintering is depicted in Fig. 1 of the accompanying drawings, and shows an even but relatively coarse covering.

During the subsequent processing of the heater, the following changes in the composition of the alumina take place.

$$\gamma\text{-alumina cubic crystals (S.G. 2.8)} \xrightarrow{800^\circ\text{ C.}} \beta\text{-alumina hexagonal crystals (S.G. 3.3)} \xrightarrow{1000^\circ\text{ C.}} \alpha\text{-alumina triagonal crystals (S.G. 3.8)}$$

The increase in specific gravity causes a volume shrinkage in the coating which results in stresses being set up. The stresses eventually cause cracks to appear in the coating. The change, however, is a continuous process, dependent on a temperature-time factor. Stages at which the changes occur are not yet fully determined, but they are not normally complete until after the heater has been used for some time in a completed discharge device.

Fig. 2 shows the change in appearance of heater wire according to the invention on removal from a thermionic valve which has been normally processed and aged. It will be seen that, while the surface of the coating has become more dense, it has become crazed with a number of small fissures.

It is found that heaters of the present invention are very considerably less brittle than those previously obtained by other electrophoretic methods, the crazing of the coated surface does not adversely affect the insulation properties of the coating and there is no tendency for the coating to flake off.

While the principles of the invention have been described above in connection with specific embodiments, and particular modifications thereof, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the invention.

What we claim is:

1. The method of manufacture of a thermionic cathode comprising the steps of electrophoretically coating the cathode heater with alumina from a bath containing eight parts by weight of γ alumina for each eight to twelve parts of α alumina, drying the coating, heating the coating between 800°–1000° C. for conversion of the γ alumina ultimately into α alumina, whereby the resultant mixture has an increased specific gravity which causes a volume shrinkage of the coating and crazing thereof with small fissures.

2. The method of manufacture according to claim 1 in which said resultant mixture of γ and α aluminas has a mean specific gravity of 3.5.

3. The cathode of claim 1, wherein the alumina coating comprises a mixture of substantially like compositions by weight of γ-alumina as cubic crystals and α-alumina as triagonal crystals with a mean specific gravity range between 2.8 and 3.8.

References Cited in the file of this patent

UNITED STATES PATENTS

1,942,879	Riddle	Jan. 9, 1934
1,975,870	Schrader	Oct. 9, 1934
2,092,815	Shaw	Sept. 14, 1937
2,164,913	Goodchild	July 4, 1939
2,442,864	Schneider	June 8, 1948
2,734,857	Snyder	Feb. 14, 1956