

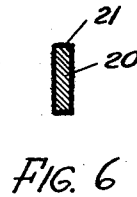
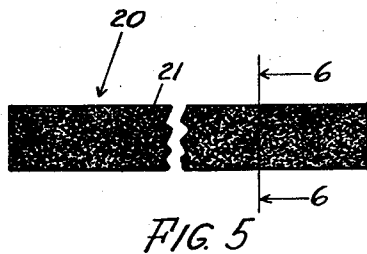
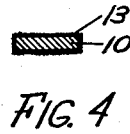
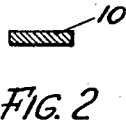
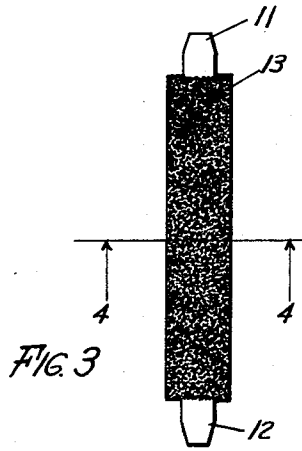
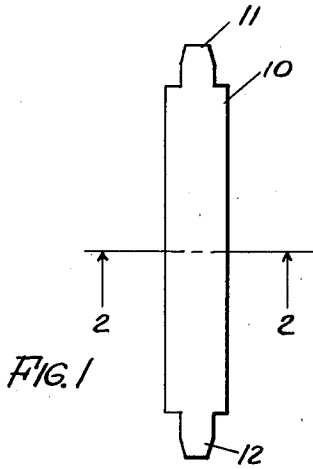
Nov. 26, 1957

G. FREEDMAN ET AL  
BLACK COATINGS FOR METAL PARTS AND METHODS FOR  
FORMING SUCH COATINGS.

2,814,574

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2 Sheets-Sheet 1



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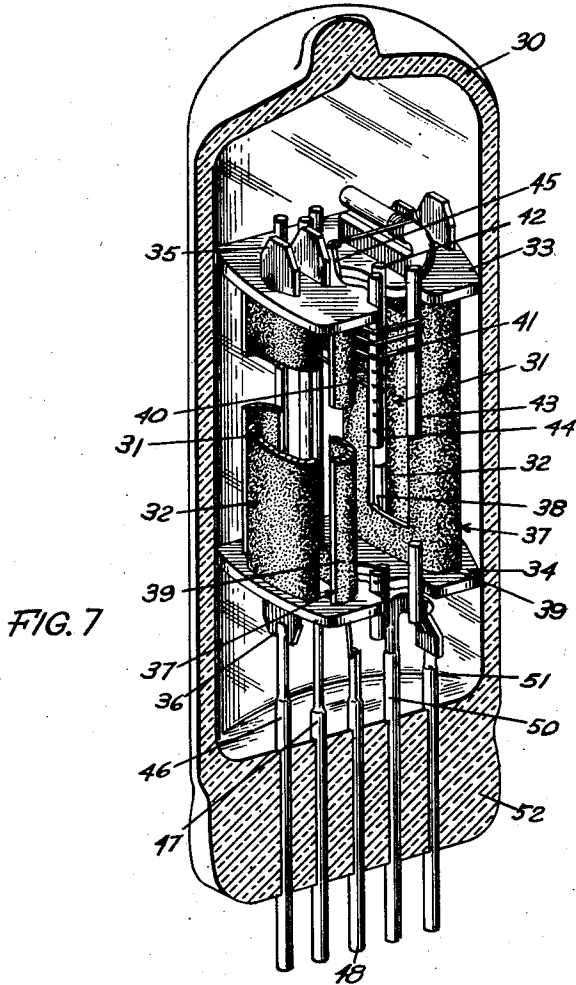
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**BLACK COATINGS FOR METAL PARTS AND METHODS FOR FORMING SUCH COATINGS**

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12 Claims. (Cl. 117—221)

This invention relates to black coatings for metal parts, especially the metal parts of thermionic discharge devices, and to methods for forming such coatings.

In thermionic tubes the parts, such as plates that carry relatively high currents, are frequently given a black coating to increase their ability to radiate heat. Such a coating may be a suspension of carbon in water, such as aquadag. However, such coatings have a tendency to crack and scale off during subsequent processing and heating. Most of the other methods used require either that the metal part be of nickel or have either a nickel or aluminum coating. Particularly in wartime, nickel and aluminum are in short supply in proportion to the demand for them. Consequently it is desirable to avoid their use. The processes of the present invention do not require nickel or nickel coated metal and yet give a coating that will not flake off upon heating or working. In addition, the resulting coating absorbs oxygen and other gases when heated in an oxidizing atmosphere and so has a getter action when the coated elements of the assembled tube are heated in subsequent processing.

By the processes of the invention, either iron or nickel tube parts are coated with a suspension of titanium dioxide and preferably either nickel or iron oxide in a mixture of a nitrocellulose binder and a wetting agent. The coated parts are heated in a reducing atmosphere, preferably of pure, dry hydrogen, at a temperature between 1300 and 1350 degrees centigrade. The result is a coating of titanium sub-oxide mixed with any added oxide. In a tube assembled from such coated parts, the residual oxygen and other gases remaining in the tube after pumping are absorbed from the atmosphere within the tube to partially oxidize the titanium sub-oxide to form a higher oxide. Thus the coating also performs the function of a getter. The addition of either ferric oxide or nickel oxide in a quantity approximately equal to the amount of titanium oxide used in the suspension will result in the coating adhering better to the metal part. Ferric oxide is used with steel parts and nickel oxide with nickel or nickel coated parts.

Other and further advantages of this invention will be apparent as the description thereof progresses, reference being had to the drawings in which:

Fig. 1 is a plan view of an uncoated piece;

Fig. 2 is a section along the line 2—2 of Fig. 1;

Fig. 3 is a plan view of a piece such as that shown in Fig. 1 after coating by the process of the invention;

Fig. 4 is a section along the line 4—4 of Fig. 3;

Fig. 5 is a plan view of a strip of metal coated by the process of the invention;

Fig. 6 is a section along the line 6—6 of Fig. 5; and

Fig. 7 is an isometric view, partly broken away, of a tube made using parts coated by the methods of this invention.

In Figs. 1 and 2, the reference numeral 10 designates the metal piece which may be of low carbon, cold rolled

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steel, nickel plated steel or nickel. The piece 10 is formed with mounting and connecting tabs 11 and 12.

A coating is prepared which, in a representative batch, comprises 100 grams of titanium dioxide suspended in a mixture of five milliliters of a wetting agent, preferably Tergitol 08, a sodium alkyl sulphate and 375 milliliters of a nitrocellulose binder, preferably composed of equal parts of butyl-alcohol and butyl-acetate with one percent of nitrocellulose. The proportions of the ingredients in the batch described above may be varied by plus or minus 20 percent and give substantially the same result. The mixture is preferably ball milled for eighteen hours to assure fine particle size and thorough mixing. The resulting coating is preferably sprayed on the parts and the sprayed parts baked in a hydrogen atmosphere at a temperature between 1300 and 1350 degrees centigrade. The lower temperature may be used when the hydrogen in the atmosphere is pure and dry. The parts are preferably held in a molybdenum boat during heating. This heating drives off the binder and reduces the titanium dioxide to a sub-oxide, changing the color of the coating from white to black. The thickness of the coating should be such that it does not add more than 0.001" to the total thickness of the base material. The adhesion of the coating to the base is improved if the solid portion of the coating consists of approximately equal parts by weight of titanium dioxide and either ferric oxide or nickel oxide. Ferric oxide is best if an uncoated steel is used for the base material and nickel oxide is used if nickel or a nickel coated metal is used for the base. The resulting coating will not readily flake off when the coated part is substantially heated or worked as in subsequent assembly of a tube from such parts. When a tube is assembled from the parts coated in this manner, the titanium sub-oxide may become oxidized by any residual oxygen present in the atmosphere in the tube. In oxidizing the coating performs the function of a getter and so may eliminate the necessity of a special structure for this purpose. It will be noted that the coating 13, shown in Figs. 1 and 3, does not extend over the tabs 11 and 12. The purpose of leaving these tabs uncoated is to facilitate the attachment of these parts to the connecting electrodes by welding or other means in the assembly of the tube mount.

If desired, a strip of metal, such as the strip 20 in Fig. 5, can be coated with a continuous coating 21. Parts may then be formed, as by stamping, from this continuous strip due to the good adhesion of the coating.

Parts for thermionic tubes may be made from parts coated in the manner described above or from strips of coated metal of the type described above and shown in Figs. 5 and 6. Such a tube is shown in Fig. 7, in which reference numeral 30 designates the envelope of a tube embodying the invention. Two plates 31, each having a coating 32 applied in the manner described above, are mounted in openings in two plates 33 and 34 of insulating material, preferably mica. Tabs 35 and 36, similar to tabs 11 and 12 shown in Figs. 1 and 3, protrude through the plates 33 and 34. Two beam forming plates 37, each formed with an opening 38 having a coating 39 formed in the manner of the invention, are also mounted in slots in the insulating plates 33 and 34. First and second grids 40 and 41 are mounted on rods 42, 43 and 44. A filament 45, that in this case also acts as a cathode, is mounted at the center of the grids 40 and 41. A lead 46 is welded to tab 36. Other leads 47, 48, 50 and 51 are welded to the other electrodes and brought out through a pinched portion 52 of the envelope 30, forming a stem. These leads are available for connection to an external circuit directly or through a socket. It will be noted that coatings 32 and 39 on the plates 31 and 37 have a

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lighter coating than the coating 13 on the plate 10 in Fig. 3. This is due to the oxidation of the titanium sub-oxide in the coating by the residual oxygen in the atmosphere within the tube when the assembled, evacuated and sealed tube is heated in the course of its production. The resulting titanium dioxide has a white color, thus lightening the color of the coating. This produces the getter function of the coating. Of course, any type of tube may be made with appropriately-shaped parts coated in the manner of the invention to give this result.

This invention is not limited to the particular details of construction, materials and processes described, as many equivalents will suggest themselves to those skilled in the art. It is accordingly desired that the appended claims be given a broad interpretation commensurate with the scope of the invention within the art.

What is claimed is:

1. A metallic body having a coating consisting of a mixture of equal parts of a sub-oxide of titanium and at least one of the group of metallic oxides consisting of ferric oxide and nickel oxide.

2. A ferrous body having a coating consisting of a mixture of equal parts of a sub-oxide of titanium and ferric oxide.

3. A nickel body having a coating consisting of a mixture of equal parts of a sub-oxide of titanium and nickel oxide.

4. A coating for metallic bodies consisting of a mixture containing twenty-one percent by weight of titanium dioxide and at least one of the group of metallic oxides consisting of ferric oxide and a nickel oxide, seventy-eight percent by weight of a nitrocellulose binder, and one percent by weight of a wetting agent.

5. A coating composition for ferrous bodies consisting of a mixture containing twenty-one percent by weight of a mixture of equal parts by weight of titanium dioxide and ferric oxide, seventy-eight percent by weight of a nitrocellulose binder, and one percent by weight of a wetting agent.

6. A coating composition for nickel bodies consisting of a mixture containing twenty-one percent by weight of a mixture of equal parts by weight of titanium dioxide and nickel oxide, seventy-eight percent by weight of a nitrocellulose binder, and one percent by weight of a wetting agent.

7. A coating composition for metallic bodies consisting of a mixture containing twenty-one percent by weight of titanium dioxide and at least one of the group of metallic oxides consisting of ferric oxide and nickel oxide, seventy-eight percent by weight of a binder consisting of one percent by weight of nitrocellulose in a mixture of equal parts of butyl alcohol and butyl acetate, and one percent by weight of a wetting agent.

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8. A coating composition for metallic bodies consisting of a mixture containing twenty-one percent by weight of titanium dioxide and at least one of the group of metallic oxides consisting of ferric oxide and nickel oxide, seventy-eight percent by weight of a nitrocellulose binder, and one percent by weight of sodium alkyl sulphate.

9. A coating composition for metallic bodies consisting of a mixture containing twenty-one percent by weight of titanium dioxide and at least one of the group of metallic oxides consisting of ferric oxide and nickel oxide, seventy-eight percent by weight of a binder consisting of one percent by weight of nitrocellulose in a mixture of equal parts of butyl alcohol and butyl acetate, and one percent by weight of sodium alkyl sulphate.

10. A coating composition for ferrous bodies consisting of a mixture containing twenty-one percent by weight of a mixture of equal parts by weight of titanium dioxide and ferric oxide, seventy-eight percent by weight of a binder consisting of one percent by weight of nitrocellulose in a mixture of equal parts of butyl alcohol and butyl acetate, and one percent by weight of sodium alkyl sulphate.

11. A coating composition for nickel bodies consisting of a mixture containing twenty-one percent by weight of a mixture of equal parts by weight of titanium dioxide and nickel oxide, seventy-eight percent by weight of a binder consisting of one percent by weight of nitrocellulose in a mixture of equal parts of butyl alcohol and butyl acetate, and one percent by weight of sodium alkyl sulphate.

12. A process for forming a black coating on metallic bodies comprising the steps of applying to the metallic body a mixture consisting of twenty-one percent by weight of titanium dioxide, and at least one of the group of metallic oxides consisting of ferric oxide and nickel oxide, seventy-eight percent by weight of a nitrocellulose binder and one percent by weight of a wetting agent, and heating the coated body to a temperature between 1300 and 1350 degrees centigrade and then cooling.

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