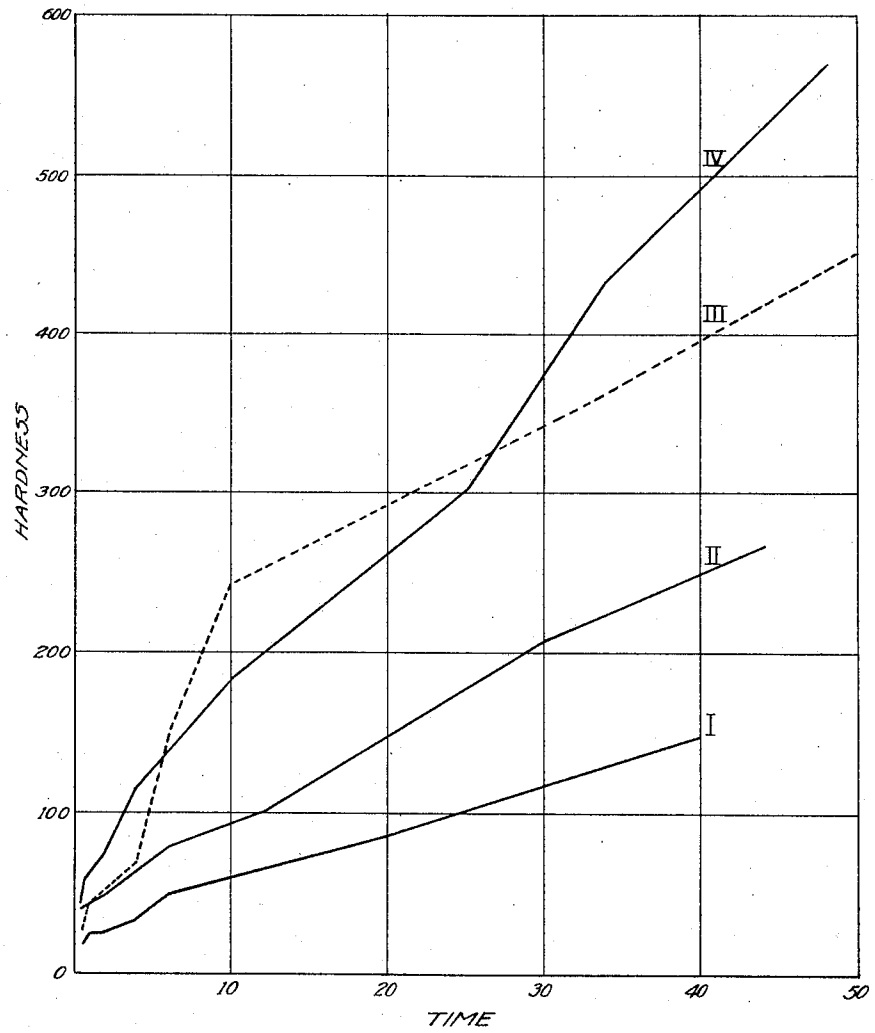
Aug. 30, 1932. H. J. MILLER ET AL 1,874,785

OXIDE COATINGS AND METHOD OF PREPARING THE SAME

Filed June 23, 1930



Inventors
Henry J. Miller
Frank J. Cahn
By George E. Mueller Atty.

Patented Aug. 30, 1932 1,874,785

UNITED STATES PATENT OFFICE

HENRY JOHANNES MILLER AND FRANK J. CAHN, OF CHICAGO, ILLINOIS, ASSIGNORS TO GRIGSBY-GRUNOW COMPANY, OF CHICAGO, ILLINOIS, A CORPORATION OF ILLINOIS

OXIDE COATINGS AND METHOD OF PREPARING THE SAME

Application filed June 23, 1930. Serial No. 463,337.

Our invention relates to oxide coatings for electron emissive surfaces and to the method of producing such coatings.

Oxide coatings for electron emissive surfaces of vacuum tubes have been used for some time. One of the outstanding weaknesses of such coatings has been their insufficient hardness and their consequent disentegration on handling and in use. The effects of the emission of electrons have a tendency to erode the electron emitting surface and thereby reduce the useful life of a tube.

An object of our invention is to provide a new and improved oxide coating and a method of producing the same.

A further object is to provide an oxide coating of great hardness.

A further object is to produce an oxide coating of fine texture and smooth surface.

Other objects and advantages will appear as the description proceeds.

The single figure of the drawing shows a series of experimental curves illustrating our invention.

In coating an electron emitting surface or cathode, barium carbonate and strontium carbonate are mixed with a binding material which consists of nitrocellulose dissolved in methyl alcohol and amyl acetate. The coating is sprayed upon the cathode by air pressure and during the spraying process practically all of the methyl alcohol and amyl acetate evaporate so that the barium and strontium carbonates with the nitrocellulose binder reach the cathode in a comparatively dry state. The cathode is mounted in the tube or envelope in this condition and during the exhaustion of the tube heat is applied to the cathode to gasify the nitrocellulose and remove carbon dioxide from the barium and strontium carbonates to convert them into oxides. ($BaCO_3$=BaO plus CO_2 and $SrCO_3$=SrO plus CO_2.)

The amount of nitrocellulose used should be as small as possible since the vaporization of this material if present in large quantities is apt to produce blow holes or disruptions in the coating which injuriously affect the emissivity of the coating. Still another reason for using as little of the nitrocellulose binder as possible is that the spacing or separation of the carbonate particles will be smaller and thus produce greater uniformity of the coating and providing a smooth surface of fine texture.

We have found that it is possible to greatly reduce the amount of nitrocellulose used as a binder in a coating mixture by employing a nitrocellulose having a high molecular weight and high viscosity and grinding the mixture for a long period in a ball mill. The method of producing nitrocellulose of high molecular weight and high viscosity is well known to those skilled in the art and will therefore not be described.

In using nitrocellulose of a high molecular weight and high viscosity we have found that the time of grinding the mixture of carbonates and nitrocellulose in a ball mill increases the hardness of the coating very much, while the grinding of a mixture containing nitrocellulose of low molecular weight and low viscosity has but small effect upon the hardness of the coating.

Referring to the drawing, the abscissas indicate the time in hours of grinding such a mixture in a ball mill and the ordinates indicate relative hardness.

Curves 1 and 2 represent the use of a nitrocellulose having a low molecular weight and low viscosity; curve 1 being of a mixture in which the nitrocellulose had a molecular weight and viscosity lower than in curve 2. Curves 3 and 4 show the effects of long grinding upon a mixture having nitrocellulose of a high molecular weight and high viscosity. It will be seen that as the time of grinding is increased for nitrocellulose mixtures of low molecular weight and low viscosity the hardness increased but slightly, and the expense of ball milling the mixture for a long period does not justify the slightly increased hardness of the resulting coating. However, as shown by curves 3 and 4, when a nitrocellulose of high molecular weight and high viscosity is used, the slope of the curve is rather steep and a very material increase in the hardness of the resulting coating is obtained. We do not wish to confine ourselves to any theory for this

phenomenon, although it seems very probable that the fact that a much smaller quantity of nitrocellulose of high viscosity may be used and still have sufficient binding properties, permits a closer positioning of the carbonate particles and results in a finer texture of the coating. Also, the fact that the gasification of the smaller amount of nitrocellulose has less tendency to disrupt the coating at the points where the gas escapes, is believed to be important.

In actual practice we have found it desirable to ball mill the mixture of carbonates and nitrocellulose for from 12 to 24 hours. The ball milling of the materials for a longer period than 24 hours results in too large a percentage of metal abraded from the ball mill being incorporated in the materials which is harmful to the product. This prolonged milling produces a very hard coating which is of sufficient hardness to very satisfactorily answer the purpose of coatings in vacuum tubes. Additional grinding beyond 24 hours does not seem to be justified by the additional cost entailed. By this method I have produced an oxide coating for cathodes which by actual test, proved to be twenty times harder than the coatings on the cathodes of similar tubes now on the market.

A formula which we have found convenient in practicing our invention consists of dissolving 15 grams of nitrocellose of high molecular weight and high viscosity in 675 c. c. of amyl acetate, and 450 c. c. of methyl alcohol. To this is added 750 grams of barium and strontium carbonates. The nitrocellulose has preferably a viscosity of the order of 80 times that of water when dissolved in amyl acetate to a 3% solution. This mixture is ground for 12 to 24 hours in a ball mill and is then sprayed or otherwise applied on the cathode. The subsequent heating of the cathode upon the exhaustion of the tube gasifies the nitrocellulose and converts the carbonates to oxides, leaving an extremely hard coating of oxides of very fine textures upon the cathode. The texture and smoothness of the resulting coating greatly enhances the emissive character of the coating and is capable of effectively withstanding the erosive effect of electron emission.

What we claim is new and desire to protect by Letters Patent of the United States is:

1. A method of producing an oxide composition which consists of dissolving nitrocellulose of high viscosity in a solvent, adding alkaline earth carbonates to the solution, grinding the resulting mixture at least 8 hours, evaporating the nitrocellulose, and converting the carbonates to oxides by the application of heat.

2. A method of producing an oxide coating which consists of dissolving less than one percent of nitrocellulose of high viscosity in a solvent, adding alkaline earth carbonates to the solution, grinding the resulting mixture for an extended period, applying the mixture to a surface, evaporating the nitrocellulose, and converting the carbonates to oxides by the application of heat and low pressure.

3. A method of producing an oxide composition which consists of dissolving a small percent of nitrocellulose of high molecular weight and high viscosity in a solvent, adding alkaline earth carbonates thereto, grinding the resulting product for an extended period, gasifying the nitrocellulose, and converting the carbonates to oxides by the application of heat.

4. A method of producing an oxide composition which consists of mixing methyl alcohol and amyl acetate, dissolving nitrocellulose of high molecular weight and high viscosity in said mixture, adding barium and strontium carbonates to the solution thus formed, milling the product for substantially 24 hours, gasifying the nitrocellulose, and converting the carbonates to oxides by the application of heat.

5. A composition for preparing oxide coatings for cathodes comprising a solvent having nitrocellulose of high viscosity dissolved therein, and fine particles of carbonates of barium and strontium intimately dispersed therein whereby a coating of fine texture and a high degree of hardness may be produced.

6. A composition for preparing oxide coatings for cathodes comprising approximately 15 grams of nitrocellulose of high viscosity, 1125 cubic centimeters of a solvent mixture, and 750 grams of barium and strontium carbonates reduced to an intimate mixture.

7. A composition for preparing oxide coatings for cathodes comprising approximately 15 grams of nitrocellulose of high viscosity, a solvent therefor, and approximately 750 cubic centimeters of barium and strontium carbonates reduced to an intimate mixture, whereby an oxide material of fine texture and great hardness may be produced.

In witness whereof, we hereunto subscribe our names this 3rd day of June, 1930.

HENRY JOHANNES MILLER.
FRANK J. CAHN.