Sept. 27, 1932. A. J. MARINO 1,879,701

PROTECTIVE COATING AND METHOD OF APPLYING SAME TO NICKEL, NICKEL ALLOYS, AND CHROMIUM IRON ALLOYS

Filed Nov. 20, 1931

Fig: 1.

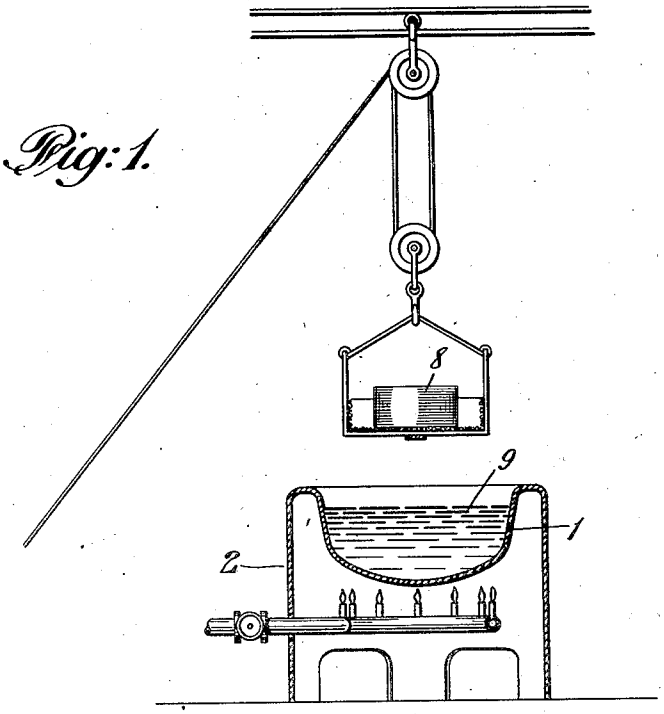


Fig: 2.

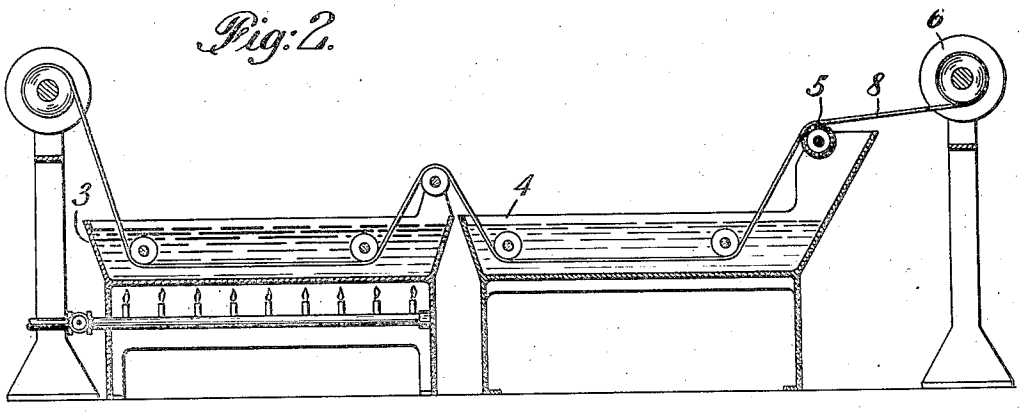
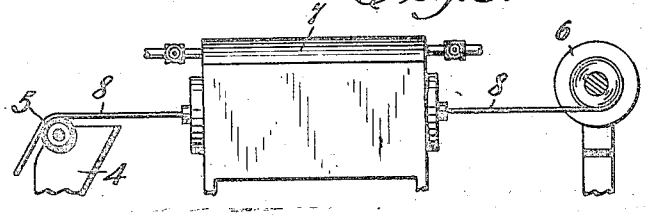


Fig: 3.



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UNITED STATES PATENT OFFICE

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PROTECTIVE COATING AND METHOD OF APPLYING SAME TO NICKEL, NICKEL ALLOYS, AND CHROMIUM-IRON ALLOYS

Application filed November 20, 1931. Serial No. 576,244.

This invention relates to a protective coating for nickel and nickel alloys and chromium alloys.

In industry where nickel alloys and chromium alloys are used it is desirable for certain purposes that they have a protective coating. Such is particularly the case with respect to the nickel iron series or the chromium iron series which are subject to rusting when moisture is present in the atmosphere. In the case of the nickel chromium alloys, frequently a coating is desired for radiation purposes such as when these alloys are utilized as heating elements. The oxide coating, however, should preferably be uniform and adherent. The natural formation of oxides by heating in air is not satisfactory particularly since in the course of manufacture of the wire and ribbon the oxide because of its abrasive action wears unnecessarily the diamond dies and other machine parts used in its production. Manufacturers have found that it is essential to draw, roll or otherwise process the alloys with the oxide coating rather than to oxidize subsequent to the manufacture because the processing causes the oxide to more firmly adhere to the alloys.

The appearance of the alloys in manufactured parts is also a problem of the industry. Certain finishes are frequently desirable such as matted or colored, for instance as blue, brown and black. Pure nickel as a black body, is used in the radio tube industry for plates, grids and other parts where a body of maximum heat radiation is necessary. There are certain difficulties in the connection with the formation of a black body surface upon nickel and to cause it to adhere to the alloy. At present, the method utilized for the formation of a black body is a carbonizing one. The carbonizing method is difficult to control and causes considerable trouble to the tube manufacturer because of the varying properties of the coating. Sometimes a matted surface is desirable and this is accomplished by sand blasting or scratch brushing. Neither of these methods are satisfactory due to expense of production.

One of the objects of my invention is to provide a coating for nickel, nickel alloys and chromium iron alloys, which can be readily applied by a simple process.

Another object of the invention is the application of a uniform coating of predetermined thickness for nickel, nickel alloys and chromium iron alloys. A still further object of the invention is to provide a coating for certain metals and alloys or for nickel, nickel alloys and chromium iron alloys which will be sufficiently adherent to permit processing of the alloys.

A further object of the invention is to provide a coating which will be sufficiently adherent and smooth so that it may be applied subsequent to certain operations such as by drawing through diamond dies, rolling down from rounds to flats for making ribbon. In other words, the coating may be applied prior to processing during processing or subsequent to the manufacture to shape or size. A further object of the invention is to provide a coating smooth and uniform which is not injurious to machine parts utilized in the manufacture of the articles made from nickel, nickel alloys or chromium iron alloys. A further object of the invention is to provide a matted surface upon nickel, nickel alloys and chromium iron alloys. A further object of this invention is to provide a coating for nickel, nickel alloys, chromium iron alloys for wire, ribbon or sheet, which will have sufficient electrical insulation properties to permit such articles to be used in contact where the voltage between turns is small.

Another object of this invention is to provide means for annealing and oxidizing nickel, nickel alloys and chromium iron alloys in the same continuous process.

Still another object of this invention is to

provide a method whereby materials can be coated either in a continuous dip process or batch process.

Referring to the drawing:

Figure 1 is a diagrammatic view of the batch method of applying the coating embodying the principles of my invention.

Figure 2 is a continuous dip method whereby wire, ribbon or sheet is continuously coated by passing through bath of coating material embodying the principles of my invention.

Figure 3 is a view of an annealing and reducing furnace.

In carrying out my invention, I propose to fuse a mixture of sodium nitrate and manganese dioxide. The temperature is then raised to the desired amount which will vary between 300 and 1000 degrees centigrade. The various temperatures are for the different alloys. The color desired, also the thickness and the annealed properties in the metal are affected by the temperature. Although I have found the following mixtures preferable:

		Per cent
(a)	Sodium nitrate	50
	Manganese dioxide	50
(b)	Sodium nitrate	60
	Manganese dioxide	40
(c)	Sodium nitrate	70
	Manganese dioxide	30

Under certain conditions different mixtures of sodium nitrate and manganese dioxide may be desirable since the different alloys require varying temperatures and a variation of the proportion of manganese dioxide can be varied to suit the alloy. In addition, the time element is affected by the proportion of manganese dioxide used as well as the temperature required, so that it may be said by controlling the time and temperature wide variations in the proportions of the mixture of sodium nitrate and manganese dioxide may be made whereby a proper coating may be had for nickel, nickel alloys and chromium iron alloys. The depth of the coating and the color are controlled by the proportion of manganese dioxide to the sodium nitrate and by the variation of the temperature and time.

In the batch process the salts are fused in the mixing pot 1 mounted in a suitable gas, oil or other type furnace 2 where the mixture 9 is brought to the desired temperature above the point of fusion and the materials to be coated or annealed and coated by immersion for the required time and then withdrawn and washed in water and dried. The drying may be in a drying chamber, a current of air spread out in the atmosphere. In the continuous process the salts are heated in the container 3 to the fusing temperature and above to the necessary working temperature the material being continuously passed through the bath at the proper speed, thence into a washing bath 4 of water over or through a wiping or drying device 5 and from there to a rewind spool 6 or container. I have found that I can utilize hard wire, ribbon or sheet 8 and by raising the temperature of the molten bath to the annealing temperature of the alloy I can anneal in the same operation. Annealing may also be done during the process but outside of the fusion bath by use of a suitable annealing furnace 7. When the annealing is done outside of the bath, see Figure 3, the atmosphere in the annealing furnace may be controlled whereby either ordinary air may be utilized which retains the color and surface as obtained by the molten bath or a reducing gas such as hydrogen may be utilized in the annealing furnace to produce a matted surface due to the reduction of the coating by the gas. The coating produced by this process adheres and forms a part of the surface of the alloys so that it may be rolled from a round wire to a very thin section of flat ribbon and still adhere without flaking or scaling. The color obtained can be varied in intensity from a brown to a black. In various industries such as electrical heating elements, it is sometimes desirable to have a wire or ribbon black coating for radiation or electrical insulation purposes. In the nickel iron or chromium iron alloys where rusting takes place, this coating prevents rusting. By my process for certain electrical uses the coating functions not only as a protective coating but also may dispense with an insulating coating since it also functions as an electrical insulation covering where the voltage between turns is small. In the radio tube industry where nickel or nickel iron alloys are used for plates or grids and the surface is blackened for heat radiation purposes and also to prevent particles of a filament adhering causes what is termed in the art as back emissions. This same property can be obtained by the use of my process producing on the nickel or nickel iron alloys a black coating having the property of increased radiation and protection against adherence of particles. The coating also is desirable in furnishing a decorative coloring as well as one that will not show tarnishing where metal is kept in stock. The coating not only adheres to the surface but is sufficiently flexible to permit of repeated bending stresses without flaking or chipping and therefore lends itself not only to the processes of manufacture of wire, ribbon or sheet, but also in the ultimate manufacture of articles in industry.

What I claim is:

1. A method for coating nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide and then dipping the alloy in the fused mixture of sodium nitrate and

manganese dioxide and then washing the alloy in water and drying same.

2. A method for coating and annealing nickel, nickel alloys and chromium alloys which comprises mixing and fusing a mixture of sodium nitrate and manganese dioxide, then raising the temperature to the annealing temperature of the alloy, then dipping the alloy in the fused mixture and then washing the coated alloy and drying same.

3. A method for coating nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide, then controlling the temperature of the fused mixture, then dipping the alloy in the fused mixture of sodium nitrate and controlling the time the alloy is allowed to remain in the fused mixture to control the depth of the coating.

4. A method for coating nickel, nickel alloys and chromium alloys which comprises fusing a predetermined mixture of sodium nitrate and manganese dioxide whereby the depth and color of the coating is predetermined by the proportion of manganese dioxide.

5. A method of forming a protecting coating on nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide, then dipping the alloy in the fused mixture and controlling the depth and color of the coating by controlling the temperature of the fused mixture, the time the alloy is in the fused mixture, and the proportion of manganese dioxide.

6. A method of forming a matted finish on nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide, then dipping the alloy in the fused mixture, then subjecting the alloy to a reducing atmosphere.

7. A method of forming a black surface on nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide, then running the alloy through the fused mixture.

8. A method of forming a black surface on nickel, nickel alloys and chromium alloys which comprises fusing a mixture of sodium nitrate and manganese dioxide, then running the alloy through the fused mixture, then washing and drying the alloy.

9. A method for forming an electrical coating for nickel, nickel alloys and chromium alloys when the voltage between turns is small comprising fusing a mixture of sodium nitrate and manganese dioxide, and then immersing the alloy in the mixture.

10. A composition to form a protective coating upon nickel, nickel alloys and chromium alloys which comprises a mixture of sodium nitrate and manganese dioxide.

11. A composition to form a protective coating upon nickel, nickel alloys and chromium alloys which comprises a mixture of 50% to 70% sodium nitrate and 50% to 30% manganese dioxide.

12. A composition to form a protective coating upon nickel, nickel alloys and chromium alloys which comprises a fused mixture of sodium nitrate and manganese dioxide.

Signed at New York in the county of New York and State of New York this 6th day of November A. D. 1931.

ANTHONY J. MARINO.