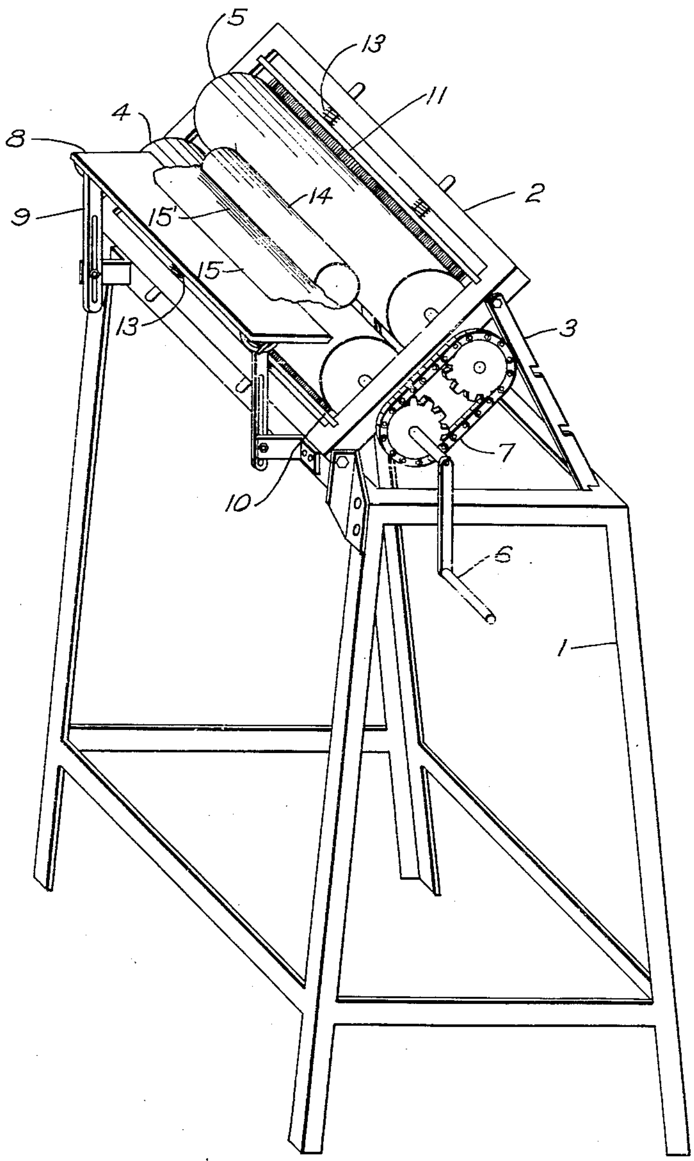
Aug. 8, 1961 L. D. EUBANK ET AL 2,994,951

METHOD OF APPLYING METALLIC COATINGS

Filed Feb. 7, 1946



Inventor

John W. Robinson
Lowell D. Eubank

By Robert A. Lavender

Attorney

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2,994,951
METHOD OF APPLYING METALLIC COATINGS

Lowell D. Eubank, South Euclid, and John W. Robinson, Brecksville, Ohio, assignors to the United States of America as represented by the United States Atomic Energy Commission

Filed Feb. 7, 1946, Ser. No. 646,168
6 Claims. (Cl. 29—529)

This invention relates to the application of protective metal coatings to rods and other cylindrical objects.

While it has long been known that metal articles may be protected by application of various metallic coatings by dipping the article to be protected into a molten metal bath of the protective metal, it has been found that for certain purposes the coatings applied in this manner are insufficiently thick to provide adequate protection for the base metal. Thus in the fission of uranium in a neutronic reactor it has been found that zinc or aluminum silicon alloy coatings may afford protection for the uranium but the durability of the coatings and their consequent life in use is much shorter than desirable. Coatings of such metals may protect the base metal for varying periods depending upon the nature of the coating and the thickness of the coating. Thus under conditions of corrosion which prevail in a water-cooled reactor, an aluminum silicon alloy coating of approximately eutectic composition on the order of five to ten mils in thickness may provide adequate protection for the base metal for a short period. However for longer periods the hot dip coating alone is inadequate to afford continuing protection for the underlying metal.

An object of the present invention is to provide heavy coatings of protective metals for various base metals. A further object of the invention is to provide a new process for the application of metallic coatings whereby substantially increased thicknesses may be secured. A further object of the invention is to provide heavy metallic coatings for uranium rods, such as employed in neutronic reactors. Further objects of the invention will become apparent from a consideration of the following description of the invention and detailed discussion of specific examples illustrating several preferred applications of the invention.

In accordance with the present invention a cylindrical object to be coated is heated to coating temperature and placed upon rotating rollers so that the rollers bear evenly against the surface of the metal object, and coating metal is then poured onto the rollers so as to form a pool in the valley between one of the rotating rollers and the cylindrical object to be coated. The rotation of the rollers is continued until the coating has been built up to the desired thickness. It has been found that by applying molten metal coatings to cylindrical objects in the described manner the thickness of the coatings is progressively increased much in the manner that a snowball increases in size but each layer of metal is firmly bonded to the underlying layer so as to provide an integral protective case of the protective metal.

The object to be coated should be heated to coating temperature prior to roller-coating. Preheating may be accomplished by dipping the object into a hot molten flux or into a non-reactive liquid, such as a liquid silicone polymer, at high temperature or into a bath of coating metal. The last method is normally preferred since it applies a preliminary coating which facilitates wetting of the object with the coating metal applied on the rolls.

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The application of the invention is not limited to any particular base metal or coating metal but may be used wherever it is desired to build up a coating heavier than obtainable by hot dip coating alone. The process is capable of building up a variety of coatings on coated as well as uncoated base metal. Thus a base metal which has been coated by hot dipping or elecroplating with one metal may be further coated by the method of the invention with a different coating metal. The invention is of special importance in the coating of uranium for use in neutronic reactors since coatings applied by conventional methods are inadequate for this purpose.

The rollers employed for carrying out the invention may be composed of any material which does not adhere to the hot coating metal or the hot base metal and which is not injured by the high temperature employed in the coating process. Rollers constructed of carbon and of asbestos cement composition have been employed satisfactorily. The size of the rollers is not critical, but to avoid excessive undulations in the coating, they are preferably considerably greater in diameter than the object to be coated. The rollers may be operated manually or automatically. For application of uniform coatings to a large number of identical objects, automatic rotation is preferred. However for the application of coatings to objects where the conditions of application are varied, as in the case where objects of different sizes are to be coated or protective coatings of different compositions or temperatures are to be applied, manual operation of the rollers permits more versatile control to suit the particular conditions involved. Speeds of rotation may vary to provide peripheral velocities from 10 to 300 or more feet per minute. In general the rate of rotation should be such that the surface of the object as it contacts the molten metal is close to or slightly below the melting point of the molten metal. This permits rapid wetting of the surface with the molten metal and addition of molten metal to the surface at a rate greater than run off of molten metal from the surface so that the desired accretion of metal on the surface is obtained.

The rollers should be kept free from accumulations of solid metal particles. This may be accomplished by frequent wiping of the rollers or by provision of brushes or swabs of material such as fibre-glass, asbestos, or silicone-polymers which are not seriously affected by the high temperatures involved.

The rollers may be heated internally if desired. However, the process may be conducted satisfactorily with rollers provided with no heating or cooling means other than exposure of the surface to normal atmospheric conditions. With some objects, such as hollow cylinders, it may be desirable to provide heating means for the forward roller and cooling means or no temperature regulation for the rear roller. For very large objects it may be desirable to provide cooling means for the rear roller with or without heating means for the forward roller. The entire process may be conducted in an atmosphere of controlled temperature and composition with or without application of radiant heat to the object or the coating metal. Conditions which assure constant radiation heat losses are desirable where a maximum uniformity of coatings is to be obtained. However, remarkably successful results have been achieved without any regulation of these factors, the heat supply being controlled merely by regulating the initial temperatures of the coating metal and the object to be coated.

During the coating procedure the metal may tend to over-run the object being coated and thus form a lip of metal extending beyond the original length of the article. This excess metal may be removed by a final rimming operation. It is usually preferable to apply a thickness of coating metal substantially greater than desired in the final coating and to machine and burnish the coating to provide a smooth highly polished finish. The trimming and machining operations may be combined. The character of the coatings at the ends of rods or tubes is better when the radius of curvature of the junction of the end faces with the cylindrical face is large than when it is small or substantially non-existent. Since the process does not coat the ends of cylindrical objects, it is preferred to carry out the process upon objects which have been previously treated to protect the ends. One highly satisfactory method for accomplishing this purpose is to provide caps or ferrules on the ends of the object prior to coating in accordance with the invention.

The invention is illustrated in the accompanying drawing showing application of coatings by means of a simple hand-operated apparatus. This apparatus comprises frame **1** which supports pivoted roller rack **2**. The rack **2** is shown held at a 45° angle to the horizontal by a pair of adjustable brackets **3**. This has been found to be a convenient working angle. The rack **2** carries two spaced asbestos cement composition rollers **4** and **5**. Roller **4** is driven directly by a crank handle **6** and roller **5** indirectly through the chain linkage **7** so that its surface speed is the same as that of roller **4**. A distributor **8** comprising a sheet of asbestos cement composition or other hard, heat-resistant material is provided in front of the forward roller **4** and supported on adjustable brackets **9** so that its position with respect to roller **4** can be regulated. It has been found convenient to set this distributor so that its upper surface is inclined a few degrees, say about 5 degrees, from the horizontal down toward roller **4** and its upper edge is substantially contiguous to roller **4**. By pouring molten metal onto the distributor **8** a more even distribution of the metal along the valley between roller **4** and the article to be coated is obtained than when an attempt is made to pour the metal directly into this valley. Brushes **10** and **11** are held by springs **13** against the rollers **4** and **5**. These brushes may be wire, fibre-glass, asbestos fibre, or other heat-resistant material. The brush holders are held in position by bifurcated ends which form guideways bearing against the ends of rack **2**.

For applying coatings by means of this equipment the article to be coated, represented as a rod **14**, is preheated, preferably by dipping in a molten bath of the coating metal and is placed in the valley between rollers **4** and **5**. The rollers are rotated by hand-crank **6** at the desired rate of rotation and additional coating metal is poured onto the distributor **8** from which it flows as a sheet **15** into the valley between rollers **4** and **5**. This sheet or pool has substantial thickness and the weight of the rod **14** depresses the sheet so that it piles up somewhat immediately in front of rod **14** to form a wave **15'** of molten metal in the larger pool **15**. It is preferred to pour out a measured quantity of the coating metal and to rotate the rollers **4** and **5** until all of the coating metal has been taken up by the rod **14** and the coating has solidified. This procedure minimizes irregularities that may result from the wave of molten metal in front of the rod if an attempt is made to remove the rod before this wave has been used up. The rod is then cooled and quenched if desired and subsequently trimmed, machined, and burnished to provide the final finish. Normally it is desirable to apply a coating about 15 mils thicker than the thickness of the desired coating and to machine off the excess metal. This procedure eliminates irregularities in the surface of the coating, and the final burnishing provides a smooth worked metal surface which appears to possess superior corrosion resistance.

The process of the invention has been found to be particularly suitable for the application of aluminum silicon coatings to metallic uranium rods. The metallic uranium is preferably provided with a blocking coat to prevent reaction of the uranium metal with the aluminum-silicon alloy to form a relatively brittle intermediate compound layer. The blocking coat may be a copper alloy or an electroplated chromium layer. Electroplated copper, iron and nickel blocking layers and hot dip coatings of zinc, and brass also have been employed with some degree of success. In addition to the aluminum-silicon alloy coatings, coatings of pure aluminum and coatings of pure zinc-aluminum alloy also have been applied by the process of the invention. When an aluminum-silicon alloy coating having approximately the composition of the eutectic is employed, the character of the coating is substantially improved by the presence of a small proportion of sodium or zinc. Thorough degassification also is beneficial for the production of sound aluminum-silicon alloy coatings.

The following examples illustrate the application of the invention to the preparation of metallic uranium rods for use in a neutronic reactor. Quantities are expressed in terms of weight if not otherwise indicated.

Example 1

A uranium rod about 8 inches long by 1.36 inches in diameter was prepared for coating by dipping in aqueous 60% HNO_3 solution at 65° C. for about 5 minutes, rinsing, and drying. The rod was promptly dipped in a bronze bath comprising 47 parts copper and 53 parts tin at a temperature of 730° C. for 20 seconds, during which the bath cooled to 680° C. The rod was removed, centrifuged 5 seconds to remove excess bronze, and dipped for 20 seconds into a molten salt bath comprising 53% KCl, 42% LiCl, 5% at 600° C. The rod was next dipped for 20 seconds into an aluminum-silicon alloy bath comprising 88 parts of aluminum and 12 parts of silicon modified by 0.1% sodium, maintained at 640° C. Upon withdrawal from this bath the rod was placed between two 5½-inch smooth asbestos cement composition rollers spaced ⅝-inch apart and 50 grams of additional modified 88/12 aluminum-silicon alloy at a temperature of 640° C. was poured onto the forward roller. The rollers were rotated at about 130–140 r.p.m. for 10 seconds to complete the application of the additional aluminum-silicon alloy. At the end of this time the coating had solidified and the rod was plunged into water to quench the alloy. When the rod had cooled, it was trimmed, machined, and polished. The resulting 30-mil coating was smooth and free from defects.

Example 2

A metallic uranium rod prepared as described in Example 1 was dipped for 1 minute in a 47% copper 53% tin bath at a temperature falling from 700° to 680° C. during the dipping period. The bronze bath was protected by about ½-inch of 53% KCl, 42% LiCl, 5% NaCl flux. Upon withdrawal from the bronze bath, the rod was centrifuged 5 seconds and plunged into a salt bath of the same composition as the flux for 20 seconds at 600° C. The rod was then dipped for 10 seconds in an unmodified aluminum-silicon alloy bath containing 88 parts of aluminum and 12 parts of silicon at 640° C. Upon withdrawal from the aluminum-silicon bath the rod was placed on the asbestos cement composition rollers and 23 grams of the same aluminum-silicon alloy and then 35 grams of alloy comprising 88 parts of aluminum, 12 parts of silicon and 1% of zinc and 0.02% of sodium both at 640° C. were poured onto the forward roller. Rolling required approximately 15 seconds to apply all of the aluminum silicon poured onto the rollers. The rod was then removed from the rollers and plunged into water to quench the coating. After quenching, the coating was trimmed, machined and buffed to a smooth even finish to provide a 30 mil coating.

Example 3

The preferred procedure comprises dipping the uranium rod through a flux of 53% potassium chloride, 42% lithium chloride, 5% sodium chloride into a molten bronze bath consisting of 53 parts of tin and 47 parts of copper at a temperature of 720° C. for 45 seconds. The rod is removed from the bronze bath and promptly immersed in a bath of molten tin at 640° C. for 20 seconds. Upon removal from the tin bath the rod is centrifuged at 500–5000 r.p.m. for about 5 seconds to remove excess tin and the ends immersed in a bath of 0.1%-sodium-modified 13X aluminum silicon alloy (Federal Specification AN–QQ–A–366, amendment 4 Al–13X) degassed by passing chlorine diluted with nitrogen through the alloy prior to introduction of the sodium. After each end of the rod has been in this bath for about 2 seconds, it is removed and aluminum caps are pressed over the ends of the rod by means of expandable dies which form a smooth fitting cap welded to the rod by the molten aluminum-silicon alloy. The rod is then again dipped in the aluminum-silicon alloy for two seconds, withdrawn, placed upon the asbestos cement composition rollers and rotated while about 33 grams of additional aluminum-silicon alloy which has been degassed and sodium-modified and is at a temperature of 800° C. is poured onto the forward roller. Rolling is effected at about 130 to 140 r.p.m. until the coating solidifies, which requires about 10 seconds. The coating is then quenched, trimmed, machined and polished as previously described.

Example 4

A metallic uranium rod about one inch in diameter was cleaned as described in Example 1, then dipped through a 53% KCl, 42% LiCl, 5% NaCl flux into a 47% copper, 53% tin bath at 740° C. and held there for 20 seconds. It was next immersed in molten tin at 400° C. for 30 seconds, withdrawn and centrifuged for 5 seconds in air. The centrifuged rod was dipped in an 88% aluminum 12% silicon bath at 640° C. for 3 seconds and then placed immediately on asbestos cement composition rollers and rolled for 5 seconds while 40 grams of 2 S aluminum at 680° C. was added. The coated rod was promptly quenched by pouring water over it and when cool was machined to a coating thickness of 30 mils.

Example 5

A metallic uranium rod about 1 inch in diameter and 4 inches long having a chromium electroplating 0.0008 inch thick thereon was dipped through a potassium, lithium, sodium chloride flux of the composition employed in Example 4 to which 10% sodium chloride had been added into a zinc bath containing 1% of aluminum maintained at a temperature of about 650° C. After one minute in the bath, the rod was withdrawn, centrifuged to remove excess molten metal and dipped into a 88% aluminum, 12% silicon bath at 640° C. for 4 seconds. The rod was withdrawn from the aluminum silicon alloy bath and placed on asbestos cement composition rollers and rolled while 35 grams of additional 88/12 aluminum silicon alloy at a temperature of 640° C. was rolled on.

Example 6

A copper electroplated uranium rod about one inch in diameter and 4 inches long was dipped into a 47% copper, 53% tin alloy bath at 718° C. for 30 seconds. The rod was withdrawn from this bath and immersed in molten tin at 500° C. for 5 seconds. It was then removed from the tin bath and immersed in an 88% aluminum, 12% silicon bath at 640° C. for 2 seconds. Upon withdrawal from the aluminum silicon bath it was placed on asbestos cement composition rollers and 50 grams of additional aluminum silicon alloy was rolled on. Rolling was continued until the coating solidified and the rod was then plunged into water to cool the coating. A thick, firmly adherent coating was thus obtained.

Example 7

A one inch diameter by four inch long metallic uranium rod prepared as described in Example 1, was dipped through a 53% KCl, 42% LiCl, 5% NaCl flux in a bath of 99% zinc, 1% aluminum at 480–500° C. for 5 minutes, withdrawn, centrifuged at 600 r.p.m. 5 seconds then dipped in a fluxless bath of 90% tin, 10% zinc at 325–335° C. for one minute. The coated rod was placed on asbestos cement composition rollers and rolled at 130 r.p.m. for about 30 seconds while an alloy of 90% tin 10% zinc at about 325° C. was poured on. The rod was then quenched in water. The total increase in weight of the rod was 8 grams.

It will be understood that we intend to include variations and modifications of the invention and that the preceding examples are illustrations only and in no wise to be construed as limitations upon the invention, the scope of which is defined in the appended claims, wherein we claim:

1. The method of coating a cylindrical metal object, which comprises supporting the cylindrical object between a pair of rollers, maintaining a pool of coating metal between the object and one of the rollers, and rotating the rollers to bring the surface of the object repeatedly into contact with the pool of coating metal, thereby progressively increasing the thickness of the coating.

2. The method of coating a cylindrical metal object, which comprises, supporting the object upon a pair of rollers, pouring molten coating metal between the object and one of the rollers at a higher temperature than said object, and rotating the rollers to bring the surface of the object repeatedly into contact with the molten coating metal, thereby progressively increasing the thickness of the coating.

3. The method of coating a cylindrical metal object, which comprises dipping the object into a molten metal bath to cover its surface with a uniform thin layer of coating metal, placing the object upon a pair of rollers, flowing molten coating metal between the object and one of the rollers, and rotating the rollers to bring the surface of the object repeatedly into contact with said coating metal, thereby progressively increasing the thickness of the coating.

4. The method of providing a protective coating on a metallic uranium rod, which comprises applying to the uranium rod a metallic barrier coating and then dipping the rod into a molten aluminum silicon alloy bath having approximately the composition of the eutectic to provide a uniform coating of the alloy over the barrier coating at least on the ends of the rod, applying aluminum end protectors to the ends of the rod, again dipping the rod into molten aluminum silicon alloy having approximately the composition of the eutectic, placing the rod between and on a pair of spaced rollers, maintaining a pool of coating metal between the rod and one of the rollers, and rotating the rollers to bring the surface of the rod repeatedly into contact with said pool of coating metal, thereby progressively increasing the thickness of the coating, then promptly quenching the coating, and subsequently machining and burnishing it to provide a smooth corrosion-resistant surface.

5. The method of coating a cylindrical uranium object which comprises dipping said object into a molten metal bath to cover its surface with a uniform thin layer of metal, placing said object upon a pair of rollers, pouring a molten coating metal between said object and one of said rollers, and rotating the rollers to bring the surface of the object repeatedly into contact with said molten coating metal, thereby progressively increasing the thickness of the coating.

6. The method of coating a cylindrical uranium object which comprises applying to said object a metallic barrier coating, dipping said object into a molten aluminum silicon alloy bath having approximately the composition

of the eutectic, placing said object between and on a pair of spaced rollers, maintaining a pool of coating metal between said object and one of said rollers, and rotating the rollers to bring the surface of said object repeatedly into contact with said pool of coating metal, thereby progressively increasing the thickness of the coating.

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