

2,858,235

METHOD OF COATING

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The present invention relates to a process for the coating of metals and other materials and the resulting products, and more particularly to a process for the coating of metal surfaces or the like to protect such surfaces when exposed to heat, oxidizing conditions, corrosive vapors, mechanical erosion, and the like.

Prior to the instant invention, many processes and coating materials have been proposed for use in protecting metallic surfaces. However, it has been found that the articles containing these coatings have been unsatisfactory in one or more of the following respects. At high temperatures, the coatings have been found to decompose and burn and thus lose all of their protective characteristics. The enamel and ceramic glazes, due to the methods of application used, have been found incapable of withstanding severe thermal and percussive shock. Such coatings have been found to be incapable of adhering well to the base metal during usage. None of the coatings nor processes of coating previously proposed has been found capable of being applied to metals and other surfaces of material having widely different expansion coefficients such as iron, steel, aluminum, copper, stainless steel, tungsten, molybdenum, magnesium, titanium, and the like, and which will adhere to such a variety of surfaces when thermal shock is imparted to the coating, such as by heating followed by sudden cooling. In such cases, the differences in the expansion of the metals and the coating occurs so suddenly as to set up enormous stresses and strains which dislodge the coatings. Further, the coatings as previously applied will not withstand flexing, bending, forming, swaging, or drawing of the coated surface without dislodging the coating.

An object of the present invention is to provide a method of coating metals and other surfaces to yield a protectively coated surface that will withstand flexing, bending, forming, swaging or drawing without dislodging the protective coating so applied.

A further object of the present invention is to provide a method of protectively coating metals and the like to yield a coating capable of protecting such materials during heat treatment.

A still further object of the present invention is to provide a method of protectively coating metals and the like whereby not only the surface of the material is coated, but wherein the coating extends to a slight depth beneath the surface, however, the core of the body of material is not affected.

A still further object of the present invention is to provide a method of protectively coating metals and the like whereby the resultant product is capable of withstanding thermal and percussive shock regardless of the differences in coefficients of the coating and the metals coated thereby.

Other objects and the nature and advantages of the instant invention will be apparent from the following description, wherein through the use of powder metallurgy techniques or the equivalent a composite material is

formed which consists of a high density core and an intimately bonded protective coating of a vitreous or ceramic material which extends to a slight depth beneath the surface of the material. In general, the process includes three broad steps, namely, the formation of a porous surface, the coating thereof with a specific type coating, and the densification of the coated body.

The metal to be protected may be obtained in the form of finely divided metallic powder and placed under suitable pressure to cause the powder to cohere into a porous body of relatively low density. Metal powders of various kinds may be employed in the practice of the invention, such as iron, chromium, nickel, copper, aluminum, silver, tin, zinc, molybdenum, tungsten, magnesium, titanium, and alloys of these metals, such as stainless steel, etc.

The more conventional methods of powder making involve the crushing and grinding of metal ingots or the like to substantially minute or microscopic powder particles, preferably of approximately 450 mesh. Metal powders are also made by reducing the purified oxide of the metals in a correct atmosphere, such as hydrogen or hydrogen and nitrogen. The deposition of pulverulent metal directly in an electrolytic tank offers an excellent source of powder.

The metal powders may be compressed either as an individual metal, as a mixture of two or more metals, or as powdered alloys. The initial compression is effected at a pressure adequate to form the powder into a coherent body of desired density so that it is in condition for the subsequent treatment. It has been found that a pressure of from 12½ to 80 tons is satisfactory, with a pressure of about 50 tons generally used. The powders may be compacted into the shape of a briquette or wafer, or directly in a mold to yield any desired shape.

As an alternative method, the present invention contemplates the coating of a metal that is already available in sheet, rod or shaped form. The surfaces of the metal may be made sufficiently porous by a sand-blasting operation, by successive exposure to an oxidizing and then a reducing atmosphere, acid etching, or any other suitable mechanical or chemical means to produce a high degree of surface porosity on the article which simulates the surface porosity found in the metal powder briquettes discussed above.

The compacted briquette or other article having a porous surface is then coated with the protective material by any of the known methods, such as dipping, spraying, brushing, soaking, wiping or flooding. The coating material is then allowed to dry. The coating and drying steps can be accomplished at room temperature or at elevated temperatures as desired. Due to the porous nature of the body being coated, the coating material will penetrate to a depth slightly below the surface into the porous mass, however, it will be confined mainly to the surface where the protection is desired and will not penetrate to such a depth where it will affect the core of the metal.

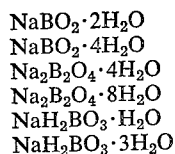
The vitreous or ceramic coating composition to be used is an important part of the invention, since not all vitreous or ceramic coating materials have been found to be entirely successful. A coating composition as described in applicant's copending application Serial No. 205,035, filed January 8, 1951, entitled "Method of Protecting Metal Surfaces, Composition Therefor, and Article Resulting Therefrom," now Patent 2,658,834, has been found particularly useful. This coating composition includes sodium meta borate, preferably in combination with clay and a reducing agent.

Actually, sodium meta borate alone as the coating composition produces a vitreous coating with a degree of protection which, for some purposes, is desirable. When heated, it forms a kind of glass or vitreous coating

in the outer pores and surface of the porous mass which acts to protect the metal surface to a fairly high temperature, as during the period of heating prior to densification of the mass. While a coating of sodium meta borate, when applied in accordance with the present invention, also gives a degree of protection where the part is to be placed in high temperature service for prolonged periods of time, the incorporation of clays, reducing agents, and other pigments with the meta borate to yield a ceramic coating improve the higher temperature protection considerably.

In the claims, it should be understood that the terms "vitreous coating" and "vitreous coating composition" are meant to include the use of sodium meta borate alone as the coating composition, the combination of sodium meta borate with other additives to yield a glass-like coating, as well as the combination of sodium meta borate with clay and other additives to yield a ceramic type coating.

The sodium meta borate utilized alone or in the coating composition can be any of the materials commonly known as sodium meta borate, hydrated or anhydrous. Following are several examples which have been found to work successfully:



Instead of adding the sodium meta borate, in the above forms, equally good results can be obtained by admixing Na_2O and B_2O_3 in mol ratios substantially equal to that existing in sodium meta borate. The sodium and boron compounds added can consist of alkalis of sodium together with oxides or acids of boron which, in combination, will give a sodium meta borate. Examples of the sodium alkali suitable for use are sodium oxide, carbonate, bicarbonate, hydroxide, or any organic sodium salt which upon thermal decomposition or ignition will give an alkaline ash of sodium oxide or carbonate. The boron compound used can be boron oxide, boric acid, borax or the like.

The borate acts as a flux for the clay, when used in combination and heated to form a ceramic coating. A suitable clay for use in the coating is a plastic clay. Such a clay, when mixed with water, assumes a plastic consistency and includes a rather narrow range of clays foremost of which are the ball clays of the ceramic industry. Clays which are not possessed of this plasticity are not suitable for use in the present invention.

The reducing agent, or oxidation inhibitor, when elected for incorporation in the coating, must be comminuted to small particle size so as to distribute itself smoothly throughout the protective layer, to reduce the tendency to separate and stratify while the coating is air drying, and subsequently to present a maximum surface to contact the corrosive gases and vapors that contact the coating. Suitable reducing agents or oxidation inhibitors include graphite, carbon black, and powdered metals, alloys or non-metals, such as iron, chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$), copper, silicon, and the like. Other oxides, pigments or the like may be incorporated, such as titanium dioxide, even if they are neither oxidizing or reducing in nature.

In the application of the material to the surface to be coated, it is preferable that water be used to effect solution of the soluble ingredients and suspension of the insoluble ingredients, using sufficient liquid to form a slurry having the consistency of paint. If, in addition, a proportion of an organic adhesive or binding agent is added thereto either with the original dry materials or with the water used for solution and dispersion a better adhesion of the wet coating to the work is secured, and upon mere drying results in a coating that will withstand

more handling and abuse than one prepared without the benefit of such adhesive material. Therefore, when applying the coating to the work it is deemed preferable to include an adhesive agent, such as dextrine, and the preferred embodiment of the invention makes use of the same. It is, of course, understood that any similar adhesive such as starch, gum, gum acacia, gum tragacanth, etc. can be utilized in place of the dextrine quite as effectively.

The inclusion of such adhesive is for the primary purpose of imparting desirable properties to the coating before heating, for upon heating the adhesive is decomposed at a relatively low temperature. However, by this time the natural adhesiveness of the coating itself begins to come into play and, of course, at high temperature the adhesiveness of the fused mass is brought into full force and effect.

In the application of this invention it has been found that the following range of proportions is satisfactory:

	Percent
$\text{Na}_2\text{O} - \text{B}_2\text{O}_3$ -----	2.5 to 100
Plastic clay -----	0 to 40
Reducing agent -----	0 to 90
Adhesive material -----	0 to 20

In a preferred embodiment, the following are used:

	Percent
Sodium meta borate octa hydrate (based on the anhydrous salt) -----	24
Plastic clay -----	39.5
Reducing agent -----	26
Organic binder -----	10.5

The following specific example is intended to illustrate the preparation of a suitable coating for use in connection with the present invention, but is not intended to limit same:

50 lbs. powdered graphite
20 lbs. dextrine
75 lbs. Kentucky ball clay

are mixed in a paddle mixer until all of the ingredients are uniformly distributed.

In a separate mixer, 95 lbs. sodium meta borate octa hydrate ($\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$) and 25 gallons water are mixed until the borate is dissolved using heat if necessary.

To this solution, the dry ingredients are added while agitating, a little at a time. When all have been added the mixture is mixed for two and a half hours until all ingredients have been thoroughly and intimately distributed. In this form the batch is ready for use.

The coated briquette or body is heated to a temperature approximating the normal forging temperature for the metal in question. The heating may be accomplished in a furnace or by passing a suitable current of electricity through the mass. The time and temperature of heating are carefully regulated for the particular metal and coating, after which the heated and coated briquette or body is densified.

The densification can be accomplished by mechanical working such as by forging, rolling or hot pressing. A pressure of approximately 300 to 500 lbs. per square inch has been found to yield good results. When forging one to three sharp blows at this pressure and temperature has been found to yield the desired densification.

During the densification, a certain amount of the coating is forced by the heat and pressure to penetrate beneath the outer surface of the metal, thus establishing a mechanical bond between the metal and the coating, and it is further believed that a partial chemical or physico-chemical bond of the metal and the coating material is formed in this area, thus increasing the bonding tendency and introducing an area of transition from pure metal on one side to coating material on the other.

It is contemplated that the coating material used will

5

be capable of being fused under the influence of the pressure and heat applied during the heating and densifying steps, and upon cooling will solidify in vitreous form and assume a metallic luster. At the elevated temperature, the coating material is soft and plastic and when subsequently struck with the great force necessary to densify the metal, it is brought into intimate contact with and is worked into the metal to a slight depth. Thus, there results an outer continuous coating over a partially continuous phase of both vitreous composition and metal confined to the area adjacent to the surface to a slight depth which is permanently held for the protection of the metal against any attack to which it is normally subject, but to which ceramics and vitreous materials are known to be resistant.

In the subsequent working of the metal, coated in accordance with this invention, such as by forming, bending, drawing, swaging or the like, this protective coating remains intact and continues to exert its protective function. In this manner, the present invention affords a method of protecting the metal while it is fabricated into rods, wires, sheets or finished articles consisting of a core of a completely dense metal, an exterior shell made up of a combination of metal and vitreous or ceramic material, and an outer coating of vitreous or ceramic material.

In certain cases, the steps of coating and densifying as described heretofore may be repeated several times as necessary to obtain the desired results.

An advantage of this process of coating is that the metal article can be subsequently worked to change its physical dimensions without the requirement for a protective atmosphere or a subsequent recoating.

It is further contemplated that the porosity required on the surface of the metal to be coated can be produced by spraying the surface with molten metal. The remaining steps in the process would be identical to those heretofore described.

The process described herein lends itself particularly well to the formation of coated filaments of tungsten or molybdenum wherein a coated rod is formed from the powdered metal in accordance with the present invention and after densification, the rod can be hot drawn into a filament which retains the protective coating held by the coated rod. Such coated articles of molybdenum, for example, have been found suitable for use in high temperature service, whereas previously molybdenum has been found unsatisfactory due to its great tendency to oxidize at high temperatures.

The following is a specific example of the process in accordance with the present invention, but is not intended to limit the same:

Molybdenum in powdered form was compressed into a briquette by cold pressing at 12½ tons. The resulting briquette was coated by brushing with a coating material having the following composition:

95 lbs. sodium meta borate octa hydrate ($\text{Na}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$)
75 lbs. Kentucky ball clay
20 lbs. dextrine
10 lbs. powdered graphite
26 lbs. titanium dioxide
25 gals. water

After air-drying the coating, the coated briquette was densified by heating to 2300° F. for fifteen minutes and a pressure of 200 lbs. per square inch was applied. The densified briquette was recoated, dried and further densified by heating to 2100° F. for ten minutes and applying a pressure of 200 lbs. per square inch. The resulting bar upon sectioning and polishing showed that the coating material had penetrated less than one quarter of the distance from the outer surface of the bar to the center thereof.

The field of application of this coating process is extremely varied and diverse and includes such applications

6

as coatings for heat treating metal wire, plates, castings, etc., coatings for jet engine exhausts, coatings for metals during welding or brazing, coatings for exhaust manifolds, coatings for casting molds and many other uses where especially high temperatures, chemical corrosion, or mechanical erosion are to be encountered.

It will be obvious to those skilled in the art that various changes may be made without departing from the spirit of the invention and, therefore, the invention is not limited to what is described in the specification, but only as indicated in the appended claims.

What is claimed is:

1. A method of protecting metal articles from oxidation at high temperatures which metal articles are in the form of a porous briquette made by compacting finely divided metal powder which comprises applying a liquid vitreous coating composition to the surface of said briquette, said coating composition containing sodium meta borate as an ingredient therein, drying said coating, and densifying said briquette under heat and pressure, said densifying being accomplished by hot forging said coated porous article at a pressure of at least 200 lbs. per square inch while the temperature of the article is approximately at the normal forging temperature of said metal, whereby the base metal of said article is densified and at the same time said coating composition has penetrated a slight depth below the outer surface of said metal and is vitrified thereon.

2. A method in accordance with claim 1, wherein the product resulting therefrom is again coated with said vitreous coating, said coating is dried, and said coated product is again densified.

3. A protectively coated metal article obtained in accordance with the method of claim 1.

4. A protectively coated metal article obtained in accordance with the method of claim 2.

5. A method of protecting a porous molybdenum article against oxidation at high temperatures which article has been formed by compacting finely divided molybdenum powder into said porous article, applying a liquid vitreous coating composition to the surface of said article, said coating composition containing sodium meta borate as an ingredient therein, drying said coating, and densifying said article under heat and pressure, said densifying being accomplished by hot forging said coated porous article at a pressure of at least 200 lbs. per square inch while the temperature of the article is approximately 2300° F., whereby the base metal of said article is densified and at the same time said coating composition has penetrated a slight depth below the outer surface of said metal and is vitrified thereon.

6. The method in accordance with claim 5, wherein said article is hot drawn into a wire, said wire still retaining the densified core of molybdenum and the coating of said vitreous material.

7. The method in accordance with claim 5, wherein said article is again coated with said vitreous coating composition and densified under heat and pressure.

8. A protectively coated metal article obtained in accordance with the method of claim 5.

9. A protectively coated metal article obtained in accordance with the method of claim 7.

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