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METHOD OF PROTECTING METAL SURFACES, COMPOSITION THEREFOR, AND ARTICLE RESULTING THEREFROM

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

This application is a continuation-in-part of applicant's copending application Serial No. 205,035, filed January 8, 1951, entitled "Method of Protecting Metal Surfaces, Composition Therefor, and Article Resulting Therefrom," patented November 10, 1953, as Patent Number 2,658,-834.

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 coating for metals and other materials capable of protecting such materials during heat treatment.

A further object of the present invention is to provide a coating which will protect metals against corrosion and is capable of withstanding thermal and percussive shock regardless of the differences in coefficients of the coating and the metals coated therewith.

A still further object of the present invention is to provide a protective coating for metals and the like which affords protection to the surface coated therewith in either a vitrified or non-vitrified form.

A still further object of the present invention is to provide a coating for metals and the like to protect against oxidizing or corrisive gases by reducing or reacting with such gases as they diffuse through the coating so as to protect the base metal or the like.

A still further object of the invention is to provide a

coating for metals and the like which is capable of withstanding flexing of the coated surface without dislodging the coating.

Other objects and the nature and advantages of the invention will be apparent from the following description.

In applicant's copending case referred to above, it was discovered that sodium meta borate in combination with a plastic clay, and an oxidation inhibitor, such as graphite, carbon black, iron or copper, yields a coating material that provided a protection to the surface on which it is applied against corrosive vapors, fumes, oxidizing gases and the like. It has now been found that sodium meta borate alone, or in certain combinations other than those specified in the copending case, yields excellent results.

The coating composition of the present invention utilizes sodium meta borate alone or in conjunction with clay, and certain additional ingredients, such as the oxides of titanium, chromium, copper, magnesium, zirconium, aluminum, calcium and the like. When such ingredients are mixed in the proper proportions, it has been found that the resulting material, when applied as a coating by any suitable means, provides a protection against corrosive vapors, fumes, oxidizing gases and the like to a wide variety of materials such as metals, all possessed of widely different characteristics. Further, when the coated metal is subjected to a temperature sufficient for the coating to vitrify and fuse, such heating can be continued considerably beyond such initial fusion point without decomposition, development of gas, formation of bubbles or otherwise developing a condition that would cause a disruption of the continuity of the coating film. Still further such vitrified coating, when subjected to severe thermal shock, tenaciously adheres to the metal surface.

The sodium meta borate utilized in the coating 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:

$NaBO_2.2H_2O$
$NaBO_2.4H_2O$
$Na_2B_2O_4.4H_2O$
$Na_2B_2O_4.8H_2O$
$NaH_2BO_3.H_2O$
$NaH_2BO_3.3H_2O$

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 alkalies 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 inclusion of the clay is not essential, since effective coatings can be obtained for certain purposes without this ingredient. The inclusion of the clay, however, results in a fused vitreous product in which the borate acts as a flux for the clay. 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 oxide or oxides to be incorporated in the coating

must be comminuted to small particles 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 to present a maximum surface. The oxides are those known as basic oxides and amphoteric oxides, namely, those that will react with acids to form salts. Suitable oxides include titanium dioxide, copper oxide, magnesium oxide, zirconium oxide, aluminum oxide, calcium oxide, chromium oxide and the like or combinations such as in chromite ($FeO.Cr_2O_3$), copper oxide and zirconium oxide, titanium dioxide and calcium oxide, and many others.

In addition to the oxide or oxides, powdered graphite, carbon black, iron or copper can be included in the composition. The resultant films after firing at considerably elevated temperatures are significantly free from the bubbles and air inclusions that characterize other compositions for the same purpose.

Additionally, this combination of ingredients appears to result in a vitreous coating possessed of considerable elasticity so that as stresses due to difference in expansions are encountered it successfully withstands any tendency of the surface to crack, check or dislodge itself.

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, gum arabic, 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
Na_2O—B_2O_3	20–100
Plastic clay	0–40
Adhesive material	0–20
Oxide or oxides	0–40
Graphite or the like	0–20

The preferred range of ingredients includes:

	Percent
Na_2O—B_2O_3	20–50
Plastic clay	20–40
Oxides or oxides	5–40
Graphite or the like	0–20
Adhesive	0–20

The following specific examples are intended to illustrate the present invention, but are not intended to limit the same:

Example 1

In a mixer, 95 lbs. sodium meta borate octa hydrate ($Na_2B_2O_4.8H_2O$) and 25 gallons water were mixed until the borate was dissolved using heat if necessary.

A strip of magnesium was coated with the material in any suitable manner and then dried. The coated strip of magnesium, which before coating was highly inflammable, could not be ignited even though there had been no vitrification of the coating.

Molybdenum coated with the above coating prevented oxidation of the molybdenum during subsequent powder metallurgy techniques up to 1600° F.

Example 2

26 lbs. powdered titanium dioxide
10 lbs. powdered graphite
20 lbs. dextrine
75 lbs. Kentucky ball clay

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

In a separate mixer, 95 lbs. sodium meta borate octa hydrate ($NaB_2O_4.8H_2O$) and 25 gallons water were mixed until the borate dissolved using heat if necessary.

To this solution, the dry ingredients were added while agitating, a little at a time. When all were added, the mixture was mixed for 2½ hours until all ingredients were thoroughly and intimately distributed. In this form, the batch was ready for use.

The surface to be coated was coated with the material in any suitable manner and then dried. The coated material even in this form was afforded protection against corrosion and oxidation, and the coating adhered well to the surface. Upon heating of the coated material, the coating will vitrify and the resulting vitrified coated surface may then be subjected to intense heat for long periods of time with sudden cooling, or alternate and repeated heating and cooling, and there is no indication of fusion, of oxidation or of wasting away of the material so coated.

It is a common failing of previous coating compositions utilizing sodium oxide-boron oxide mixtures that beyond their fusion points they tend to undergo a decomposition or evolution of gas due to vaporization or some similar phenomenon whereby bubbles are created in the otherwise smooth protective surface and which upon disruption causes a break in the continuity of the coating with exposure of bare uncoated surface. In accordance with the present invention, the utilization of a ratio of Na_2O to B_2O_3 substantially the same as that existing in sodium meta borate, in conjunction with the ingredients specified above, resulted in a coating without this failing, and having a myriad of desirable properties.

The preferred composition results in an increased fusion point as compared to the fusion point of the fluxing agent. Whereas sodium meta borate fuses at 1771° F., the coating in accordance with this invention does not fuse until much higher temperatures are reached. Metal coated with sodium meta borate alone and heated to the fusion point of the meta borate results in an immediate evolution of gas and blistering of the flux along with distinct evidence of the oxidation or burning of the metal. In contrast, when metal is coated with this coating composition, the coating can be fused and heated considerably beyond the fusion point to much higher temperatures without any evolution of gas or other disruption of the film and with full protection of the metal against the corrosive and oxidation influences of air and gases.

As illustrative of the wide range of metals having different expansion coefficients to which this coating material has been applied successfully are the following:

Metal:	Coefficient $\times 10^{-6}$
Aluminum	18.35
Copper	14.09
Iron	8–10
Steel	10–13
Stainless steel	9–12

It is to be understood that the inclusion of other in-

gredients such as various oxides, pigments, etc. to produce a decorative effect, color opacity, or other physical change, such as change in fusion point, will suggest itself to those versed in the art and that any such modification does not detract or alter the basic invention embodied herein.

Further examples of coating compositions that have been used successfully are:

Example 3

	Percent
Sodium meta borate	37.5
Kentucky ball clay	37.5
Titanium dioxide	12.5
Dextrine	12.5

Example 4

	Percent
Sodium meta borate	46
Kentucky ball clay	35
Titanium dioxide	12
Dextrine	7

Example 5

	Percent
Sodium meta borate	33
Kentucky ball clay	39
Titanium oxide	2
Aluminum oxide	15
Dextrine	11

Example 6

In Example 3 above, substitute aluminum oxide, magnesium oxide, zirconium oxide, calcium oxide, or copper oxide for the titanium dioxide.

Example 7

	Percent
Sodium meta borate	38
Kentucky ball clay	28
Titanium dioxide	6
Graphite	19
Dextrine	9

Example 8

	Percent
Sodium meta borate	38
Kentucky ball clay	28
Chrome ore	6
Graphite	19
Dextrine	9

Example 9

	Percent
Sodium meta borate	27
Kentucky ball clay	20
Copper oxide	33
Graphite	13
Dextrine	7

The field of application of this coating material is extremely varied and diverse and includes such applications as coatings for heat treating metal wire, plates, castings, etc., coating for jet engine exhausts, coatings for metals during welding or brazing, coatings for exhaust manifolds, coatings for casting molds, and many others.

It will be obvious to those skilled in the art that various changes may be made without departing from the spirit of the invention.

What is claimed is:

1. A composition of matter for use as a protective coating for oxidizable metals consisting essentially of 20% to 50% by weight sodium meta borate, 20% to 40% by weight plastic clay and 5% to 40% by weight of at least one metal oxide.

2. A composition of matter for use as a protective coating for oxidizable metals consisting essentially of 20% to 50% by weight sodium meta borate, 20% to 40% by weight plastic clay, 5% to 40% titanium dioxide and up to 20% graphite.

3. A coating composition in accordance with claim 1 wherein sufficient water is present in addition to the solid constituents to bring the material to the consistency of paint.

4. A magnesium article having a protective coating on the surface thereof, said protective coating consisting essentially of a solution of sodium meta borate.

5. A magnesium article having a protective coating vitrified on the surface thereof, said protective coating consisting essentially of 20% to 100% by weight sodium meta borate, up to 40% by weight plastic clay, and up to 40% by weight of a metal oxide.

6. A metal article having a protective coating vitrified on the surface thereof, said protective coating consisting essentially of 20% to 50% by weight sodium meta borate, 20% to 40% by weight plastic clay and 5% to 40% by weight of at least one metal oxide.

7. The method of protecting a magnesium surface subjected to elevated temperatures which consists essentially of coating the surface with a composition consisting essentially of a solution of sodium meta borate, and drying the coating thereon.

8. The method of protecting a metal surface subjected to elevated temperatures which comprises coating the surface with a composition consisting essentially of water and as the solid constituents thereof 20% to 50% by weight sodium meta borate, 20% to 40% by weight plastic clay and 5% to 40% by weight of at least one metal oxide, sufficient water being present to render the mixture to the consistency of paint, drying the coating thereon, heating the coated base until the coating melts, and thereafter allowing it to cool until solidified.

9. The method of protecting a metal surface subjected to elevated temperatures which comprises coating the surface with a composition consisting essentially of water and as the solid constituents thereof 20% to 50% by weight sodium meta borate, 20% to 40% plastic clay, 5% to 40% by weight of at least one metal oxide, up to 20% by weight graphite, and up to 20% by weight of an organic viscid gummy adhesive material, sufficient water being present to render the mixture to the consistency of paint, drying the coating thereon, heating the coated base until the coating melts, and thereafter allowing it to cool until solidified.

10. A molybdenum article having a protective coating on the surface thereof, said protective coating consisting essentially of a solution of sodium meta borate.

11. A molybdenum article having a protective coating vitrified on the surface thereof, said protective coating consisting essentially of 20% to 100% by weight sodium meta borate, up to 40% by weight plastic clay, and up to 40% by weight of a metal oxide.

12. A method of protecting a molybdenum surface subjected to elevated temperatures which consists of coating the surface with a composition consisting essentially of a solution of sodium meta borate, and drying the coating thereon.

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