

1

3,178,322

METAL PREHEAT-TREAT COATING

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5 Claims. (Cl. 148-22)

This application is a continuation-in-part of my application Serial No. 823,313, filed June 29, 1959, now abandoned for Metal Preheat-Treat Coating.

This invention relates to a composition and method for preventing oxide scale formation during the heat treatment of steels particularly stainless steels, and various other metal alloys. It is more specifically concerned with a composition which can be easily applied to metal surfaces to protect them from oxidation and other degenerative processes during heat treatment and which, depending upon the metal to be protected, either spalls upon cooling or is readily removable by immersion in standard solutions for substantially reduced periods of time to leave a bright metal finish.

The heat treatment of various metals and principally steels, copper, copper alloys, and those now generally referred to as superalloys, give rise to oxidation and alloy reactions which markedly deteriorate the surfaces of the heated articles. These reactions not only cause the destruction of a portion of the surface metal but also result in the formation of a heavy layer of metal oxide scale. In most cases this scale can only be removed by a costly and time-consuming sand blasting operation. Where conventional protective coatings are used and scale formation is not, therefore, as aggressive as is normal, the oxide scale must be eliminated by immersion and retention in acid pickling baths for extended periods of time.

When carbon steels are subjected to heat treatment excessive oxidation of the surface is normally encountered and may greatly reduce the overall dimensions of the piece being heat treated. When this occurs, it is necessary to remove the oxide scale layer which forms by machining or by some other means in order to obtain a surface having the physical characteristics of the parent metal.

Where scale forms, or other surface modifying reactions occur upon heating, an article cannot be heat treated in its final form. Furthermore, since machining often alters the mechanical properties of the metal, it will be impossible, in many instances, to obtain the exact surface condition desired unless it is possible to heat-treat an article in its final form.

Although oxide scale pre-heat-treat inhibitors are known to the art, none of the conventional compositions function in a scale preventative capacity insofar as steels, and especially the precipitation hardenable and corrosion resistant steels, are concerned. The most that is accomplished by such compositions is a reduction and slight modification in the character of the scale which is formed on heat treatment. A sand blasting or rather severe acid pickling of the treated article is still required. It is also well known that the scale which normally forms in the heat treatment of superalloys has heretofore been impossible to remove except by abrasive means. These alloys are generally comprised of nickel, chromium and cobalt as major constituents and are discussed in the ASM, Metals Handbook (1948), on pages 566-569.

It is, therefore, a principal object of this invention to provide a protective coating composition and method which will eliminate the foregoing deficiencies of known heat treat techniques and coating compositions. A further object is to provide a composition and method for protecting the surface of metal articles during their heat treatment. Still another object of this invention is to provide a metal article having a coating which protects the surface during heat treatment of the metal. Another

2

object of this invention is to provide a composition and method which completely prevent the formation of an oxide scale and eliminates undesirable changes such as carburization and other surface reactions occurring during the heat treatment of stainless steels. A further object is to furnish a composition and method which inhibit the formation of scale as the result of heat treatment of superalloys and to so modify any scale which does form to permit its ready removal by acid pickling. Still another object is to provide a pre-heat-treat coating composition which not only protects the surface of the stainless steels against carburization and the formation of oxide scale, but also spalls readily from the surface of the coated article during cooling to expose a bright-surfaced, heat-treated article. An additional object of the invention is to provide a protective coating composition which permits the heat treatment of metal articles in their final shape and form.

These as well as other objects will become apparent from the following detailed description of the invention.

The objects of this invention are in part accomplished by providing a glass-ceramic heat treatment protective coating composition for metal surfaces, which composition comprises a non-metallic aluminum constituent, a silicon oxide constituent, a non-metallic lead constituent, and a non-metallic boron constituent. The composition may be prepared by blending oxides of aluminum, silicon, lead, and boron or, alternatively, by mixing compounds containing one or more of the aluminum, silicon, lead, and boron constituents. The oxygenated compounds of the constituents are preferred ingredients of the composition. For example, a coating composition of this invention may be prepared by blending 40 parts of alumina with from 60 to 75 parts of silica, 120-130 parts of litharge, and from 40 to 50 parts of boric anhydride. Alternatively, compositions of this invention may be prepared by blending together appropriate quantities of oxygenated compounds, ceramic frits and glass compositions containing oxygenated compounds of aluminum, silicon, lead, and boron. For example, a composition of this invention may be prepared by blending 150 parts of kaolin containing approximately 39 percent by weight aluminum oxide, 45 percent by weight silicon dioxide, and 16 percent water with about 300 parts by weight of a ceramic frit prepared from a lead borosilicate glass and which contains approximately 60 to 65 percent lead oxide, 10 to 15 percent silicon dioxide, and 20 to 25 percent boric anhydride.

The protective coating of this invention ordinarily contains from 10-40 percent aluminum constituent, based on aluminum oxide, from 10-40 percent silicon constituent, based on silicon dioxide, from 20-70 percent lead constituent, based on plumbous oxide, and 5-25 percent boron constituent based on boric anhydride. In a preferred embodiment of the invention, the proportion of boron constituent as boric anhydride is from 14-18 percent and the amount of the lead constituent, as lead oxide, is from 40 to 50 percent. These relative percentage figures are with respect to the total aluminum, silicon, lead, and boron content of the composition calculated as the respective oxides. When other constituents are present in the composition they do not affect the relative ratios of aluminum, silicon, lead, and boron constituents present.

Other compositions of this invention are prepared with the inclusion of a halide flux such as calcium chloride or barium chloride, a binder and a diluent.

The compositions of this invention, when applied to a metal surface, protect the metal during heat treatment and have the advantage of spalling from the metal without the necessity of complicated, expensive, or damaging after-treatments.

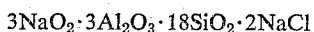
3

In a particular embodiment of this invention, the composition may be provided by mixing an aluminum silicate, such as an alkali metal-aluminum silicate (e.g., petalite) or an alkaline earth aluminum (e.g., calcium silicate aluminum silicate), in conjunction with a lead and boron-containing fluxing constituent which functions as an interstitial filler material for the silicate component. In this embodiment of the invention, the relative proportions of silicon, aluminum, boron, and lead constituents are as stated above.

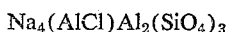
It is often desirable to provide the aluminum and silicon constituents of the composition as a single mineral or compound which is an oxygenated compound containing aluminum and silicon, ordinarily referred to as a silicate. The silicon constituent may be supplied as a silicate which contains no aluminum. The particular silicate which is utilized in this composition is not of any critical significance since any silicate falling within the indicated group will work satisfactorily. It is, therefore, not essential that the silicate be perfectly pure, although the purer the silicate the better the results. Exemplary of the silicates which may be used are aluminum silicate, which is the preferred material, magnesium silicate, calcium silicate, and barium silicate. These, as well as other usable silicates, form the major constituents of such minerals as kaolin, feldspar, talc, bentonite, ball clay and chain clay, all of which can be used in this coating composition. It is, however, preferred to use kaolin since it is the purest form of aluminum silicate available in mineral form.

A coating composition which is constituted of a silicate selected from the above class will not function in the desired manner without the inclusion of a boron and lead-containing fluxing constituent. In an embodiment of the invention this constituent is selected from the class consisting of (a) lead borate and (b) lead oxide and boric acid. The latter two compounds produce lead borate upon heating and, therefore, function in the same manner as lead borate. While it is not intended to be limited by the following explanation of the purpose of the borate constituent, it is believed that it acts as an interstitial filler material for the silicate and, therefore, provides a coating which is almost completely impervious to the passage of oxygen at the high temperatures to which the coated article will be subjected during heat treatment. The borate constituent also serves to lower the melting temperature of the coating composition and additionally provides for a lower initial temperature of protection. It thus increases the range of protection to from about 800° F. to about 2350° F.

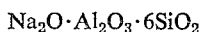
The aluminum, silicon, boron, and lead constituents of the composition may be provided as minerals and compounds containing one or more of the constituents in conjunction with oxygen, halogen, and an alkali or alkali earth metal. Thus, the composition of this invention may be prepared from compounds and minerals selected but not limited to the following: Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$; cyanite, Al_2SiO_5 ; danburite, $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$; datolite, $\text{Ca}(\text{BOH})\text{SiO}_4$; ganomalite, $4\text{Ca} \cdot \text{O}6\text{PbO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$; harmotome, $(\text{K}_2\text{Ba})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$; hydromephe-lite, $\text{HNa}_2\text{Al}_3\text{Si}_3\text{O}_{12} \cdot 3\text{H}_2\text{O}$; kaliophyllite, KAlSiO_4 ; kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; marialite,



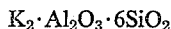
matlochite, $\text{PbO} \cdot \text{PbCl}_2$; mendipite, $2\text{PbO} \cdot \text{PbCl}_2$; ortho-clase, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$; petalite, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$; quartz, SiO_2 ; sassolite, $\text{B}(\text{OH})_3$; sodalite,



wollastonite, CaSiO_3 ; mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$; calcium alu-minum silicate, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; albite,

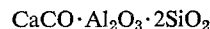


nephelite, NaAlSiO_4 ; potassium aluminum silicate,

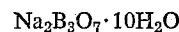


4

potassium aluminum borate, $\text{K}(\text{AlO})_2(\text{BO}_2)_3$; amalcite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; andalusite, Al_2SiO_5 ; andesine, $(\text{CaO}, \text{Na}_2\text{O})\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$; amorphite,



amorthoclase, $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$; apophyllite, $\text{K}_2\text{O} \cdot 8\text{CaO} \cdot 16\text{SiO}_2 \cdot 16\text{H}_2\text{O}$; axinite, $\text{HCa}_3\text{Al}_2\text{BSi}_4\text{O}_{16}$; ba-rysilite, $\text{Pb}_3\text{Si}_2\text{O}_7$; bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; borax,



chabazite, $\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 8\text{H}_2\text{O}$; pyroboric acid, $\text{H}_2\text{B}_4\text{O}_7$; orthoboric acid, H_3BO_3 ; metaboric acid, $\text{B}_3(\text{OH})_3$; boric anhydride, B_2O_3 ; lead metaborate, $\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$; various lead oxides; lead meta silicate, PbSiO_3 ; and the like.

The binding composition employed can be any organic polymeric, resinous, or plastic material which will serve to bind the particles of the other constituents together so as to form a continuous film on the surface of the metal to which it is applied. Hence, the binding composition can be composed of acrylate resins, polymeric epoxy resins, polyurethanes, alkyd resins, copolymers of various resins, or other similar materials. The preparation of these resins is well known to those skilled in the art and can be found in such text books as "Organic Chemistry," by Fieser & Fieser, published by D. C. Heath & Co., Boston. Non-limiting examples of acrylate resins which can be used in the coating are methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, diethyleneglycolmethacrylate, and methylethacrylate. An example of an alkyd resin is the condensation product of glycerol and phthalic anhydride. Other alkyd resins are well known to those skilled in the art. An example of an epoxy resin is a glycidyl polyether resin obtained by the reaction of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)propane. This produces a polymer in which the molecular units have terminal epoxy groups. Other epoxy resins prepared by the reaction of epichlorohydrin with polyhy-dric alcohol such as 1,2,3-trihydroxypropane are well known in the art. An example of a polyurethan is a diisocyanate of propylene glycol of the general formula $(\text{ONC}-\text{C}_3\text{H}_6-\text{O}-\text{C}_3\text{H}_6-\text{O})_n\text{C}_3\text{H}_6-\text{CNO}$, wherein n is a number taken from the series 0, 1, 2, 3, . . . , and having an average molecular weight of substantially 2500.

The diluent used in the preparation of this invention may be any of the well known diluents employed with resins and polymers in the paint industry. These include lower aliphatic ketones, lower alkyl esters of lower ali-phatic acids, benzene, and lower alkyl substituted ben-zenes, all containing up to about 14 carbon atoms. Non-limiting examples of these diluents are acetone, methyl-ethyl ketone, diethyl ketone, diisopropyl ketone, octyl pentyl ketone, methyl acetate, butyl acetate, octyl acetate, methyl propionate, octyl hexanoate, benzene, toluene, xylene, ethyl benzene and tert.-butyl-benzene. In addition, water may be used as the diluent where the binder is compatible therewith, such as methyl cellulose.

The amount of binder employed in the composition of this invention may vary from about 1 to about 5 percent, based on the total of inorganic solids employed. The exact amount of binder employed depends upon the de-gree of adherence necessary to maintain the coating on the metal surface during heat treatment. Since the or-ganic binder employed decomposes at the heat treatment temperature, it is preferred to employ only the amount of binder absolutely required. Excess binder is undesir-able because, upon decomposition, it may tend to form carbides of the metals in the particular alloy being treated. A preferred ratio of binder to inorganic solids in the com-position of this invention is 2 to about 4 percent.

The amount of binder employed may also be deter-mined as a ratio of the silicate constituent of the coating composition. The ratio of the silicate constituent to resin in the coating composition can vary from about 10 to 1 to about 2 to 1. At least 10 weight percent of resin based on the total weight of the silicate constituent is required

in order to impart sufficient adhesive quality to the coating material to permit it to stick to the metal and thus prevent oxygen from coming in contact with the surface of the metal during the period when the coated metal article is being brought up to the temperature at which the organic constituents of the coating are burned off in the furnace at the beginning of the heat treatment cycle. On the other hand, the amount of resin should be no more than about half the amount of silicate constituent since coatings which contain resin in excess of this amount tend to form blisters during the burning off of the organic material at the beginning of the heat treatment cycle. It is preferred to use 12 parts of resin for every 100 parts of silicate.

The resin may contain various customary plasticizers, the nature and amount of which are well known to those skilled in the art and will not be here discussed.

The amount of diluent employed with the coating can vary from 1 to 10 times the amount of solids present in parts by weight. The amount of diluent can be varied to conform to the desired manner of application, as for example, brushing, spraying, or dipping. A ratio of solids to diluent of 1 to 1 is found to be satisfactory when the coating is spread on the surface to be protected with a spatula. For spray application, it is found that the composition is of the proper consistency when the ratio of solids to diluent is about 1 to 10. Still greater amounts of diluent may be employed if desired. Ordinarily however, amounts in excess of that which would give a ratio of solids to diluent of 1 to 10 give no additional advantage and only increase the amount of diluent that must be evaporated from the coating.

An essential constituent of the composition of this invention, when it is desired to produce a coating which will readily spall from the surface of stainless steels, copper and copper alloys, is a metal chloride selected from the class consisting of calcium chloride and barium chloride. This constituent modifies the thermal coefficient of expansion of the coating to alter it substantially from that of the above noted alloys. When calcium or barium chloride is incorporated in this composition, the coating completely shatters and drops from the heat treated surfaces during its cooling cycle to leave a bright metal finish which requires no clean-up operations.

Nevertheless, inclusion of the calcium or barium chloride constituent will not cause the coating to spall completely from the heat treated surfaces of any of the superalloys. While the coating performs its protective function better if calcium or barium chloride is incorporated, it is not essential to add one of them when the coating is intended for use with the superalloys. This is also true insofar as stainless steel and the other alloys are concerned since, in many instances, it may be desired to retain the coating on the metal surfaces during a heat treatment which includes a multiplicity of heating and cooling cycles. For example, a commonly used heat treatment for a stainless steel such as PH15-7Mo, requires heating the metal to 1900° F. for 30 minutes, followed by cooling to room temperature, heating to 1750° F. for 10 minutes, cooling to -100° F. for 8 hours, reheating to 1075° F. for 60 minutes and finally cooling to room temperature. If the coating is one which will spall upon cooling, it will be necessary to recoat the article between heating cycles. There are, on the other hand, many situations in metal treatment where a single heating cycle is employed, as where a full anneal is accomplished between metal forming operations. For these reasons, the coating composition of this invention encompasses two specific embodiments, one containing calcium or barium chloride and one excluding these components.

Where the coating of this invention is used to protect the superalloys during heat treatment, a simple dip for 10 minutes or less in an acid pickling bath, such as one consisting of approximately 20 percent nitric acid and 5

percent hydrofluoric, will accomplish coating removal without difficulty. It should be remembered that no coating compositions, prior to the instant one, have been developed which can be removed from the superalloys without use of abrasive means. Furthermore, such conventional coatings fail in their protective function, whereas the coating of this invention affords sufficiently complete protection to practically eliminate oxide scale formation.

In addition to a particular coating composition and a process for heat treating metals, this invention also provides coated metal articles in which the coating protects the surface from oxidation at ambient atmospheric conditions as well as at elevated temperatures. In this manner, metal articles which are to be heat treated may be protected from oxidation for long periods of time prior to the actual treatment of the articles at elevated temperatures.

A coating composition of this invention comprises 100 parts of an aluminum silicate; from 50 to 400, and preferably 200, parts of a lead and boron-containing constituent such as (a) lead borate, (b) a mixture of lead oxide and boric acid, and (c) a lead borosilicate glass frit; from 1 to 50, and preferably 12, parts of a binder; and from 0 to 50, and preferably 20, parts of a fluxing agent selected from the class consisting of calcium chloride and barium chloride, all by weight of the total solids. It will also be found necessary to incorporate sufficient diluent to provide spreadable consistency to the composition. A preferred composition is one containing 13 percent kaolin, 25 percent of a mixture of 85 percent lead oxide and 15 percent boric acid, 1.5 percent of acryloid resin, and 60 percent toluene. A particularly preferred embodiment of the invention employs a lead borosilicate frit containing 60-65 percent lead as lead oxide, 20-25 percent boron as B_2O_3 and 10-15 percent silicon as SiO_2 .

The general process for the preparation of the coating employed in this invention consists of incorporating the constituents in a ball mill and grinding for a sufficient period of time to reduce the particle size of the solids to less than approximately 100 mesh as measured by the Taylor standard sieve. It is preferred to employ a ball mill lined with ceramic material and having ceramic tumbling balls therein. After removal from the mill, the composition may be diluted with additional diluent to whatever consistency is desired. The metal article which is to be heat treated is then coated with this coating composition by spreading, brushing or spraying so as to provide a coat having a thickness of from about 0.25 to about 5 mils and preferably from 0.25 to 0.5 mil. The coating is then allowed to air-dry from about one to about 10 minutes in order to allow the excess diluent to evaporate. The coating is sufficiently dry when it is firm to the touch and exhibits no tackiness. The coated metal article is then ready for heat treatment. If the metal article is to be subjected to a single heating cycle for purposes of giving it a full anneal, it may be placed in a furnace at ambient temperature and then heated to bring the coated article first up to a temperature at which the organic material in the coating is decomposed and burned off, leaving a film having no carbon or hydrogen therein. This usually occurs at from about 400° F. to 600° F. Following this, more heat is applied to bring the article to the particular heat treatment temperature desired for the metal concerned. After the heat treatment, the coated metal article is air-cooled until it is brought to ambient temperature. Upon cooling to room temperature, the coating will begin to peel and drop from the surface of the stainless steel specimen at about 500° F. Spalling will continue until no coating remains adhered to the surface and a bright metal finish is revealed. On the other hand, when an article composed of the same metal is subjected to the same heat treatment without the coating of this invention, the amount of scale formed is extremely thick and heavy and very

7

difficult to remove. When known coatings are used, the scale which is, nevertheless, formed is of less thickness but is still difficult to remove. With most such compositions, the scale can only be removed by mechanical means or by pickling in aqueous mineral acid solutions such as those consisting of hydrofluoric and nitric acids for extended periods of time.

The following examples will more clearly illustrate the composition, process, and articles of this invention.

Example I

A coating composition was prepared by mixing together 150 parts of kaolin with 255 parts of lead oxide, 45 parts of boric acid, 30 parts of calcium chloride, 18 parts of acrylic resins and 500 parts of toluene, milling this mixture in a porcelain ball mill for a period of about 48 hours, removing the composition from the mill, washing the mill out with 250 additional parts of toluene and adding the mill wash to the final composition. This composition was then sprayed onto an Inconel X article and the excess toluene permitted to evaporate at room temperature, leaving a film 0.25 mil thick. Inconel X is a trademark for a super-alloy containing from 70 to about 77 weight percent nickel, 14 to 16 percent chromium, 2.25 percent titanium, 0.7 percent cobalt, 0.4 percent aluminum, 5 percent iron, 0.3 percent manganese, with minor amounts of silicon, copper, carbon and sulphur making up the balance. The coated Inconel X article was then placed in an electric furnace which was at ambient temperature and heat was slowly applied, raising the temperature of the metal article to the decomposition point of the coating. Prior to reaching a temperature of about 700° F., the carbonaceous materials had been oxidized and driven off, leaving a fused anhydrous silicate film on the surface of the metal as shown by subsequent spectral analysis. The application of heat was continued, raising the temperature to 1625° F. The furnace, containing the Inconel X article, was maintained at this temperature for 4 hours. The heat treated article was then removed from the furnace and cooled in air to ambient temperature. As the specimen cooled, excess coating spalled. Analysis of the remaining surface film showed that it comprises a fused coating containing aluminum silicate, lead borate and calcium chloride. Although the coating adhered to the surfaces and was continuous in nature, photomicrographs indicated the absence of any intergranular penetration of the Inconel X surfaces. The part was then heat aged by being placed back in the furnace at a temperature of 1300° F. and maintained at that temperature for 10 hours, and then air-cooled. Upon removal from the furnace the article was immersed in an aqueous acid solution containing 5 weight percent hydrofluoric acid and 20 weight percent nitric acid for a period of 10 minutes. This removed the remaining coating, leaving a shiny smooth surface.

Example II

The procedure of Example I was repeated using a film 0.5 mil thick with the modification that the coated Inconel X article was placed in a furnace which was maintained at about 1625° F. The hydrocarbon portion of the coating immediately burned off leaving a fused aluminum silicate-lead borate-calcium chloride film on the surface. The sample was maintained in the furnace for a period of 4 hours, which was sufficient to relieve all stress within the metal. Thereafter, the article was removed and cooled as in Example I. The film was found to be 0.5 mil thick and upon immersion in the acid solution of Example I for a period of 15 minutes the scale was removed, leaving a shiny smooth surface.

Example III

The procedure of Example II was repeated using a film 5 mils thick with the modification that the furnace was maintained at a temperature of 1925° F. for full anneal

8

purposes. After full anneal for 30 minutes and subsequent cooling, excess film spalled and the remainder of the fused coating was found to be substantially 0.5 mil thick and was readily removed upon immersion in the acid solution.

Example IV

A coating composition was prepared as in Example I employing 50 parts of china clay, 150 parts of lead borate, 10 parts of barium chloride and 3 parts, all by weight, of an alkyd resin obtained by reacting glycerol with phthalic anhydride. The coating composition contained one part of methylethyl ketone diluent to one part of the solids. The composition was applied with the aid of a putty knife to the surface of a H-11 type steel sheet measuring $\frac{3}{8}$ " x 6" x 24" so as to provide a film substantially 2 mils thick. The general composition of the H-11 type steels, in percent by weight, is approximately 0.40 percent C, 5 percent Cr, 1.3 percent Mo, 0.5 percent V plus small amounts of Mn, Si, and other alloying elements, with the balance being iron. The coated piece of steel was allowed to stand exposed to the atmosphere for a period of six months without any indication of deterioration of the film or of corrosion of the steel beneath the film. The sheet was next placed in a furnace and maintained at a temperature of 1850° F. for a period of one-half hour. The sheet was cooled to ambient temperature and as cooling progressed below about 500° F. or 600° F., spalling of the coating became more and more apparent until a surface, containing no coating, remained at room temperature. No coating removal was required.

A steel sheet was heat treated as in Example IV, but without a protective coating. An oxide scale formed on the surface which required abrasive cleaning for removal.

Example V

The procedure of Example I was repeated in the preparation of a coating composition consisting of 150 parts of feldspar, 200 parts of lead borate, 30 parts of calcium chloride and 25 parts of an epoxy resin obtained from the reaction of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)propane in equimolar quantities. The ratio of n-heptane diluent to combined resin and solids was substantially 10 to 1. This composition was sprayed onto a René 41 specimen containing 51 weight percent Ni, 11 weight percent Co, 10 weight percent Mo, 19 weight percent Cr, and 3 weight percent Ti to provide a film substantially 0.5 mil in thickness. The film was allowed to air-dry about 5 minutes and then the coated specimen was placed in a furnace maintained at 1950° F., where it was kept for 30 minutes. Following this, the specimen was air-cooled and the coating on the heat treated specimen was found to be substantially 0.5 mil in thickness. This scale was removed from the surface by immersion in the acid solution described in Example I.

Heat treatment of uncoated René 41 at 1950° F. for one-half hour as in Example V produced oxide scale which could not be removed by immersion in the acid solution but had to be removed by abrasive methods.

Example VI

A high carbon tool steel rod measuring 1 inch in diameter and 3 inches in length was coated with the composition described in Example I to a depth of 1 mil. The analysis of this tool steel was 0.72 percent C, 0.25 percent Mn, 0.20 percent Si, 40 percent Cr, 18.25 percent W, 1.5 percent V, with the balance Fe. The coated rod was then placed in a furnace maintained at a temperature of 1550° F., where it was soaked for 30 minutes. The specimen was then removed from the furnace and placed in a 2350° F. furnace where it was retained until it reached furnace temperature. It was then quenched in oil, and water-washed to remove oil. The specimen had a bright, shiny metal finish. It was later coated with a composition identical to that of Example

I except that no calcium chloride was included. After the diluent evaporated from the coating, the specimen was placed in a furnace maintained at a temperature of 1050° F. and retained therein for a period of two hours, after which it was air-cooled to room temperature. This same 1050° F. cycle was repeated in order to give the specimen the desired temper. After air-cooling was completed, the specimen was immersed in a conditioning bath, prepared in accordance with Patent No. 2,861,015, and containing 50 percent sodium hydroxide and 1 percent sodium dichromate and retained therein for 5 minutes. Visual and micrographic examination of the specimen showed the surface to be bright and shiny and indicated a complete absence of any decarburization or other surface degenerated conditions. The Rockwell C hardness of the specimen was 64.

Example VII

The procedure of Example VI was repeated with an identical specimen but without application of any coating. During the heat treatment to 2350° F., excessive scaling and carburization to a depth of .020 inch per surface occurred.

Examples VI and VII illustrate the substantial advantages obtained in employing the coating of this invention to protect a metal during heat treatment. While, in Example VII, a scale which was 1/2" thick formed as the result of heat treatment, no scale formed on the specimen pre-coated with the composition of this invention, nor did any carburization occur.

Example VIII

Following the procedure of Example I, a coating composition of this invention was prepared by milling 300 parts of glass ceramic frit containing 60-65 percent lead oxide, 10-15 percent silica, and 20-25 percent boric anhydride, with 150.5 parts kaolin, 30 parts calcium chloride, and 600 parts of toluene. After milling, the mill was washed with additional toluene and the toluene wash was combined with make-up toluene to add an additional 100 parts of toluene to the composition. Prior to adding the wash and make-up toluene, 18.3 parts of acrylic binder were dissolved therein. In this way, a portion of the silicon constituent was added to the mixture along with the boron and lead constituents and the majority of the silicon constituent was added to the composition along with the aluminum constituent.

An alternate method for preparing compositions of this invention is to combine the minerals or compounds used to provide the various constituents and form therefrom a frit by firing the mixture to an appropriate temperature. This combined frit is then milled and the diluent and binder added after milling. The relative proportions of boron constituent, lead constituent, silicon constituent, and aluminum constituent employed in the composition of this invention vary depending upon the melting point desired for the final composition. The melting point desired depends upon the nature of the heat treatment to be used. When a high melting point is required, the composition will be higher in the aluminum and silicon constituents, while for a low melting composition large amounts of the lead and boron constituents are employed.

Although this invention has been fully described and illustrated, it will be understood that this disclosure is for purpose of exemplification and is not to be taken by way of limitation, the spirit and scope of the invention being limited only by the terms of the appended claims.

I claim:

1. A metal preheat-treat coating composition consisting essentially of about 12 percent kaolin; 24 percent of a lead borosilicate frit containing 60-65 percent lead oxide, 10-15 percent silicon dioxide and 20-25 percent boric an-

hydride; 2.5 percent calcium chloride; 1.5 percent acryloid resin; and 60 percent toluene.

2. A process for heat treating a stainless steel article comprising applying a coating to the surfaces thereof, the coating composition consisting essentially of oxygenated inorganic nonmetallic constituents of aluminum, silicon, boron and lead, containing 10-40 percent aluminum constituent, based on aluminum oxide, 10-40 percent silicon constituent, based on silicon dioxide, 20-70 percent lead constituent, based on lead oxide, and 5-25 percent boron constituent, based on boric anhydride; heating the coated article to fuse said coating; thereafter heat treating said coated stainless steel article at a predetermined temperature, and subsequently cooling said coated stainless steel article to room temperature.

3. A process for heat treating an article constructed of a superalloy comprising applying a coating to the surfaces of said article, the coating composition consisting essentially of 100 parts of aluminum silicate, from 50 to 400 parts of a mixture of lead oxide and boric acid, from 1 to 50 parts of a polymeric organic binder, and sufficient diluent to give the composition a spreadable consistency; heating said coated article to a temperature sufficient to fuse said coating; thereafter heat treating said coated metallic article at a predetermined temperature; subsequently cooling said article to room temperature, thereby causing spalling of excess fused coating, and finally immersing said article in an acid solution to completely remove any remaining traces of coating.

4. A process for heat treating a stainless steel article, the process comprising applying a coating composition to the surfaces of said article; heating the coated article to fuse the coating; thereafter heat treating the coated article to a predetermined temperature, and subsequently cooling the coated article to room temperature; said coating composition consisting essentially of 100 parts of an aluminum silicate; from 50 to 400 parts of a lead and boron containing constituent selected from the class consisting of (a) lead borate and (b) a mixture of lead oxide and boric acid; up to about 50 parts of calcium chloride as a fluxing agent; from 1 to 50 parts of a polymeric organic binder, and sufficient diluent to give the composition a spreadable consistency.

5. A process for heat treating a stainless steel article, the process comprising applying a coating composition to the surfaces of said article; heating the coated article to fuse the coating; thereafter heat treating the coated article to a predetermined temperature, and subsequently cooling the coated article to room temperature thereby causing the coating to spall completely from said surfaces and to leave said surfaces scale-free and non-carburized; said coating composition consisting essentially of about 12 percent kaolin; 24 percent of a lead borosilicate frit containing 60-65 percent lead oxide, 10-15 percent silicon dioxide and 20-25 percent boric anhydride; 2.5 percent calcium chloride; 1.5 percent acryloid resin; and 60 percent toluene.

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