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METHOD OF HEAT TREATING METALS EMPLOYING AN OXIDATION SCALE INHIBITOR

Edward B. Schneider, Canoga Park, Calif., assignor to North American Aviation, Inc.

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This invention relates to a process of heat treating metals so as to inhibit oxidation scale formation. More particularly, this invention relates to a process of covering metal surfaces during heat treating to inhibit scale formation.

When metals are heat treated, a thick oxide scale forms on the surface. This scale not only represents the destruction of a fraction of the metal at the surface of the article but it is also very difficult to remove. In order to remove this oxide film, it is usually necessary to sandblast the article, a costly and time consuming procedure.

It is therefore the object of this invention to provide a method for protecting the surface of metal articles during heat treating. Another object is to provide a process which inhibits scale formation on the surface of metal articles during heat treating. It is likewise an object of this invention to provide a process of heat treating metal articles which reduces the amount of scale formed on the surface of the metal. Another object of this invention is to provide a process for heat treating metal articles employing a coating composition which inhibits oxide scale formation during heat treatment and which can be readily removed by acid action after heat treatment. Still other objects of this invention will become apparent from the discussion which follows.

The above and other objects of this invention are accomplished by the process of heat treating metal articles comprising applying to the surface to be heat treated an organic ammonium clay compound in which at least one of the hydrogens on the nitrogen is replaced by an organic radical.

The type of clay mineral to be used may vary. For optimum scale inhibition in the process of this invention, it is best to use a bentonite clay, a constituent of which is montmorillonite.

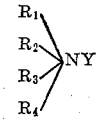
It is preferred to use an organic ammonium clay compound in which all four hydrogens on the nitrogen atom have been replaced by hydrocarbon groups. Hence, an embodiment of this invention is a process of heat treating metal articles comprising applying to the surface to be heat treated a coating composition consisting essentially of (1) a quaternary ammonium bentonite compound in which each of the hydrogens on the nitrogen atom has been replaced by a hydrocarbon group, (2) an organic binding composition and (3) an organic hydrocarbon diluent wherein the ratio of quaternary ammonium bentonite compound-to-binder composition is from about 10:1 to about 1:5 and the amount of diluent is sufficient to give the composition a spreadable consistency, heating the coated article to a temperature sufficiently high to decompose said coating composition at the outset of said heat treating, covering the surface with fused bentonite and thereby inhibiting oxidation of the surfaces during heat treating.

Non-limiting examples of metals that are satisfactorily protected from excessive scale formation by this process are iron; nickel; cobalt; steel; various chromium, nickel and carbon steels; molybdenum; titanium; and alloys of

these metals. Upon removal of the heat treated coated metal articles from the furnace, it is found that the thickness of the scale formed on the surface is only a fraction of the amount of scale formed when a similar metal article is heat treated under comparable conditions without the protective coating employed in this process. The scale that does form in carrying out the process of this invention is modified so that it is not as adherent as is the case when no coating is used, and upon pickling the treated metal article in an aqueous acid solution containing a mixture of hydrofluoric and nitric acids, the surface film is completely removed leaving a shiny smooth surface.

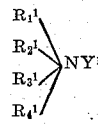
The coated metal article may be gradually heated to a temperature sufficiently high to decompose the coating composition covering the surface with fused bentonite film and thereby preventing oxidation of the surface during subsequent heat treating. Alternatively, the coated article is placed in a furnace at an initial temperature sufficiently high to decompose the coating composition at the outset of the heat treating, forming a film of fused bentonite on the metal surfaces. This prevents excessive oxidation of the surfaces during the heat treating.

One of the components of the coating composition employed in the process of this invention is an organic ammonium bentonite compound represented by the general formula



wherein Y is a clay substituent; N is nitrogen; each of R_1, R_2, R_3 and R_4 is selected from the class consisting of hydrogen and an organic radical, said organic radical having from 1 to about 20 carbon atoms; and wherein not more than 3 of said R_1, R_2, R_3 and R_4 groups are hydrogen atoms.

It is preferred to employ a hydrocarbon substituted ammonium bentonite clay composition represented by the general formula



wherein the N is nitrogen; Y^1 is a clay substituent such as bentonite including montmorillonite, a component of bentonite; the R^1 groups may be the same or different and represent hydrocarbon groups which have replaced hydrogen atoms attached to the nitrogen atom and are selected from the class consisting of alkyl, cyclo-alkyl, alkenyl, cyclo-alkenyl, aryl, arylkyl and alkaryl groups having from 1 to about 20 carbon atoms.

Non-limited examples of mono-hydrocarbon substituted ammonium bentonite are 2-ethylhexylammonium bentonite hexadecylammonium montmorillonite, dodecylpyridinium bentonite, octadecylammonium bentonite, etc. Examples of dihydrocarbon substituted ammonium clay compounds are di - 2 - ethylhexylammonium bentonite, methylnaphthylammonium bentonite, didodecylammonium bentonite, etc. Examples of tri-hydrocarbon substituted ammonium bentonite compounds are trioctadecylammonium bentonite, methylcyclohexyldodecylammonium bentonite, dimethyloctadecylammonium montmorillonite, etc. Non-limiting examples of tetra-hydrocarbon-substituted ammonium bentonite compounds which constitute a component of the coating composition employed in the process of this invention are tetramethylammonium bentonite, dimethyldiethylammonium montmorillonite, dimethyldioclodecylammonium benton-

ite, methyltributylammonium montmorillonite, dimethyldodecylbenzylammonium bentonite, tetrabutylammonium bentonite, methyltrieicosylammonium bentonite, diethyldiphenylammonium bentonite, trimethylnaphthylammonium monmorillonite, dibutyldicyclohexylammonium, bentonite, diethyldiisohexenylammonium bentonite, dipropenyldioctadecylammonium bentonite, dimethyldipropenylammonium bentonite, dimethyldi(2,4-di-heptylphenyl)ammonium bentonite.

Other organic ammonium clay compounds which are employed in the process of this invention are compounds in which the organic substituent on the nitrogen atom is an ether containing hydrocarbon, i.e., the substituent contains one or more —C—O—C— groups therein, as for example, ethylhexoxypropylammonium bentonite, octylphenoxyethoxyethyldimethylammonium bentonite, etc. Other ammonium clay compounds include rosinammonium bentonite, pyridinium bentonite, etc.

The amine: clay ratio in the organic ammonium clay compound can have a value of 50 to 200 milliequiv. amine per 100 grams of clay. It is preferred to use a clay composition in which the amine: clay ratio is 75–115 milliequiv. amine per 100 grams of clay in order to obtain better scale inhibition and modification upon heat treating of metals coated with a composition of the clay compound. Especially preferred is a clay compound in which the amine: clay ratio is substantially 80 milliequiv. amine per 100 grams of clay, the theoretical base exchange value for the combination.

The above hydrocarbon substituted ammonium bentonite compounds are made by the process substantially as described in Kolloid-Zeitschrift 137. Band, Heft 1, Seite 40 (1954) and in U.S. 2,531,427. The hydrocarbon substituted ammonium bentonite is in a powdered form of a particle size such that it will pass through a 200 mesh screen.

The binding composition employed with the bentonite compound can be any polymeric, resinous, or plastic material which will serve to bind the particles of the organic ammonium clay compound 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, polyurethans, alkyd resins, copolymers of various resins, and the like. 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, ethylmethylacrylate, n-propylmethacrylate, diethyleneglycolmethacrylate, methylethacrylate, etc. An example of an alkyl 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 polyhydric 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 $ONC—C_3H_6—O[C_3H_6—O—]_nC_3H_6—CNO$ 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 the coating used in 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 aliphatic acids, benzene, and lower alkyl substituted benzenes, 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, methylacetate, butylacetate, octylacetate, methyl propionate, octyl hexanoate, benzene, toluene, xylene, ethyl benzene, tert.-butyl-benzene, etc.

The ratio of the bentonite compound-to-resin in the coating composition can vary from about 10:1 to about 1:5. It is found that at least 10 weight percent of resin based on the total weight of bentonite compound plus resin 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 treating cycle. On the other hand, the amount of resin should be no more than about five times the amount of bentonite compound since coatings which contain resin in excess of this amount tend to form blisters during the burning off of the organic material at the begining of the heat treating cycle period. The preferred ratio of organic ammonium clay compound-to-resin is 2:3.

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

The amount of diluent employed with the coating can vary from 1 to 10 times the amount of combined bentonite and resin compound in parts by weight. The amount of diluent can be adjusted to suit the particular application, namely, brush application, spraying, dipping or other appropriate means for spreading on the coating on the surface. A ratio of combined bentonite compound and resin-to-diluent of 1:1 is found to be satisfactory when the coating is spread with a spatula on the surface to be protected. For spray application, it is found that the composition is of the proper consistency when the ratio of solids to diluent is about 1:10. Still greater amounts of diluent may be employed if desired, however, ordinarily amounts in excess of that which would give a ratio of solids-to-diluent of 1:10 give no additional advantage and only increase the amount of diluent that must be evaporated from the coating.

Small amounts of low boiling organic compounds such as from about 0.1 to about 5 weight percent ethyl alcohol based on the weight of the diluent, may be added to aid in the subsequent evaporation of the diluent from the coating.

In addition to a process for heat treating metals, an embodiment of this invention 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 treating of the articles at elevated temperatures. Therefore, an embodiment of this invention includes a metal article having a coating consisting of a quaternary ammonium bentonite composition of the type described hereinabove, and an organic binding composition in which the ratio of bentonite compound-to-binding composition is from about 10:1 to about 1:5.

As stated hereinabove, the hydrocarbon groups on the quaternary ammonium bentonite compound can have from 1 to about 20 carbon atoms and are selected from a class consisting of alkyl, cyclo-alkyl, alkenyl, cyclo-alkenyl, aryl, arylkyl and alkaryl groups. For example, an embodiment of this invention comprises an article consisting of a metal such as iron, stainless steel, various carbon steels, Inconel X, titanium, cobalt, etc., in other words, any metallic article having a coating consisting of dimethyldioctadecyl ammonium bentonite admixed with

methylmethacrylate resin. The ratio of the bentonite compound to resin can vary from 10:1 to 1:5. A coating which is found to be especially suited for protecting metal surfaces is one in which the ratio of dimethyldioclodecyl ammonium bentonite-to-methylmethacrylate is 2:3 and metal articles coated with this composition constitute a preferred embodiment of this invention.

The general process for the preparation of the coating employed in this invention consists of mixing the clay compound, having a particle size such that it will pass through a 200 mesh screen, with the resin and a portion of the diluent sufficient to make a composition having a paste consistency and then subjecting this to milling for about 2 to 10 hours in a ball mill. It is preferred to employ a ball mill lined with ceramic material and having ceramic tumbling balls therein. The mixing in the ball mill serves to thoroughly mix the bentonite compound with the resin. After removal from the mill, the composition is diluted with additional diluent to the desired consistency. 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., preferred 0.5 to 2 mils. The coating is then allowed to airdry for a short period of time of from about one to about ten 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 treating. As stated above, the metal article may be placed in a furnace originally at ambient temperature and then heat applied to bring the temperature of the coated article first up to a point at which the organic material in the coating is decomposed and burned off, leaving a fused anhydrous bentonite film having no carbon, hydrogen or ammonium therein. This usually occurs at a temperature of substantially 500° F. to 700° F. Following this, more heat is applied to bring the article to the heat treating of Inconel X, the metal is heat aged or hardened at a temperature of substantially 1300° F. for 10 hours. For stress relieving, it is maintained at a temperature of substantially 1625° F. for a period of 4 hours, while annealing is performed by subjecting the metal to a temperature of substantially 1925° F. for 10 to 20 minutes. After the heat treatment, the coated metal article is air cooled until it is brought to ambient temperature. It is found that only a minor amount of scale is formed on the surface of the metal when the metal is covered with the bentonite film. On the other hand, when an article composed of the same metal is subjected to the same heat treatment without the bentonite film the amount of scale formed is many times greater than the scale formed on the coated article. The fused bentonite film and scale formed on the coated article is readily removed by subjecting it to the action of aqueous mineral acid solutions such as aqueous solutions of hydrofluoric and nitric acids for a period of from about 10 to about 30 minutes. When, however, the same metal is heat treated without the bentonite film, the oxide scale is not only formed in manifold greater quantities but it cannot be removed by acid solutions. Instead, it must be sandblasted, vapor blasted, or machined off.

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

Example I

A coating composition was prepared by mixing together two parts of dimethyldioctadecyl ammonium bentonite with three parts of methylmethacrylate resin and 20 parts of toluene, milling this mixture in a porcelain ball mill for a period of about four hours, removing the composition from the mill, washing the mill out with 20 additional parts of toluene and adding the mill wash to the final composition. The bentonite compound, resin and toluene were then subjected to agitation by stirring until a substantially homogeneous composition was obtained. This composition was then sprayed onto an Inconel X article and the excess toluene permitted to evaporate at ambient temperatures leaving a film 0.25 mil thick. The Inconel X is a trade name for metal containing from 70 to about 77 weight percent nickel, 14–16 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 silicone, 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. At a temperature of substantially 600° F., the resin and the hydrocarbon radicals on the bentonite compound were oxidized and the nitrogen and water also driven off leaving a fused anhydrous bentonite or anhydrous aluminum silicate film on the surface of the metal as shown by subsequent spectral analysis. The application of the heat was continued, raising the temperature to substantially 1625° F. The furnace and the Inconel X article was maintained at this temperature for substantially four hours. The heat treated Inconel X was then removed from the furnace and cooled with a stream of air to ambient temperature. As the specimen cooled, the excess coating spalled and was thus removed. However, a part of the coating was found to have fused with a small amount of scale which had been formed during the heat treating. The scale that had formed on the surface of the Inconel X was found to be substantially 1 mil thick. Analysis of the surface scale showed there was no hydrocarbon, nitrogen or water present and that only aluminum silicate, aluminum oxide, silica, and components of the Inconel X made up the film indicating that the film consisted mainly of fused bentonite. It was then heat aged by being placed back in the furnace at a temperature of substantially 1300° F. and maintained at that temperature for ten hours, and then air cooled. Upon removal from the furnace, the surface appeared white and smooth. The article was then immersed in an aqueous acid solution containing 3 weight percent hydrofluoric acid and 35 weight percent nitric acid for a period of substantially ten minutes. This removed the scale leaving a shiny smooth surface.

Good results are also obtained when ethylhexoxyammonium bentonite is employed in the process of Example I and 1 weight percent ethyl alcohol based on the weight of the diluent is used in the coating composition.

Example II

The procedure of Example I was repeated using a film 0.5 mils thick with the modification that the coated Inconel X article was placed in a furnace which was maintained at a temperature of substantially 1625° F. The hydrocarbon portion of the coating immediately burned off. The nitrogen and water was also driven off leaving a fused bentonite film on the surface. The sample was maintained in the furnace for a period of substantially four hours 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 substantially 1 mil thick and upon immersion in the acid solution of Example I for a period of substantially fifteen minutes the scale was removed leaving a shiny smooth surface.

Good results are obtained when dodecylpyridinium ammonium bentonite is employed in the process of Example II.

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 substantially 1925° F. for annealing purposes. After annealing for 10 to 20

minutes and subsequent cooling, the excess anhydrous fused bentonite film spalled and the remainder of the fused bentonite coating was found to be substantially 1 mil thick and was readily removed upon immersion in the acid solution.

Example IV

A coating composition was prepared as in Example I employing hexadecyl ammonium bentonite having an amine:clay ratio of 50 milliequiv. amine per 100 grams of clay, and alkyd resin obtained by reacting glycerol with phthalic anhydride. The ratio of bentonite compound-to-resin was 10:1. The coating composition contained one part of methylethyl ketone diluent-to-one part of combined bentonite compound and resin. The composition was applied to the surface of a 43–40 steel billet measuring 6" x 6" x 24" with the aid of a putty knife so as to provide a film substantially 2 mils thick. The composition of the 43–40 steel in parts by weight is substantially 0.37–0.44 carbon, 0.6–0.95 manganese, 0.2–0.35 silicon, 1.55–2.0 nickel, 0.65–0.95 chromium, 0.2–0.3 molybdenum, and 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 visible indication of deterioration of the film or of corrosion of the steel beneath the film. The billet was next placed in a furnace and maintained at a temperature of substantially 1900° F. for a period of substantially six hours. It was then placed on a hand mill and reduced to a sheet .050 inch thick. The sheet was cooled to ambient temperature and was found to have a scaly layer on the surface approximately 1 mil thick. This film was removed by immersion in an acid solution as described in Example I leaving a smooth surface.

A steel billet was heat treated as in Example IV and reduced, but without a protective coating. An oxide scale formed on the surface which was reduced to a powder by the action of the hand mill. The scale still adhering to the surface after the hammer mill processing required blasting for removal.

Good inhibition and modification of the scale is also obtained when the procedure of Example IV is repeated with octylphenoxyethoxyethyldimethylammonium montmorillonite in which the amine:montmorillonite ratio is substantially 200 milliequiv. amine per 100 grams of montmorillonite.

Example V

The procedure of Example I was repeated in the preparation of a coating composition consisting of tetraeicosyl ammonium bentonite and an epoxy resin obtained from the reaction of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)propane in equimolar quantities. The amine:clay ratio in the ammonium bentonite compound was substantially 200 milliequiv. of amine per 100 grams of clay. The ratio of bentonite compound to resin was substantially 1:5. The ratio of n-heptane diluent to combined resin and bentonite compound was substantially 10:1. This composition was sprayed onto a titanium specimen containing 6 weight percent aluminum, 4 weight percent vanadium, and 90 weight percent titanium to provide a film of substantially 2 mils in thickness. The film was allowed to airdry for a period of substantially five minutes and then the coated titanium speciman was placed in a furnace maintained at substantially 1700° F. where it was kept for a period of about thirty minutes. Following this, the specimen was water quenched and the scale on the heat treated titanium was found to be substantially 1 mil in thickness. This scale was likewise removed from the surface of the titanium by immersion in the acid solution as described in Example I.

Heat treating of uncoated titanium at 1700° F. for a period of ½ 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 vapor blasting.

Good results are likewise obtained when the amine:clay ratio of the organic ammonium compound employed in Example V is 75 milliequiv. of amine per 100 grams of clay, and also when the ratio is 115 milliequiv. of amine per 100 grams of clay.

Example VI

A piece of 10–20 steel measuring 3" x 1" x ½" was coated with the composition described in Example I to a depth of 1 mil. The coated piece of steel was then placed in a furnace maintained at a temperature of 1800° F. where it was kept for a period of substantially one hour. The coated piece of steel was then removed from the furnace and air cooled to ambient temperature. The scale on the heat treated specimen was found to be from 1–3 mils in thickness over the surface of the metal. The heat treated coated steel article was then immersed in a hydrofluoric-nitric acid bath for a period of substantially ten minutes as described in Example I. This removed the scale leaving a smooth surface. The 10–20 steel used in this experiment has the following composition in percentage by weight: 0.18–0.23 carbon; 0.30–0.60 manganese; a maximum of 0.04 phosphorous, up to 0.05 sulphur, and the balance being composed of iron.

Example VII

The procedure of Example VI was repeated with a piece of 10–20 steel without coating it with the hydrocarbon substituted ammonium bentonite composition. During the one hour heat treatment at 1800° F., a porous powdery layer, 8 mils thick, of iron oxide developed on the surface of the steel specimen.

Examples VI and VII above illustrate the substantial advantage obtained in employing a coating of organic ammonium bentonite compounds on a metal being heat treated. The thickness of the scale in Example VI was from 1–3 mils while that in Example VII was 8 mils thick, a decrease of from 166 percent to 500 percent in the thickness of the oxide scale when a protective coating is used.

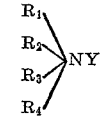
The ratio of amine:clay in organic ammonium bentonite compounds employed in Examples I, II and III was substantially 80 milliequiv. of amine per 100 grams of bentonite.

One of the advantages of the process of this invention is that metal ingots or billets can be forged to more even and accurate tolerances because of the substantial absence of oxide scale formation. Another advantage is that the loss of metal is reduced also due to the lack of excessive scale formation when the metals are heat treated in the presence of a coating made of an ammonium bentonite compound. Still another advantage is that the fused bentonite film formed on the metal surfaces at high temperatures can be easily removed with a considerable saving in both time and labor. The practice of this invention also provides metal articles having a protective coating which shields them from corrosive attack by oxygen and other elements.

Although the invention has been described and illustrated in detail, it is to be understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of this invention being limited only by the terms of the appended claims.

I claim:

1. The process of heat treating metal articles comprising applying to the surface to be heat treated a coating composition consisting essentially of (1) an organic ammonium clay compound represented by the general formula



wherein Y is clay substituent; N is nitrogen; R_1, R_2, R_3 and R_4 are selected from the class consisting of hydrogen and an organic radical; and wherein not more than 3 of said R groups are hydrogen atoms; (2) an organic binding composition and (3) an organic hydrocarbon diluent wherein the ratio of organic ammonium clay compound-to-binder composition is from about 10:1 to about 1:5 and the amount of diluent is sufficient to give the composition a spreadable consistency, heating the coated article to a temperature sufficiently high to decompose said coating composition at the outset of said heat treating, covering the surface with fused bentonite and thereby inhibiting oxidation of the surfaces during heat treating.

2. The process of heat treating metal articles comprising applying to the surface to be heat treated a coating composition consisting essentially of (1) a quaternary ammonium bentonite compound in which each of the hydrogens on the nitrogen atom has been replaced by a hydrocarbon group, (2) an organic binding composition and (3) an organic hydrocarbon diluent wherein the ratio of quaternary ammonium bentonite compound-to-binder composition is from about 10:1 to about 1:5 and the amount of diluent is sufficient to give the composition a spreadable consistency, heating the coated article to a temperature sufficiently high to decompose said coating composition at the outset of said heat treating, covering the surface with fused bentonite and thereby inhibiting oxidation of the surfaces during heat treating.

3. The process of claim 2 wherein each of said groups on said quaternary ammonium bentonite has from 1 to about 20 carbon atoms.

4. The process of claim 2 wherein each of said hydrocarbon groups on said quaternary ammonium bentonite is selected from the class consisting of alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, arylkyl and alkaryl groups having from 1 to about 20 carbon atoms.

5. The process of claim 2 wherein each of said hydrocarbon groups on said quaternary ammonium bentonite is selected from the class consisting of alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, arylkyl and alkaryl groups having from 1 to about 20 carbon atoms and said binding composition is an acrylate resin.

6. The process of heat treating metal articles comprising applying to the surface to be heat treated a coating composition consisting essentially of (1) a quaternary ammonium bentonite compound in which each of the hydrogens on the nitrogen atom has been replaced by a hydrocarbon group, (2) an organic binding composition and (3) an organic hydrocarbon diluent, wherein the ratio of quaternary ammonium bentonite compound-to-binder composition is from about 10:1 to about 1:5 and the amount of diluent compound is sufficient to give the composition a spreadable consistency, heating the articles at an initial temperature sufficiently high to decompose said coating composition at the outset of the heat treating, forming a film of fused bentonite on the metal surfaces and thereby preventing excessive oxidation of the metal surfaces.

7. A process of heat treating metal articles comprising applying to the surface to be heat treated a coating composition consisting essentially of dimethyldioctadecyl ammonium bentonite, a methylmethacrylate resin binding composition, and a toluene diluent wherein the ratio of quaternary ammonium bentonite compound-to-binder composition is from about 10:1 to about 1:5 and the amount of toluene is sufficient to give the composition a spreadable consistency, heating the coated article to a temperature sufficiently high to decompose said coating composition at the outset of said heat treating, covering the surface with fused bentonite and thereby preventing oxidation of the surfaces during heat treating.

8. The process of claim 7 wherein the ratio of said bentonite compound-to-said resin is 2:3.

9. The process of claim 7 wherein the ratio of bentonite:resin:toluene is 2:3:40.

10. A metal article having a coating consisting of a quaternary ammonium bentonite compound in which each of the hydrogens on the nitrogen atom has been replaced by a hydrocarbon group and an organic binding composition in which the ratio of bentonite compound-to-binding composition is from about 10:1 to about 1:5.

11. An article as defined in claim 10 in which the hydrocarbon groups on said quaternary ammonium bentonite have from 1 to about 20 carbon atoms.

12. The article as defined in claim 11 wherein the ratio of said bentonite compound-to-said resin is 2:3.

13. An article as defined in claim 10 in which said hydrocarbon groups on said quaternary ammonium bentonite compound is selected from the class consisting of alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, arylkyl and alkaryl groups having from 1 to about 20 carbon atoms and said binding composition is an acryate resin.

14. A metal article having a coating consisting of dimethyldioclodecyl ammonium bentonite and methylmethacrylate resin wherein the ratio of said bentonite compound-to-said resin is from about 10:1 to about 1:5.

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