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COATED METALLIC ARTICLE FOR USE AT ELEVATED TEMPERATURES

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6 Claims. (Cl. 117—53)

This invention relates to the protection of metallic articles against scaling and oxidation at elevated temperatures.

It is among the objects of the invention to provide metallic articles, especially ferrous metal articles, with a surface coating which is refractory, is resistant to scaling and oxidation at high temperatures in oxidizing atmospheres, is cheap and easily produced from readily available materials, and greatly increases the life of metallic articles exposed to oxidation at elevated temperatures.

A particular object is to provide such a coating which is coherent and is strongly bonded, or adherent, to the underlying metal, and which is resistant to destruction by the stresses to which the article is subjected in use.

Other objects of the invention are to provide a method of producing coatings of the type referred to, and to provide materials for making such coatings and for practicing the method provided by the invention.

Yet another object is to provide a method of operating ferrous metal articles at elevated temperatures whereby oxidation and scaling are repressed and the life of such articles is thereby prolonged.

Yet other objects will appear from the following description.

The invention is predicated upon my discovery that its stated objects are attained by fusing on the surface of the article which is to be protected a coating of a mixture of cast iron enamel ground coat, at least one non-acidic scale-resisting refractory material which when bonded by the fused ground coat renders the coating refractory and resistant to scaling, and silica. Preferably, nickel oxide is used as the scale-resisting protective refractory, either alone or with another non-acidic refractory, or for less severe service an oxygen compound of chromium, such as chrome ore, may be used. For most purposes it is advantageous to use both nickel oxide and chrome ore, although other non-acidic refractory materials such as aluminum oxide, burned magnesite, bauxite, diaspore, kaolin, fire clay and similar refractory materials may be used with nickel oxide in place of the chrome ore.

The term "cast iron ground coat" is used herein for brevity to refer to the well-recognized class of ground coat enamel compositions used for cast iron and steel (see, for example, "Enamels" by A. I. Andrews, pages 188–94). These are widely used and readily available wherever enameling operations are performed, so that the term will be understood by those skilled in the art. Any of the standard cast iron enamel ground coats may be used in preparing the mixtures used in the practice of the invention. For many purposes I now prefer to use the ground coats used in wet process cast iron enameling, which are sometimes called bisque ground coats. These adhere satisfactorily, as I have found, to both iron and steel in both sheet and cast form, and when used in accordance with the invention provide coatings which satisfactorily protect the metal without attacking it further, even at 2100° F. Coatings made using bisque, or wet process cast iron, ground coats afford equally satisfactory protection at both moderately elevated and high temperatures and are therefore preferred for most purposes in the practice of this invention, although their composition may need to be adjusted somewhat for use at moderately elevated temperatures, e. g. at 1000° to 1500° or 1600° F., as will appear.

Most of the cast iron ground coats are free from or very low in cobalt oxide. This is desirable where the article is to be used at more than moderately elevated temperatures, say above about 1500° or 1600° F. They are desirable also for service in which the coated article is stressed or shocked to any great extent. The ground coats commonly used with sheet steel or sheet iron are less desirable for coating articles which are used at more than moderately high temperatures, say above 1500° F., because they seem to exhibit a progressive action upon the underlying metal when exposed for long periods at such temperatures.

The cast iron enamel ground coats used in the practice of the invention themselves afford little resistance to scaling, for example of iron and steel articles, at elevated temperatures, as actual tests have demonstrated. I have found, however, that they serve admirably, particularly when their refractoriness is increased by admixture with silica, as a matrix, or vitrified medium for suspending substantial amounts of scale-resisting refractory materials which act to prevent or reduce oxidation and scaling of metals, e. g. iron and steel, covered by such coatings, whereby the life of such articles under exposure to elevated temperatures is increased greatly.

As indicated above, the best results are obtained with coating materials made from enamel ground coat, preferably bisque ground coat, and substantial amounts of nickel oxide and chrome ore or other similar oxygen compound of chromium. Chrome ore is preferred, however, be-

cause it produces particularly refractory coatings. Most suitably the chrome ore used is one which contains from 50 to 60 per cent of chromic oxide. While the exact reason for this is not certain, I now believe that this is due in part to reaction of the nickel oxide, perhaps with silica or with chrome, and to the substantial amounts of magnesia and alumina which occur in most chrome ores.

The proportions in which the enamel ground coat, scale-resisting refractory material such as nickel oxide and chrome ore, and silica are mixed in the compositions provided by and used in the practice of the invention will vary somewhat depending upon the exact composition of the ground coat and also upon the particular conditions to which the coated article is to be exposed, so that limits can not be set for all compositions falling within the scope of the invention. However, it will be understood that more refractory coatings are necessary in the case of articles exposed to extremely high temperatures or extremely oxidizing atmospheres than where the coated article is used under less severe scaling conditions. Also, the specific examples given hereinafter will indicate clearly to those skilled in the art how this is to be done. Again, resistance to scaling is increased generally, as my tests have shown, by progressive increase in the amounts of nickel oxide, or of nickel oxide and/or other scale-resisting refractory material, and of silica relative to the amount of ground coat, although the coating composition should not contain too large a proportion of nickel oxide or other similar refractory material because the resultant fused coating may thereby be mechanically weak. I have found, for example, that for many purposes the use of from 2 to 4 pounds of nickel oxide per gallon of enamel ground coat slip will produce a satisfactory fused coating that is mechanically strong and highly resistant to scaling of the underlying metal.

When compositions comprising mixtures of cast iron enamel ground coat, silica, and, for example, nickel oxide and chrome ore are fired on a metallic base the ground coat fuses and the nickel oxide and chrome ore become dispersed throughout the glassy medium thus formed. Upon cooling the fused ground coat solidifies and forms a matrix for the other ingredients which act to protect the underlying metal in much the same manner as oxide formed on the stable surface chromium and chromium-nickel irons and steels acts to prevent oxidation and scaling at high temperatures. In addition to thus holding the protective, or scale-resisting, refractory material in place to exert its anti-scaling function, the ground coat serves also as a coating impervious to oxygen and carbon, but as noted above, this alone is insufficient protection for the metal. The ground coat cooperates, however, with the protective refractory to greatly reduce oxidizing attack of the metal. Tests have shown, for example, that the life of parts exposed to high temperatures may be increased as much as 300 per cent in this way. Hence plain carbon parts may be caused to have the life of more expensive alloy steels.

From what has been said it will be understood that an important factor is the provision of vitrified coatings that are durable and will resist cracking and spalling during use of the protected article. Nickel oxide has a high coefficient of expansion, and the use of large amounts may cause the coefficient of expansion of the vitrified coating to be so different from that of the base as to create a tendency for the coating to crack or spall, for example under repeated heating or cooling. For that reason silica, preferably as quartz, is added, its low coefficient tending to offset the increase that would otherwise be caused by the scale-resisting, or protective, refractory material. Preferably the silica is used in an amount to compensate for the high coefficient of nickel oxide so that the coefficient of the vitrified coating will approach that of iron. Generally speaking, one pound of silica is equivalent to two pounds of nickel oxide for this purpose. Silica is useful also because it increases the refractoriness of the coating.

As an example, a mixture useful for coating ferrous metal articles such as annealing box covers and other parts exposed to high temperatures comprises a mixture of 8 pounds of bisque ground coat, 2 pounds of black nickel oxide, and 1 pound each of chrome ore and silica, all in finely divided condition. This mixture is formed into a slurry with 4 pints of water.

In addition to their anti-scaling properties, these coatings are of dark color so that heat efficiency of articles such as annealing boxes, heat treating containers, and the like is improved.

The compositions used in the practice of the invention may be applied dry, if desired for any reason, for example by dredging. Most suitably, however, the composition is worked up with water to provide a slurry which may be applied with a brush, or to provide a slip of consistency appropriate to application by dipping, spraying or slushing. An important factor is the forming of a relatively thick layer of the mixture, to form a thick vitrified coating. After the composition has been applied to the article it is dried, if need be, following which it is fired at a temperature such as to fuse the composition to the underlying metal. For most purposes firing at temperatures of about 1600° to 1900° F., depending upon the composition of the coating material, will suffice. The time of firing will vary according to the mass of the metal and to allied factors, but generally longer firing is necessary than in ordinary enameling operations, say 30 minutes to 1 hour at 1650° F. In any case, the firing is conducted at a temperature and for a time to fuse the composition satisfactorily on its metal base. When using bisque ground coat the article should be placed in a furnace which is at firing heat, or at least heated well toward it, rather than to heat it up in a cold oven, to obtain the best adherence.

Although the invention is applicable to the protection against scaling and oxidation at elevated temperatures of articles of various metals and for various uses, it is particularly applicable to the treatment of ferrous metal articles such, for example, as annealing boxes and covers, oven parts, retorts, crucibles, normalizing furnace parts, carburizing boxes, zinc and salt baths, and the like. For maximum adherence and maximum protection against scaling it is preferred to thoroughly remove scale and the like from the surface of the article prior to applying the coating composition, as by pickling the article or sand blasting the surface which is to be coated.

The fused coatings produced in the practice of the invention are coherent, adherent, and highly resistant to scaling and oxidation of the underlying metal, and they are of sufficient mechanical strength to minimize disruption of the coating under shock and other stresses to which articles,

such as annealing boxes and covers and the like, may be normally subjected. Micro-examination of coatings produced in the practice of the invention indicates the strong adherence to be due to intergranular penetration of the coating, and there is reason to believe that in the firing operation some portion of the coating composition is actually reduced to elemental metal which may alloy with the underlying metal and serve to improve the adherence between the latter and the fused coating. Be this as it may, the preferred compositions are resistant to spalling upon bending of the coated article although where the coating does break or spall the surface has an enameled appearance and offers continued resistance to scaling.

The benefits to be derived from the invention have been demonstrated amply by both laboratory and actual commercial tests. In one series of laboratory tests there was used a coating composition comprising 12.5 parts by weight of bisque ground coat, 2 parts by weight of powdered nickel oxide, and 1 part by weight of powdered chrome ore. This mixture was thoroughly stirred with water to provide a mix of the consistency of paint so that it could be applied with a brush. The composition thus prepared was applied to specimens of pickled sheet steel (0.0265 inch thick), and to specimens of black sheet (0.126 inch thick). The coated specimens were fired at 1850° F. for one hour, following which they were heated for varying periods of time, up to one hundred hours, at 1300°, 1500° and 1700° F. in the oxidizing atmosphere of an electric furnace. These tests showed that the fused coating decreased oxidation of the underlying steel about thirteen to about fifteen times as compared with uncoated specimens of the pickled steel, and about seven times in the case of the black sheet. The tests demonstrate, therefore, the great resistance to scaling provided through the practice of the invention as well as the benefit to be derived from initially pickling or otherwise removing scale prior to forming the coating.

Another composition which gave satisfactory results consisted of a mixture in water of about 13 pounds of a standard enamel ground coat, from 1 to 3 pounds of nickel oxide, and from ½ to 1 pound of chrome ore.

Still another composition which may be used for some purposes consists of about 11 pounds of standard enamel ground coat milled with 2 pounds of water to which there are added from 3 to 6 pounds of powdered chrome ore.

Yet another composition may be made by grinding from ½ to 1 pound of ground coat with water, about 10 pounds of powdered chrome ore or chrome ore and nickel oxide being added. The amount of water is desirably such as to provide a paste which may be applied by brushing.

In yet another test a coating composition in accordance with the invention was applied to an annealing cover used in commercial practice at 1600° to 1675° F. Untreated covers scale so rapidly in this particular plant that their life may be only four heats, and at best it does not exceed thirteen heats. The cover provided with a coating in accordance with this invention after thirteen heats and more than 3000 hours' exposure was apparently in as good condition as when it was first placed in service, and there is no indication that this cover will fail at any predictable time in the future.

Steel inner annealing covers used in a strip mill were treated according to the invention. After 26 heats of 80 hours each at the annealing temperature of 1650° F. they were unchanged in appearance. Untreated covers, in comparison, had scaled badly and were in need of repairs.

In another test half of a pressed steel cyanide pot was treated according to the invention. The unprotected half failed eventually, but at that time the treated half retained almost its original thickness.

Pyrometer tubes immersed in a salt bath used in one plant lasted about 5 days before failing. When the tubes were treated according to the invention their life was 34 days.

The compositions may be mixed dry and then mixed with water when they are to be used. Or, if preferred, there may be used ground coat slips, the ingredients which characterize the invention being added when coating work is to be done. Or, chrome ore may be milled in the enamel slip, if desired, but the nickel oxide should not be added until shortly before use because it tends to settle out and harden.

As indicated above, the compositions described specifically should be fired on the articles at temperatures of at least about 1600° F. Once fired on they will protect the articles at lower or higher temperatures. For some purposes, however, it may not be feasible to fuse the coatings at such temperatures, or for reasons of economy it may be wished to fire at lower temperatures. For example, with parts used at, say, 1100° to 1400° or 1500° F. it may be desired to fire the coating on in the furnace in which the part is used. Satisfactory results may be had in such cases by modifying the cast iron enamel coating composition by adding cobalt oxide or molybdic oxide, which cause the material to become satisfactorily fused and bonded to the article at such moderately elevated temperatures. Such modified compositions, which are thus like sheet iron and sheet steel ground coats, should not be used with articles that are normally exposed at 1600° F. or higher in regular use. In the use of these modified coatings removal of mill scale or the like from the article is not necessary because they appear to fuse through it to the metallic base.

This application is a continuation-in-part of my copending application Serial No. 295,936, filed September 21, 1939.

According to the provisions of the patent statutes I have explained the principle and method of practicing my invention, and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. That method of treating a metallic article to render it resistant to oxidation at elevated temperatures which comprises applying to said article a coating of an unfritted mixture of chrome ore and cast iron enamel ground coat frit substantially free from cobalt compounds, and heating the coated article to vitrify said frit and form a vitrified coating bonded to the underlying metal, said chrome ore being dispersed through said vitrified frit coating which acts as a matrix therefor, and the coating thus formed protecting the underlying metal against oxidation and scaling at high temperatures.

2. A method according to claim 1, said mixture containing also nickel oxide and silica in an amount to compensate for the high expan-

sion coefficient of said oxide, and said oxide being likewise suspended in the vitrified frit coating.

3. A composition for coating metal articles to render them resistant to oxidation and scaling at elevated temperatures comprising an unfritted mixture of a major proportion by weight of cast iron enamel ground coat frit substantially free from cobalt compounds, and a substantial proportion by weight of chrome ore.

4. A composition according to claim 3, said composition containing also substantial amounts of nickel oxide and silica.

5. As a new article of manufacture, a metal article adapted for use at elevated temperatures under oxidizing conditions, said article having its exposed surface provided with an adherent and coherent fused protective coating of cast iron enamel ground coat substantially free from cobalt compounds and having dispersed therethrough and suspended therein, as a matrix, a substantial proportion of chrome ore.

6. An article according to claim 5, said coating containing silica in excess of the amount present in the frit forming said coating, and the coating having also suspended therein nickel oxide.

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