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DARK COLORED STAINLESS STEEL SURFACES

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ABSTRACT OF THE DISCLOSURE

A process for producing oxide coated stainless steel having an oxide coating impregnated with an alkali metal silicate to improve resistance to wear.

This invention relates generally to improved surfaces of stainless steel, and more particularly to an improved black surface on stainless steel.

The commercial demand for black or other dark-colored stainless steels to compete with other metals such as aluminum, brass and copper has increased considerably in recent years. Of special interest are processes which will afford the surface a black or other dark color finish that does not detract from the metallic appearance of the metal, i.e., a process which will not result in a surface which has a painted look. Black or other dark colors on stainless steel surfaces are normally produced by a variety of oxidation processes which provide a thick oxide of a black or dark hue. Various processes for producing such black surfaces have been well known for many years, but have had very little commercial application, particularly in the architectural field where the stainless steel is to be used out of doors. The reason for this lack of success is that the oxide films so produced are not sufficiently resistant to corrosion, abrasion or other service factors which tend to remove the coating. Attempts have been made to improve the coating by applying lacquers, waxes, oils and the like. However, none of these materials has provided anything approaching a stabilized or permanent coloring which will resist outdoor exposure, and in fact some of these substances actually impair certain properties of the oxide coating.

It is therefore a principal object of this invention to provide an improved process for producing a permanent, weather-resisting, dark oxide coating on stainless steel.

A related principal object of this invention is to provide a stainless steel member which has on its surface a tightly adherent, dark, weather-resisting, permanent oxide coating.

Still a further object of this invention is the provision of an improved process for treating black oxide coatings which will render them abrasion-, weather-, and corrosion-resisting.

Yet an additional object of this invention is the provision of a process of treating black oxide coatings which will improve their apperance and render them resistant to abrasion, corrosion and weather.

These and other objects together with a fuller understanding may be had with reference to the following specification and appended claims.

Methods of producing deep, black coatings on stainless steel have been well known for many years. Basically there are two types of processes which are used to produce deep, black coatings. In one of these methods, the stainless steel article or member is cleaned and then immersed in a bath of a molten salt, normally sodium and/or potassium dichromates or sodium and/or potassium nitrates or the like, at temperatures ranging from about 600° F. to 950°

F. Examples of this type of blackening process are described in U.S. Patents Nos. 2,394,899 and 2,431,986.

In the other type of process, the stainless steel member is immersed in an aqueous bath of an alkali hydroxide with or without additives which catalyze or accelerate the oxidation reaction on the stainless steel. These aqueous baths are operated at temperatures of from about 220° F. to 310° F. These aqueous baths can be divided into alkaline baths, acid baths and electrolytic baths. Examples of processes using aqueous alkaline baths are described in U.S. Patents Nos. 2,476,780 and 3,142,592. Processes using aqueous acid baths are described in U.S. Patents Nos. 2,172,353, 2,219,554, 2,283,170, 2,283,171 and 2,521,580. An example of electrolytic aqueous baths is found in U.S. Patent No. 2,957,812.

Various modifications and variations of these two general types of processes have been utilized, such as electrolysis in molten salt baths and spraying of the chemical of the molten bath salts on the surface of the stainless steel, followed by heating of the stainless steel with the salt thereon to temperatures above the fusion points of the chemicals. An example of this latter variation is described in U.S. Patent No. 3,005,729.

Both of these types of processes have found some limited success in blackening the surface of small parts which are not exposed to severe atmospheric conditions. However, these processes have not been utilized to any great degree in the areas of larger decorative members such as architectural panels and automotive trim. There are several reasons for the lack of commercial utilization thereof in these areas. First, the oxide coating produced by these processes is somewhat soft and is rather easily abraded from the surface. Also, many of these processes produce an oxide that actually lowers the corrosion resistance of the stainless steel and therefore the parts cannot be utilized in any atmosphere or environment where corrosion is a factor. Also, one of the biggest drawbacks has been that the black film or coating produced by these processes has a slightly milky or opalescent appearance with a slightly blue or brown cast and does not have a deep, rich, lustrous, black apperance such as is characteristic of paints and enamels. In small parts, this lack of a deep, rich, lustrous, black appearance can be overcome by oiling or waxing the surface. Since the black oxides produced by these processes are generally quite porous, the oil or wax is absorbed into the surface resulting in a sealing of the coating which enhances the richness of the black oxide. However, this oil or wax treatment is only temporary in that the oil or wax will eventually be degraded by the action of ultraviolet light and corrosive elements present in the atmosphere, and the surface will revert to its original condition after having been blackened with the oils or waxes having been leached out. Therefore, such oiled, waxed or other organically treated blackened stainless steel surfaces are unsuitable for exterior use or use in normally corrosive environments encountered by stainless steel.

According to this invention, a black oxide coating on stainless steel produced by any of the conventional methods or variations thereof or other methods of blackening may be made permanent and given a rich, deep, lustrous appearance by treating the porous oxide with an aqueous solution of an alkali metal silicate followed by a stabilizing heat treatment. This treatment may be accomplished by dipping the stainless steel having the oxide coating thereon into a solution of the alkali metal silicate or by spraying, flowing, rolling or otherwise applying the sodium silicate solution to the oxide coating and thereafter performing the stabilizing heat treatment preferably at temperatures from about 300° F. to about 1000° F. The applied alkali metal silicate solution, which may be potassium or lithium silicate but which is preferably sodium silicate be-

cause of its ready availability and inexpensiveness, is absorbed essentially completely into the porous oxide and acts to seal the oxide; when the absorbed alkali metal silicate is heated to above 300° F. it becomes insoluble and, therefore, will not be leached out by the action of the weathering influences as are the waxes, oils, lacquers and other organic materials. This silicate treatment in addition to rendering the blackened oxide film on the surface a much deeper, richer, and more lustrous black color also helps to even out non-uniformities in apperance of the surface caused during the oxidation process. Also the silicate treatment removes the milky or opalescent appearance of the surface, contributing to the deep, rich, lustrous appearance.

Any of the methods of blackening described above may be used in connection with this invention. The choice of the particular method is determined by the type of article or surface to be blackened and the use to which the article is to be put. For architectural panels or articles for exterior use, a blackening process has been developed which, when used in conjunction with the silicate treatment of this invention, produces excellent results; and, although this process was developed for architectural panels, it has very wide use for many other articles. In this blackening process the surface of the stainless steel to be blackened is coated with an aqueous solution of sodium dichromate or potassium dichromate which has been thickened with "Methocel" (a trade name of Dow Chemical Company of Midland, Mich., for methyl cellulose). The article with the coated surface is heated to a sufficiently high temperature for a sufficient time to cause an even black oxide coating to be formed. To achieve a good, deep, uniform, black color, it is normally necessary to heat to temperatures between 950° F. and 1050° F. Below 950° F. the color tends to be grayish or brownish and often non-uniform and above 1050° F. the oxide tends to be non-uniform and has a propensity toward turning green. It is also preferred to use a solution of sodium dichromate rather than potassium dichromate inasmuch as the sodium dichromate is much more soluble in water. There should be at least about 10% sodium dichromate in the solution and the concentration may range all the way up to a completely saturated solution. The amount of "Methocel" added as a thickening agent will vary depending upon the surface and the article's size, etc. Also, a wetting agent such as "Wetanol" may be added. ("Wetanol" is a modified sodium lauryl sulfate manufactured by Glyco Products Company, Empire State Bldg., New York, N.Y.) A typical formulation of the blackening solution is as follows:

Sodium dichromate	grams	3,000
"Methocel" (4,000 cps.)	do	10
"Wetanol" (10% solution)	milliliters	10
Water	do	2,000

Analysis of the black oxide film obtained on a stainless steel article utilizing the preferred solution described above and heated between 950° F. and 1000° F. indicated that the oxide consists almost entirely of alpha Fe_2O_3 with traces of alpha iron or chromium. The composition of black oxide films produced by the other processes vary widely from hydrated oxides of iron to oxides such as Fe_3O_4. Also, the thickness of oxide films produced by these various blackening methods range from more than 1,000 angstroms up to about 500,000 angstroms depending upon the method used and the conditions of oxidation. The black oxide coatings produced by the preferred method described above normally range in thickness from about 5,000 angstroms to 25,000 angstroms.

The blackened stainless steel is treated in a solution of alkali metal silicate. In order to get effective amounts of alkali metal silicate into the coating, there should be at least 10% of the alkali metal silicate in solution. It has been found that the best solution strength is between 30% and 60% by volume of alkali metal silicate in water. A wetting agent such as "Wetanol" can be employed in amounts up to about 10%.

The following examples illustrate this invention.

EXAMPLE 1

AISI Type 302 stainless steel panels with a dull mat finish were cleaned by scrubbing with an alkaline cleaner and rinsed in clear water. The panels were dried and then sprayed with a sodium dichromate solution having the composition described above. The coated panels were placed in a furnace at 1000° F. for ten minutes after which they were cooled and scrubbed with water to remove the excess sodium dichromate solution and any loose oxide. These panels were then dried at room temperature which resulted in a black oxide film on the surface thereof greater than 1,000 angstroms in thickness. The oxide had a dull gray-black appearance. The oxide coated surfaces were then sprayed twice with 30% sodium silicate solution in water, the panels being dried at room temperature between the two sprayings. After the second spraying, the panels were heat treated for five minutes at 800° F. to make the oxide coating permanent.

EXAMPLE 2

AISI Type 430 stainless steel panels with a bright annealed strip finish were cleaned by scrubbing with an alkaline cleaner and rinsing in clear water. They were then pickled for ten seconds in an aqueous solution of 15% nitric acid and 3% hydrofluoric acid maintained between 180° F. and 200° F. The panels were then rinsed and immediately immersed in a solution of 568 grams of Houghto-Black No. 16 chemical (a trade name of a blackening chemical sold by E. F. Houghton & Company, Philadelphia, Pa.) in 1,183 milliliters of water, operated at a temperature of between 240° F. and 250° F., for ten minutes. After rinsing in water and drying at room temperature, the panels had a fairly uniform gray-black surface. The panels were then treated by flowing with a 10% solution of sodium silicate in water and given a stabilizing heat treatment for thirty minutes at 500° F. The resultant surface had a deep, highly reflective, black appearance which had a "black mirror" character.

The greatly improved surface appearance of the blackened surfaces treated with alkali metal silicate solution over that of the untreated blackened surface is readily apparent to the eye. Certain aspects of this improvement in surface appearance quality can also be measured quantitatively. To demonstrate this, panels of steel blackened as described in Example 1, but not treated following the blackening, were compared with panels of samples blackened and treated with sodium silicate solution as described in Example 1. This comparison was accomplished by meaurements of gloss made by a Hunter Lab Model D 16 Multipurpose Glossmeter (an instrument manufactured by Hunter Associates Laboratory, McLean, Va.). Measurements were made on both of these samples of specular gloss at 45° and diffuse reflectance with the incident light source at 45° and with the measuring photocells at 20° and 0°. The table below lists the results of these measurements.

TABLE.—EFFECT OF SILICATE TREATMENTS ON TYPE 304, 2D VB FINISH, BLACKENED BY DICHROMATE COATING METHOD (1000° F. FOR TEN MINUTES)

	Color			Gloss		
	L	A	B	Specular 45°	Diffuse 20°	Diffuse 0°
As blackened (no treatment)	21.0	0.0	−1.9	0.1	4.5	4.4
Treated, 30% sodium silicate solution	21.9	+0.5	−0.7	0.4	9.1	2.9

From this table it can be seen that the specular gloss has changed very little and that the specular gloss is in fact quite low on both samples, indicating that both of these surfaces have almost no specular reflectance at all.

However, diffuse reflectance at 20° indicates the effect which is seen visually by the eye. Reflectance by the sodium silicate treated panel at this 20° angle is more than double the reflectance of the blackened and untreated sample. This great increase in reflectance is the phenomenon that gives the visual impression of a deeper, richer and more lustrous black surface. The other visual effect of the sealing sodium silicate treatments, i.e., that of evening out non-uniformities, cannot be measured quantitatively by instruments but can easily be observed visually.

Measurements with a Hunter Lab Sphere Color Difference Meter (also manufactured by Hunter Associates Laboratory, McLean, Va.) indicate that the sodium silicate treatment does not change the actual color of the coating. However, the improvement in the richness and luster of the oxide removes the milky or opalescent appearance present. The following tests were performed on panels blackened as described in Example 1 above but not treated with sodium silicate and also with samples of panels blackened and treated with sodium silicate as described in Example 1 above. Also, samples blackened as described in Example 1 above and rubbed with linseed oil, a conventional prior art practice of treating blackened surfaces, were used for comparison.

Resistance to solvents

Samples of panels having surfaces of each of the three conditions, i.e., blackened and untreated, blackened and treated with linseed oil and blackened and treated with sodium silicate according to this invention, were immersed in both toluene and lacquer thinner for 24 hours. After treatment, the blackened and untreated surface and the blackened and treated with sodium silicate surface were both unaffected; however, the surface which was blackened and treated with linseed oil had turned to an uneven, unattractive whitish color and had become porous.

Resistance to chemicals

Samples of panels having surfaces of each of the three conditions were tested by placing drops or smears of the following reagents on the surface of the panel, which reagents were removed by washing after 24 hours: 10% nitric acid, 10% sulfuric acid, 10% hydrochloric acid, 30% sodium hydroxide, lubricating oil, lipstick, glazing compound and cement. After 24 hours the blackened and untreated surface had been attacked by the sulfuric and hydrochloric acid which removed the coating. This panel was also stained by the glazing compound and there were slight stains from the lubricating oil and lipstick. The cement also removed the black oxide coating. The surface was unaffected by the other reagents. The panel blackened and treated with linseed oil was attacked by the nitric acid, sulfuric acid, hydrochloric acid, sodium hydroxide, cement and glazing compound. The surface of this panel was also slightly stained by lipstick and oil. The surface was unaffected by the other reagents. The panel blackened and treated with sodium silicate according to this invention was very slightly attacked by hydrochloric acid and slightly attacked by the cement. This panel was unaffected by any of the other reagents.

Resistance to salt spray

Samples of panels having surfaces of each of the three conditions were exposed for 100 hours in a standard 5% salt spray test. The blackened and untreated surface and the surface blackened and treated with sodium silicate according to this invention were unaffected. The surface blackened and treated with linseed oil was badly streaked and mottled in appearance.

Resistance to outdoor exposure

Samples of panels having surfaces of each of the three conditions were exposed in an Atlas Weather-Ometer for 206 hours. The blackened and untreated surface and the surface blackened and treated with sodium silicate according to this invention were unaffected. The surface blackened and treated with linseed oil was reduced back to its condition before treatment, i.e., the linseed oil had been almost completely removed during the exposure.

Resistance to abrasion

Samples of panels having surfaces of each of the three conditions were abrasion tested on a Taber Abraser, using CS–10 wheels with a load of 1,000 grams. On the blackened and untreated surface after ten cycles, most of the black oxide had been removed revealing bright stainless steel substrate. The surface blackened and treated with linseed oil showed break-through at ten cycles and the black oxide was substantially removed after twenty cycles. The surface blackened and treated with sodium silicate solution according to this invention showed break-through only after 100 cycles.

In addition to the quantitative tests above, the blackened surface treated with sodium silicate according to this invention proved to be resistant to organic solvents such as benzene, petroleum ether, acetone, xylene, alcohol, carbontetrachloride, methyl ethyl ketone and trichlorethylene. Other panels blackened and treated with sodium silicate according to this invention were exposed in an Atlas Weather-Ometer for more than 10,800 hours without substantially any signs of deterioration. This is equivalent roughly to more than 36 years of actual outdoor exposure.

Also, panels having surfaces blackened and treated with sodium silicate according to this invention can be formed to a certain extent. For example, such panels can withstand sharp 90° inside and outside bends and in some gauges withstand 180° flat bends without showing any break-through of the coating. The blackened coating treated with sodium silicate according to this invention will not chip or crack when the panels are sheared or stretcher leveled, nor does the coating tend to spall or chip upon impact.

The term stainless steel, as applied in the present specification, is intended to include all the steels classified by the Ameriuan Iron and Steel Institute as being standard grades of stainless steel. These include the type 400 series stainless steels that contain chromium in amounts of from about 10%, by weight, to about 30%, by weight, and generally less than 1% carbon, such as AISI Types 410 and 430 and additionally the AISI Type 300 series which contain, in addition to Cr and C, a nickel content of from 6% to 30% which renders the steel structure "austenitic," such as AISI Types 301, 302 and 304, and the 200 series steels which contain not only nickel in amounts of 1% to 10%, but also up to about 30% Mn and 0.60% N_2 as additional austeni.izers. Such various stainless steel analyses may contain additionally, as impurities or alloying ingredients, small amounts of P, S, Cu, Mo, Se, B, Be, Co, W, Ti, Cb, Ta, V, Zn, Al, Si, rare earths, etc. All stainless steels, however, contain chromium within the range of from about 10% to 30% and carbon up to about 1%. The Cr content in every instance is the element that primarily effects the essential property of oxidation and corrosion resistance, and consequently the article of the present invention may be broadly said to be composed partly of a steel that consists essentially of carbon in an amount up to about 1%, chromium from 10% to 30% and the balance iron.

Although several embodiments of this invention have been described, various adaptations and modifications can be made without departing from the scope of the appended claims.

We claim:

1. A process for providing a dark lustrous surface on stainless steel comprising the steps of producing a porous oxide film integrally bonded to the surface of the stainless steel article of a thickness greater than about 5,000

angstroms by oxidizing with an aqueous solution of alkali metal dichromate and heating to a sufficiently high temperature for sufficient time to cause an even black oxide coating to be formed thereon, treating the oxide coating with a solution consisting essentially of an alkali metal silicate to fill the voids of the oxide coating, and baking said treated oxide coating at a temperature between 300° F. and 1000° F.

2. The process according to claim 1 wherein said alkali metal silicate is sodium silicate.

3. A process of claim 2 wherein the sodium silicate solution contains at least 10% sodium silicate.

4. The process of claim 2 wherein the sodium silicate solution contains from about 30% to about 60% sodium silicate.

5. A process of claim 2 wherein said sodium silicate solution contains up to about 10% of the wetting agent.

6. The process of claim 1 wherein the oxide coating is between about 5,000 and 25,000 angstroms thick.

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