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METHOD OF IMPROVING CORROSION RESISTANCE OF STAINLESS STEEL

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This invention relates to improving the corrosion resistance of stainless steel surfaces and particularly to a method of improving the corrosion resistance of polished stainless steel articles.

In the process of producing stainless steel for commercial applications, it is usually desirable to obtain the maximum possible corrosion resistance properties. This is particularly the case where the stainless steel is to be exposed to corrosive environments such as outdoor applications, particularly building and automobile trim. Buffing and polishing stainless steels effect an attractive and desirable bright metallic finish which is ideal for such applications, and also improves the corrosion resistance of the stainless steel surface. However, exposure to ordinary corrosive atmospheric conditions, such as industrial atmospheres, or in the case of automobile trim exposure to the corrosive effects of salts employed for highway use, invariably causes corrosion of the stainless steel utilized for such purpose and shortens the life and attractiveness of stainless steel articles. Methods of improving the corrosion resistance of such articles are constantly being sought and any improvement obtained in securing improved corrosion resistance is of importance in this field.

Many coatings have been developed which increase the corrosion resistance of stainless steel surfaces; however, a majority of them detract from the desired bright metallic finish and are relatively unattractive and therefore are undesirable. Transparent finishes such as lacquers, plastics and waxes offer only temporary protection and soon erode or peel away, exposing the stainless steel to the corrosive environment.

It has now been found that by means of the present invention improved corrosion resistance of stainless steel articles may be obtained while retaining the natural bright metallic luster.

It is an object of the present invention to provide a stainless steel article that exhibits improved corrosion resistance.

It is also an object of the present invention to provide a means of improving the corrosion resistance of bright and lustrous stainless steel without destroying the beauty of the natural metallic finish.

It is a further object of the present invention to provide a method of filling the microscopic pits and voids normally found on the surface of conventionally polished stainless steel with a material that will prevent nucleating corrosion in the vicinity of such pits and voids.

Other objects and advantageous features of the present invention will be obvious from the following description.

In the practice of the present invention stainless steel is given a chromate film or finish such as is conventionally applied to zinc and cadmium coated steel articles. The coated stainless steel is then polished with a fine grit polishing powder or by buffing to bring back the bright and lustrous metallic finish. Polishing is controlled so that the stainless steel surface is not reduced more than about 2 mils and for optimum results, not more than 0.6 mil. Such a stainless steel treated in the manner described exhibits corrosion resistance far superior to untreated stainless steel surfaces.

Chromate formations such as are applied in the method of the present invention are well known for coating zinc and cadmium coated steel. Processes for obtaining a chromate film involve contacting the cleaned surface of the article being treated with an aqueous solution that contains chromic acid plus a reducing agent. The reducing agent may be one of the mineral acids such as hydrochloric and sulfuric acid but also may be an organic acid such as formic acid. While the article is being withdrawn from the aqueous solution, it acquires a thin gelatinous-like coating which is subsequently permitted to dry or is cured by heating at a low temperature of about 200° F. or 300° F. Such a film offers protection to the zinc or cadmium coating from corrosive breakdown. These coatings are commonly referred to as chromate coatings and are believed to be composed of a material of the formula

$$Cr_2O_3.CrO_3+H_2O$$

The chromate films may be applied to carbon steel surfaces that are not coated with such materials as zinc and cadmium. Processes for accomplishing this are taught in U.S. Patents Nos. 2,768,103 and 2,768,104, issued to Schuster et al. These processes involve contacting a treated steel, such as Blackplate, with an aqueous chromic acid bath plus a reducing agent. The steel surface is first cleaned by a pretreatment, such as solvent and alkaline cleaning, pickling, nitric acid etching, phosphatizing, oxide coating, etc., and is thereafter chromate coated by contacting the surface with aqueous chromic acid plus reducing agent, such coating being then dried or cured.

Particularly desirable results are obtained when a clean surface of carbon steel is contacted for at least one second with an aqueous solution consisting essentially of about ½ to about 30% chromic acid and about ¼% to 25% of a reducing agent. Preferred reducing agents are those that do not form stable oxidation products or water soluble salts with the chromic acid. Both the chromic acid and the reducing agent may be applied simultaneously from the same solution or the reducing agent may be applied separately after coating. Representative reducing agents are the straight chain polyalcohols such as glycol, glycerine, mannitol, sorbitol and sugars generally, as well as conventional reducing agents such as potassium iodide, phenol, hydroquinone, phosphorus acid, hydroxylamine sulfate, triethanolamine, and the like. Hydrogen, methane, formaldehyde vapors, ethyl alcohol vapors, and similar gaseous reducing agents may be utilized in lieu of or supplementary to the agents mentioned previously. The concentration of reducing agent in the solution should be less than the concentration of chromic acid and the solution bath temperature should be preferably between about 50° F. and 200° F. The length of time the carbon steel article is held in the solution is not critical but should be for a time of at least one second. As the metal is withdrawn from the solution it is found that a gelatinous film is carried on the surface of the metal, which film is subsequently dried. Drying is preferably accomplished within the temperature range of from 200° F. to 300° F.

In accordance with Patent No. 2,768,103 particularly desirable results are obtained when the carbon steel is etched with a nitric acid bath prior to chromate coating. Such a practice has been found to be nonbeneficial when coating stainless steel. Chromate coated stainless steel exhibits a variety of colors depending on the thickness of the coat. Heavy coatings create interference patterns which are objectionable. Lighter coatings are bluish gray and very light coatings (10 to 20 mg. per square foot) exhibit a yellowish cast.

In the present invention stainless steel is chromate coated. It has been found that surface preparation, such as is required in the processes of coating carbon steels taught by the Schuster et al. patents, is not necessary when chromate coating stainless steels. While it is desirable for the stainless steel to have a clean surface, no special etching or oxidizing steps are required. The preferred CrO_3 bath and coating conditions are substantially the same as those employed in Patent No. 2,768,104. The chromate coated stainless steel is polished sufficiently to remove any outward appearance of the film, leaving a metallic bright appearance. However, care must be taken that not all of the film is completely removed. This film is actually only a few millionths of an inch thick. Polishing should not remove more than about 2 mils from the surface of the stainless steel. Optimum results are obtained when the surface is reduced 0.6 mil or less. Excellent results have been obtained when only about 0.1 mil of the stainless steel surface has been removed by polishing. Polishing is preferably accomplished with very fine grain materials, such as 320 grit or finer, in that coarse polishing materials will scratch the surface of the stainless steel. However, even a scratched surface will exhibit some improved corrosion resistance if chromate coated before polishing. Buffing may follow grit polishing or the entire polishing may be accomplished by buffing with a cloth wheel of conventional manufacture.

A distinct advantage of an embodiment of the present invention is the fact that the chromate coating is applied to the stainless steel in its sheet or strip form and before conventional forming operations. Thus, stainless steel sheet or strip is chromate coated before a drawing operation is applied to the coated sheet and the drawn or otherwise formed article is buffed in the conventional manner without performing any additional operations not ordinarily performed after drawing. Stainless steel articles fabricated from the chromate coated stainless steel sheet or strip as by drawing or otherwise mechanically deforming the sheet into the shape and size of the articles and which are thereafter polished as taught herein, exhibit superior corrosion resistance to identical articles formed in an identical manner from the same stainless steel but which have not been chromate coated and polished, or if chromate coated, have not been polished. The polishing, as by buffing as described, effects a redistribution of the chromate coating to effectively fill the pits and voids normally present in the surface of stainless steel sheet as well as fine cracks or voids in the chromate coating that may have been formed by reason of the mechanical deformation applied during the fabrication of the article.

Stainless steel that may be treated in accordance with the present invention includes all of the ferrous base metals commonly referred to as stainless steel such as the AISI types of the 200, 300 and 400 series. Such steels contain, among other alloying ingredients, mainly chromium within the range between 10% and 35%. The stainless steels to which the method of the present invention is applicable many contain the usual impurities such as silicon, phosphorus, sulfur, copper, tin, etc. These elements are usually present in quantities of less than 1%; however, larger quantities of these elements may be added for special effects. For example, up to 3% silicon or up to 1% sulfur may be purposely employed. Other alloying additions include up to 35% nickel, up to 20% manganese, and up to about 5% of molybdenum, tungsten, titanium, columbium, vanadium and cobalt. Carbon is usually below about .25%. There also may be traces of rare earths. Nitrogen is usually present as an impurity but up to 0.60% may be purposely added.

Polished and buffed stainless steel as normally produced contains numerous microscopic pits and voids which are believed to be the cause of corrosion. These pits or voids act to nucleate or initiate corrosion when the steel is exposed to corrosive conditions. The present invention improves the corrosion resistance of stainless steel in that the voids normally present are filled with a material which will not permit their nucleating corrosion. Although polishing restores the bright and lustrous metallic finish, it does not remove the entire coating, as sufficient chromate film is retained and flowed into the pits and voids to give a smooth surface and to improve corrosion resistance.

The method of the present invention is particularly applicable to stainless steels with bright and lustrous finishes in that dull finishes do not lend themselves to light polishing and buffing after chromate coating and will not provide significantly improved corrosion resistance unless polished and buffed to a point where the chromate coat is entirely removed. It is desirable to apply the method of the present invention to stainless steels that exhibit a polish at least equivalent to or brighter than a No. 4 finish. A No. 4 finish on stainless steel is well known in the steel industry as a ground finish obtained by employing about 120 to 150 grit materials. The present method is particularly applicable to finer finishes such as automobile grade stainless steel strip. The finish of this material is obtained by a final cold rolling through extra smooth rolls after the usual cold rolling, annealing and pickling operations. Such a finish is generally of higher luster and smoothness than a No. 4 finish. Excellent results may be obtained on No. 7 and No. 8 stainless steel finishes which are ground and buffed surfaces. The method is also equally applicable to lustrous finishes obtained initially by means other than mechanical such as electropolishing and bright pickling.

The following specific examples are given to illustrate the process of the present invention and in no way limit the invention to the exact methods set forth.

Specimens of type 430 stainless steel strip that exhibited a bright and lustrous finish were cleaned in an electrolytic alkaline bath. Some of the specimens were chromate coated by immersing them in an aqueous solution that contained about 2.0% chromic acid (CrO_3) and about 0.66% cane sugar at room temperature (about 70° F.). The chromate coatings were then cured by heating the specimens in an oven until they reached a temperature of 400° F. A coating weight of about 40 milligrams per square foot was obtained. Coated and uncoated specimens were formed into Erichsen cups with a deformation of 7 millimeters and some specimens of each were given a light buff. All the samples were exposed to 20% salt spray (20%, by weight, NaCl in water). Results were as follows:

Sample	Result
1. Uncoated, unbuffed	A number of small rust spots appear in 48 hours.
2. Uncoated, buffed	No rust spots at 48 hours; some spots appear after 72 hours.
3. Coated, unbuffed	Rust spots appear on deformed area after 165 hours.
4. Coated, buffed	No rust spots after 600 hours.

As shown by the above data the chromate coated and buffed samples show highly superior corrosion resistance to samples that have been either coated but not buffed, buffed but not coated or untreated.

Flat specimens of type 430 stainless steel were given a chromate coating as described above. These flat samples were cleaned, immersed in the aqueous solution previously described, dried, polished and submitted to a 20% salt

spray (an aqueous solution of 20% of NaCl) at room temperature. Results were as follows:

Table I

Test No.	Polishing Operation [1]	Metal Removed By Polishing, Mils	Results—48 Hrs.	Results—113 Hrs.
1	Coated but not buffed	0	No rusting or pitting	No rusting or pitting.
2	Coated and lightly buffed	0	do	Do.
3	No coating, lightly buffed	0	do	1 medium, 5 small and 50 fine spots.
4	No coating, no buff	0	A number of small rust spots after 16 hrs.	Numerous rust spots and general corrosion.
5	Coated and heavily buffed	0	No rusting or pitting	3 fine rust spots.
6	Coated and polished with 320 grit alumina and buffed.	0.1	do	4 fine rust spots.
7	Coated and polished with 240 grit and 320 grit alumina and buffed.	0.6	do	1 small, 40 fine spots.
8	Coated and polished with 180+240+320 grit alumina powder and buffed.	1.0	2 fine rust spots	15 small, 30 fine spots.
9	Coated and polished with 120+180+240+320 grit alumina powder and buffed.	1.5	No rusting or pitting	5 small, 5 fine, 450 very fine spots.
10	Coated and polished with 60+120+180+240+320 grit Al_2O_3 powder and buffed.	2.0	1 small rust spot	1 medium, 10 small, 20 fine and numerous very fine spots.

[1] Polishing was conducted with commercial grade polishing belt of successive grit sizes as indicated.

It may be seen from the examples of Table I that although the advantages of polishing and buffing chromate coated stainless steel are not so pronounced as where drawing or forming operations after coating have taken place, it is obvious that beneficial corrosion resistance is obtained. Test No. 2 showed equivalent corrosion resistance to test No. 1 although buffing had substantially restored the natural metallic luster of the stainless steel surface. Also it can be seen that all the examples that had been coated and polished or buffed showed superior corrosion resistance to test No. 4 which was an untreated specimen as tested. Also, all the specimens showed some superior corrosion resistance to Example 3 which was a buffed but otherwise untreated sample. All samples except sample No. 1 showed a bright and lustrous automobile grade strip finish. Sample No. 1 had such a finish but exhibited a chromate coat.

We claim:

1. The method of providing improved corrosion resistance to a bright stainless steel article normally having microscopic pits and voids therein which comprises, providing said article with a chromate film comprising an in situ formed film of hydrated mixed chromium oxides mechanically polishing said article so as to reduce the surface thereof not more than 0.6 mil so as to remove the appearance of said chromate film while flowing the chromate to insure the filling of the microscopic pits and voids therewith.

2. The method of producing a formed stainless steel article with improved corrosion resistance which comprises, applying to the surface of a stainless steel alloy normally having microscopic pits and voids therein an in situ formed film of hydrated mixed chromium oxides, mechanically forming said alloy into the desired shape and mechanically polishing the surface of said formed stainless steel so as to remove the appearance of said film while flowing the said film to insure the filling of the microscopic pits and voids therewith.

3. The method of producing a formed stainless steel article with improved corrosion resistance which comprises, applying to the surface of a stainless steel alloy normally having microscopic pits and voids therein an in situ formed film of hydrated mixed chromium oxides, mechanically forming said alloy into the desired shape and mechanically polishing the surface of said formed stainless steel so as to reduce the surface thereof not more than 0.6 mil so as to remove the appearance of said film while flowing the said film to insure the filling of the microscopic pits and voids therewith.

4. The method of producing a formed stainless steel sheet or strip normally having microscopic pits and voids on the surface thereof with an aqueous chromic acid solution containing from about ½% to about 30% CrO_3 and from about ¼% to 25% of a reducing agent that will partially reduce the CrO_3 film that remains on said surface upon removal from the contacting solution so as to effect an in situ formed film of hydrated mixed chromium oxides on said surface, removing the contacted surface from the solution so that said film remains on the surface, drying said film, mechanically forming said steel into the desired shape and polishing the surface of said formed stainless steel so as to reduce the surface of said article not more than 0.6 mil so as to remove the appearance of said film while flowing the said film to insure the filling of the microscopic pits and voids therewith.

5. The method of producing a formed stainless steel article with improved corrosion resistance which comprises, contacting a bright clean surface of stainless steel normally having microscopic pits and voids therein with a chromic acid solution containing from about ½% to about 30% CrO_3 at a temperature of about 50° F. to about 200° F., removing the contacted surface from the solution so that a film of the solution remains on the surface, drying said film on said surface while chemically reducing a portion of the chromic acid in the film so as to effect an in situ formed film of hydrated mixed chromium oxides, mechanically forming said stainless steel and polishing the surface of said formed stainless steel so as to reduce the surface of said article not more than about 0.6 mil so as to remove the appearance of said film while flowing said film to insure the filling of the microscopic pits and voids therewith.

6. A method for improving the corrosion resistance of chromium type stainless steel alloys which comprises applying to the surface of said alloys an in situ formed coating of hydrated mixed chromium oxides and then buffing down the coating until its presence is not apparent to the eye.

7. A method for improving the corrosion resistance of chromium type stainless steel alloys which comprises contacting said alloys with an aqueous chromic acid solution containing from about ½% to about 30% CrO_3 and from about ¼% to about 25% of a reducing agent which will reduce CrO_3 to form substantially water insoluble salts therewith so as to form an in situ coating of hydrated mixed chromium oxides on said alloys and then buffing down the coating until its presence is not apparent to the eye.

8. A method for improving the corrosion resistance of chromium type stainless steel alloys which comprises, con-

tacting said alloys with an aqueous chromic acid solution containing from about ½% to about 30% CrO_3 and from about ¼% to about 25% of sugar so as to form an in situ coating of hydrated mixed chromium oxides on said alloys and then buffing down the coating until its presence is not apparent to the eye.

9. A method for improving the corrosion resistance of chromium type stainless steel alloys which comprises, contacting said alloys with an aqueous chromic acid solution containing from about ½% to about 30% CrO_3 and from about ¼% to about 25% of polyalcohol so as to form an in situ coating of hydrated mixed chromium oxides on said alloys and then buffing down the coating until its presence is not apparent to the eye.

10. A method for improving the corrosion resistance of chromium type stainless steel alloys which comprises,

contacting said alloys with an aqueous chromic acid solution containing from about ½% to about 30% CrO_3 and from about ¼% to about 25% of potassium iodide so as to form an in situ coating of hydrated mixed chromium oxides on said alloys and then buffing down the coating until its presence is not apparent to the eye.

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