Nov. 26, 1963 L. K. SCHUSTER ET AL 3,112,231

PROTECTIVE COATING

Filed June 20, 1957

Fig. 3.

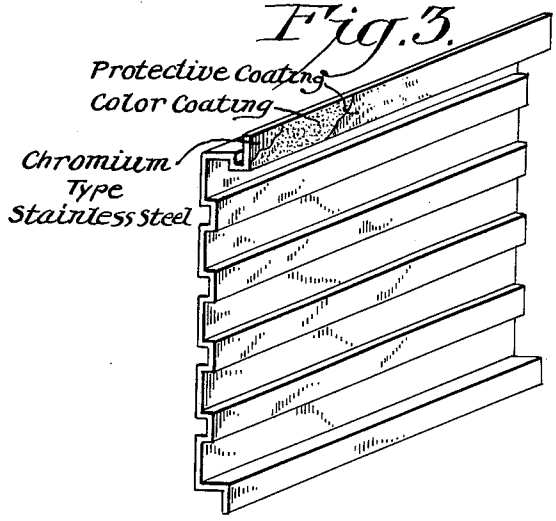


Fig. 1.

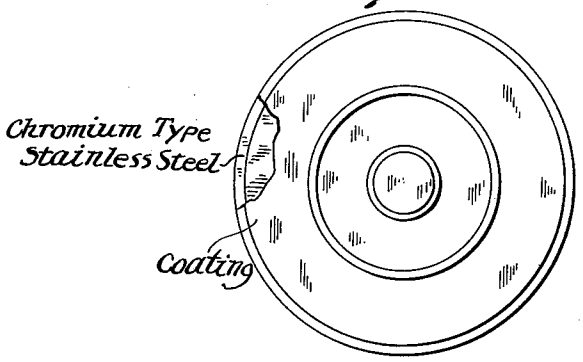
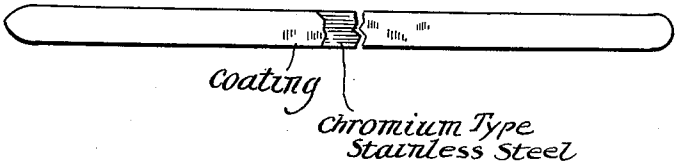


Fig. 2.



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PROTECTIVE COATING

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The present invention relates to protective coating of chromium type stainless iron alloys.

Although the above alloys are generally quite corrosion resistant, one object of the present invention is to improve this resistance. Other objects include the provision of protectively coated alloys of the above type.

The above as well as still further objects of the present invention will be more clearly understood from the following description of several of its exemplifications, reference being made to the accompanying drawings in which:

FIG. 1 is a side view of an automotive type wheel hub cap;

FIG. 2 is a corresponding view of an automobile body trim strip; and

FIG. 3 is a perspective view of an external metal building panel.

In certain forms of automotive and building construction, it is desirable to provide trim and other exposed surfaces in the form of metal that does not require painting and is generally free of maintenance problems. Very desirable metals for this purpose are the chromium type stainless iron alloys. These are ferrous alloys having from about 10 to 25% chromium content, little or no nickel, and may have carbon, phosphorus, sulfur, silicon, molybdenum, aluminum, copper or other alloying ingredients in amounts up to about 5% each. The low nickel content is a significant feature of these alloys since this reduces their cost and avoids the supply problems associated with the use of nickel in non-strategic constructions.

It has been discovered that the chromium type stainless iron alloys, although quite satisfactory from maintenance considerations, suffer serious pitting in certain environments, e.g. in salt air or in contact with building plaster, and this pitting is sharply reduced or entirely prevented by a coating of an in situ formed combination of hydrated mixed chromium oxides, the coating having from 20 to 60% chromium by weight, about 40 to 95% by weight of the chromium being trivalent, the remainder being hexavalent, and the coating weighing from about 1 to 200 milligrams per square foot of surface that it covers.

The coating is readily made by applying to the metal surface an aqueous solution essentially of chromic acid and a compatible reducing agent for the chromic acid, and the coated surface is then heated to a temperature of from 250 to 450° F. to cause the reducing agent to react with the chromic acid and leave a water-insoluble layer, the proportions of reducing agent and chromic acid being such that from about 40 to 95% of the chromium in the chromic acid is reduced to trivalent form, and the final layer weighs at least about 1 milligram per square foot of surface. Coating weights of 1 to 10 milligrams per square foot are preferred inasmuch as heavier coatings impart a colored appearance which generally includes irregular optical interference patterns and may therefore be objectionable for some purposes.

The properties of the coating can be varied by the type of reducing agent, its amount, and the reduction temperature. The reducing agent is preferably one that does not leave water-soluble salts in the final coating layer. Compatible reducing agents are those that when present in the

above proportions do not cause any precipitation during the period in which the solution is kept as a solution, and are not driven off by the heat treatment, before they are oxidized. Organic polyalcohols are very effective reducing agents, and examples of specifically desirable polyalcohols include sucrose, invert sugar, dextrose, glycols, polyglycols such as diethylene glycol, glycerine, mannitol, sorbitol, triethanolamine and tartaric acid. Other reducing agents such as citric acid and hydroxylamine salts, such as hydroxylamine sulfate and even phosphorous acid and KCNS are also suitable. The reducing agent should not be so stable that it cannot be oxidized by the chromic acid, at least when it reaches the final baking temperature.

A coating bath containing both the chromic acid and the reducing agent should not be permitted to stand long enough to form deposits of insoluble chromium compounds before the bath is applied to the surface and cured, that is, subjected to the final heat treatment. To avoid this, the dwell of the reducing agent in contact with the chromic acid solution should be of limited duration. The chromic acid and the reducing agent can even be applied as by spraying from a common spraying jet, solutions of the separate ingredients being mixed together only just before spraying.

The reducing agents listed above do not react very rapidly and can be stored in a chromic acid solution for at least one day at room temperature (80° F.) without deterioration.

In general, polyalcohols and their oxidation products are suitable reducing agents. These contain a carbon atom to which is linked an alcohol group that is not protected against oxidation, and such structure appears to be effective regardless of the remainder of the molecule, so long as the materials are not too volatile, that is, they should boil at temperatures well above 212° F.

The amount of reduction depends upon the type and amount of reducing agent used and temperature of reduction. A general rule to follow is the higher the reducing agent content and the higher the reduction temperature the more reduction of the hexavalent chromium in the chromic acid. Coatings with 40 to 70% reduction of the hexavalent chromium are more highly colored, having a brown to brownish green appearance. Coatings having conversions of hexavalent chromium to trivalent chromium from about 70 to 95% are extremely insoluble in water and in all types of corrosive media likely to be encountered. Moreover, these highly converted coatings are almost colorless when in coating weights below 5 milligrams per square foot.

The more highly converted coatings can be produced by selection of the correct amount of reducing agent as well as the proper conversion temperature. A general rule is to use a lower CrO_3-to-reducing agent ratio, a higher reduction temperature, and most effective, a combination of both. For coatings of highest conversion, it is preferable to incorporate the least amount of reducing agent and to use the curing operation to effect maximum conversion. For example, to obtain a 1 milligram per square foot coating having 95% reduction, it is better to use, in the case of sucrose, a ratio of 3 parts by weight of CrO_3 to one part by weight of sucrose cured at 388° F., than one part by weight of CrO_3 to one part by weight of sucrose cured at 275° F. Curing temperatures above 450° F. produce coatings that give less protection against pitting. A curing temperature of 325° to 390° F. gives best results with coating weights of 1 to 10 milligrams per square foot. In the upper portion of this coating weight range (above 5 milligrams per square foot) somewhat higher temperatures ranging to 425° F. are also extremely effective.

The percentage of trivalent chromium in the coating can be determined by dissolving it in a 2 to 40% aqueous

solution of NaOH by weight at 160° F. or higher, titrating the hexavalent content of the resulting solution with sodium thiosulfate in the presence of potassium iodide, and subtracting this content from the total chromium content which is determined by oxidizing another dissolved coating sample with H_2O_2 and again titrating with sodium thiosulfate in the same way.

In general the greater the trivalent chromium content, the more insoluble the coating and the more resistant it becomes to chemical attack. However, the greater resistance to attack requires longer treatment for dissolution of the coating in the above analytical procedure. The hexavalent chromium content appears to be reduced somewhat during the more severe dissolving operations because of the chemical action on the metal. Apparently the nascent hydrogen generated by the reaction effects the reduction. The hexavalent chromium content that any coating bath provides can also be determined by applying the coating bath in exactly the same way to other metals, or to surfaces like glass, which do not interfere with the analysis. Glass, even if attacked by alkali, does not appear to cause any change in the hexavalent chromium content. Coatings on glass can be dissolved in more concentrated alkali, such as those containing 40% NaOH by weight, and the coating formed on glass appears to be identical to that formed on metal.

The coating solution can be applied by immersion, flooding, spraying, roller coating, electrostatic spraying, etc. Roller coating, immersing, and flooding are particularly suitable for continuous coating of strip metal. The thickness of the coating depends upon the concentration of the solution, and if applied by roller coating, the roll pressure and roll surface characteristics also affect the thickness of the final coating.

It has been found advantageous to incorporate in the coating solution a small amount of wetting agent in the order of .005 to 0.3% by weight to improve the wettability of the metal surface by the coating solution. With such a wetting agent in the treating solution, the surface of the metal is more uniformly and more rapidly wetted so that the entire treatment time is held to a minimum. The final coating is also more uniform and precleaning problems are minimized. Furthermore, oxidizable wetting agents such as are formed by condensing 3 mols of ethylene oxide with p-(n-octyl)phenol, may be use to take the place of some of the reducing agent. Long-chained alkyl sulfates are suitable and tertiary butyl alcohol will be effective although it does not cause any appreciable reduction and is generally required to be in higher concentration, e.g. 0.5%, to provide really effective wetting. In general, however, anionic, cationic or non-ionic wetting agents including quarternary ammonium compounds of long-chain alkyl or aralkylamines, can be used.

In some cases, where metals are difficult to wet, the amount of wetting agent used may lead to foaming. This difficulty may be minimized by adding to the bath an anti-foaming agent such as water-solubilized alkyl phosphate type wetting agents. For example, a 0.001% addition of monolauryl phosphate completely esterified with octaethylene glycol, to a bath containing 0.006% of the above-mentioned octyl phenyl polyethylene oxide alcohol wetting agent, gives very effective wetting without foaming difficulties.

The following examples indicate some of the ways in which the invention can be practiced.

Example I

AISI Type 430 stainless steel, bright automotive finish .02 inch thick in coil form, was processed through the following steps:

(*a*) Cathodically clean in an aqueous solution containing 16 grams KOH per liter at 140–160° F., at a current density of 40 amperes per square foot for 6 seconds.
(*b*) Tap water rinse.
(*c*) Clean anodically in an aqueous solution containing 16 grams KOH per liter at 140–160° F., at a current density of 40 amperes per square foot for 6 seconds.
(*d*) Tap water rinse.
(*e*) Pass strip between grooved rubber rolls flooded with an aqueous solution containing 0.3% CrO_3 and 0.1% cane sugar at 75° F., thereby leaving a uniform film of the solution on the sheet.
(*f*) The filmed strip is then heated to a temperature of 390° F., by passing it for 2½ seconds between banks of ceramic gas burners heated red hot by burning gas.

The resulting cured coating weighs 6 milligrams per square foot and a sample of the coated metal exposed to a salt spray cabinet, 20% NaCl at 95° F., shows no corrosion after 1 month's exposure. Uncoated samples from the same stock are badly covered with corrosion products after a 1 week's exposure to the same treatment.

Example II

Six groups of 3 inch by 5 inch AISI Type 430 stainless steel panels, bright automotive stock, .025 inch thick, were cleaned by brushing in an aqueous solution containing per liter 25 grams Na_2HPO_4, 5 grams NaOH, and 5 grams of the wetting agent made by condensing 3 mols of ethylene oxide with p-(n-octyl)phenol, at 180° F. for 1 minute. After rinsing with water the cleaned panels are coated by dipping them in an aqueous solution containing CrO_3 and enough cane sugar so that the weight ratio of CrO_3/sugar is maintained at 3/1. Each group of panels was coated with a different solution as specified below. The coated panels were then heated in an electric furnace for 9 seconds to attain a temperature of 350° F. on the surface. The following table shows the percent of CrO_3 used, the cured coating weight per square foot, the appearance of the coating, and the performance in salt spray exposure.

Percent CrO_3	Coating Weight, mg./sq. ft.	Coating Appearance	Performance in Salt Spray at 95° F., 20% NaCl, 1 month
Untreated			Very poor performance—surface covered with rust.
.1	1	Not noticeable	Slight and localized corrosion.
.25	5	Almost colorless	Slight and localized corrosion.
.5	8	Very light brownish tinge uniform.	Very slight and localized corrosion.
1.6	27	Light blue uniform coating.	No corrosion.
2.8	56	Light purple coating	Do.
6.0	96	Optical interference pattern.	Do.
11.0	212	do	Do.

Example III

Several 3 inch by 5 inch Type 430 stainless steel panels as in Example II were cleaned, coated and cured as described in Example II, except that in all cases 1.5% CrO_3 acid was used with various types and amounts of reducing agents as listed below:

Reducing Agent Used	Weight Ratio: CrO_3/Reducing Agent	Performance in Salt Spray Exposure 20% NaCl, 95° F., 1 month
H_3PO_3	3/1	Practically no corrosion.
H_3PO_3	3/2	Do.
H_3PO_3	1/1	Do.
Triethanolamine	3/1	Do.
Do	4/1	Do.
Glycerol	3/1	Do.
Do	1/1	Do.
Ethylene Glycol	3/1	Do.
Do	1/1	Do.
Polyethylene glycol having an average molecular weight of 1500.	3/1	Do.
Do	1/1	Do.
Citric Acid	3/1	Do.
Do	1/1	Do.
Cane Sugar	3/1	Do.
Do	2/1	Do.
Uncoated		Badly covered with rust.

Example IV

To demonstrate how the color and appearance of the chromium-containing coating can be influenced by varying ratios of CrO_3 to reducing agent and varying conversion temperatures, a series of panels of dull finish AISI Type 410 stainless steel was treated in the following different ways, using otherwise identical techniques and the same (3%) concentration of CrO_3 and the same reducing agent (triethanolamine).

Weight Ratio of CrO_3 to Triethanolamine	Peak Curing Temp., °F.	Percent Conversion to Trivalent Cr	Appearance
7/1	325	40	Brown.
6/1	325	55	Ligh Brown.
6/1	425	75	Very Light Brown.
4/1	425	91	Greenish Tint.
3/1	425	95	Colorless.

A feature of the present invention is that very little time is needed for the application of the chromium-containing coating. The solution of chromic acid and reducing agent need only be in contact with the metal surface long enough to wet it properly, and the curing operation need be no longer than required to attain the desired surface temperature. Even a fraction of a second at the specified curing temperature is sufficient. Some time may be required to reach that temperature depending upon the rate at which heat is supplied, the thickness and mass of metal, and the manner in which heat is supplied. Any source of heat is applicable. The selection depends upon the desired conversion speed, shape of article to be heated, gauge, etc. Suitable heating sources include infrared lamps, cut-type ceramic or tubular metal gas burners heated to incandescence, ordinary gas burners, induction heating, hot air, and the like.

Curing temperatures below 250° F. do not provide the striking results of the invention. For example, if the solution of chromic acid and reducing agent is merely permitted to dry at 212° F., the coating is not nearly as resistant to chemicals and in most cases is even soluble in water. The solubility of the coating cured at 212° F. may diminish somewhat upon standing for several days, but it does not approach that of a coating cured pursuant to the invention.

By reason of the high speed with which the coatings of the invention can be applied, they are readily incorporated in conventional metal manufacturing or metal coating production lines. Such lines operate at speeds sometimes as high as 600 feet per minute or higher, and at such speeds even a one-minute treatment would require quite a few hundred feet of additional line length.

The chromium-containing coatings of the present invention are very effective in weights as low as 1 milligram per square foot of coated surface, or as high as 100 or even 200 milligrams per square foot. Coatings heavier than about 50 milligrams per square foot do not seem to add too much to the protection that is afforded, and are not desirable when the coated metal is to be sharply deformed, as by a drawing operation. Even the 50 milligrams per square foot coatings do not withstand drawing operations too well unless the conversion percentage is 70 or lower.

Coatings that have been cured at temperatures of up to 375° F. can have their weights determined very rapidly by merely dissolving such coating from a sample portion of the coated metal. A 20% solution of sodium hydroxide in water at 200–212° F. for 1½ minutes is effective for this purpose. The panel is weighed both before and after the coating removal and the weight loss gives the coating weight. If desired the coating weight can also be determined by dissolving it off in the above manner and adding to the resulting solution an excess of sodium peroxide or hydrogen peroxide. The peroxide is permitted to react to completion after which the solution

is diluted to a standard volume and its color checked against a standard by means of a colorimeter. So long as the precursor coating solution has a substantially unchanged composition, the chromium content shown by the colorimeter will indicate the amount of coating on the tested section. This relationship holds if before the testing the coating is cured at a temperature at least as high as 250° F. A curing below this temperature leaves a product with somewhat higher moisture content, and a suitable correction would then be needed. At or above 250° F. the moisture content of the coating appears to be substantially constant.

Instead of colorimetrically determining the chromium content of the solution in which the coating is dissolved, this content can be obtained by titrating the solution with sodium thiosulfate as referred to above.

The coatings when cured at temperatures of about 400° F. or higher are resistant to solution by sodium hydroxide, and sodium hydroxide solutions of 30 or even 40% strength may be needed. Such strong solutions dissolve some of the metal, however, and a correction should then be applied. The correction can be obtained by filtering off the iron hydroxide formed in the solution, preferably after the peroxide treatment and after the peroxidized solution is neutralized with sulfuric acid and then made slightly alkaline with ammonia. From the weight of the iron hydroxide filtered off, and the analysis of the steel, the chromium dissolved from the steel is determined. It appears that the chromium and iron are dissolved substantially simultaneously by the treatment so that the correction is capable of good accuracy both for the colorimetric chromium analysis as well as for the overall coating weight determination. A similar correction can be used with the other steels such as chromium-free alloys, but there the dissolved iron does not significantly interfere with the colorimetric chromium determination and no iron separation or correction is needed except for the overall coating weight determination.

For the purpose of checking the coating during a continuous coating operation, the coating weight can be more readily determined by lowering the curing temperature over a small portion of the metal surface so that a sample of that localized surface can have its coating more readily dissolved off. Where the metal is in the form of elongated sheets coiled up, such a low curing temperature can be restricted to one or both ends of the coil, for example. The remainder of the metal can be cured at the best curing temperature, which is generally up near 390° F.

The above analytical procedures are also suitable for determining coating weights on other metals including plain carbon steels.

The coatings of the present invention need not be relied on to impart any characteristic color to the base metal. This metal can be itself colored as by plating with a different metal such as copper, or by applying to its surface an adherent colored coating such as in situ formed metal oxide or sulfide. The following examples show how the coatings of the present invention improve the corrosion resistances of such colored products.

Example V

Panels as in Example II were given the following treatment:

(1) Clean cathodically in an aqueous solution containing 5% by weight Na_2CO_3 at 160° F. for 30 seconds, employing a current density of 80 amperes per square foot.
(2) Rinse with tap water.
(3) Dip in an aqueous solution containing 20% by weight H_2SO_4 for ½ minute at 150° F. to activate the steel surface (remove passive film).
(4) Rinse with tap water.
(5) Electroplate about .00002 inch copper on the metal surface using Rochelle salt copper cyanide bath. The

Rochelle salt copper cyanide bath contains the following constituents:

3.5 ounces per gallon copper cyanide
4.6 ounces per gallon sodium cyanide
4.0 ounces per gallon Rochelle salts (potassium sodium tartarate $KNaC_4H_4O_6 \cdot 4H_2O$)
4.0 ounces per gallon sodium carbonate

The conditions of plating used were 3 amperes per square foot, 75° F., 7 minutes.

(6) Rinse in tap water and dry by air blast.

Some of the above treated panels after the final rinse and before drying, were coated with an aqueous solution containing 2.1% CrO_3, .7% cane sugar and .005% of the above-mentioned octyl phenyl polyethylene oxide alcohol wetting agent. The solution was rolled on the panels and the applied film cured to attain a temperature of 425° F. on the steel surface (9 seconds—1500° F. electric furnace).

Example VI

Other copper plated panels of Example V after the final rinse, were dipped in a blackening bath containing 1 part by volume of saturated $(NH_4)_2S$ solution and 1 part by volume water, for 30 seconds at 75° F. followed by a tap water rinsing and drying. Some of these blackened panels were also given the final coating and curing as in Example V.

Example VII

Other copper plated panels of Example V after the final rinse were subjected to a bluing treatment by immersing them in an aqueous solution of—

75 grams per liter potassium chlorate
75 grams per liter ammonium nitrate
2 grams per liter copper nitrate

at 180° F. for 10 seconds, followed by tap water rinsing and drying. Some of these blued panels were also given the chromium oxide coating treatment of Example V, except that ½% CrO_3 and .17% sugar was used.

The following table gives the color and salt spray performance of the panels made in Examples V, VI and VII.

Treatment	Color	Performance in Salt Spray 20% NaCl, 90°F. 24 hours
Copper plate of Example V.	Copper color	Completely discolored and moderately covered with corrosion products.
Copper plate plus chromium oxide coating of Example V.	Bronze color	No change in appearance. No corrosion.
Sulfided copper coating of Example VI.	Black	Badly rusted throughout.
Sulfided copper coating and chromium oxide coating of Example VI.	do	Slight local pit corrosion.
Blued copper coating of Example VII.	Blue	Badly discolored and pit corrosion throughout.
Blued copper coating and chromium oxide coating of Example VII.	Bluish-yellow	Very slight corrosion and changing color.

Various colors can also be imparted to the above stainless steels by means of heat or by treatment in fused baths such as a mixture of equal weights of sodium nitrate and potassium nitrate at 300° C. Colors starting with a beautiful gold at about 500° F. to a blue at 1000° F. and black at higher temperatures, can be produced by mere heating in air. These oxide films, however, are quite easily corroded and in themselves lower the corrosion resistance of the stainless steel. Application of the chromium oxide coating on top of these oxides, however, markedly increase corrosion resistance, as in the following:

Example VIII

AISI Type 420 stainless steel panels .025 inch thick were solvent cleaned with trichlorethylene and then subjected to a heating operation by placing in an electric

furnace for ½ minute at 1500° F. The resulting color was gold. Some of these panels were dip coated with a ¼% CrO_3 or ½% CrO_3 using a CrO_3/sugar weight ratio of 3/1 and curing them in a furnace to attain a temperature of 390° F. on the surface (9 seconds in a 1500° F. source). The ¼% CrO_3 solution gave a 5 milligram per square foot coating weight, and the ½% CrO_3 a 10 milligram per square foot coating. The gold color was thereby made somewhat deeper. Panels were subjected to a salt spray cabinet for 100 hours using 20% NaCl at 90° F., with the following results:

Treatment	Salt Spray Performance after 100 hours
Gold color by heating	Badly corroded.
Gold color by heating plus chromium oxide coating (5 milligrams per square foot).	Almost no corrosion.
Gold color by heating plus chromium oxide coating (10 milligrams per square foot).	Almost no corrosion.

Alkaline solutions of $KMnO_4$ in water also impart a gold color to the above stainless steels, probably by oxidizing the surface. This oxide is more protective than the thermal oxide coating. However, here again the corrosion resistance is sharply improved by applying the chromium oxide coating on top.

Example IX

(1) Clean cathodically .010 inch thick panels of 17% chromium steel (0.40% carbon, no other significant ingredients) in aqueous 5% by weight Na_2CO_3, 160° F., 30 seconds, using a current density of 80 amperes per square foot.
(2) Rinse in tap water.
(3) Immerse for 5 minutes in an aqueous solution containing 10% by weight $KMnO_4$ and 10% by weight NaOH at 190° F.
(4) Rinse in tap water.
(5) Dip in a solution containing 1% by weight CrO_3 and 0.3% by weight cane sugar, drain 30 seconds, and cure in a furnace to attain a temperature of 400° F. on the surface.

The resulting coating has an orange tint and offers excellent protection to the stainless steel.

Another suitable technique for coloring stainless steels treated in accordance with the present invention is by dipping in a strong aqueous solution of sulfuric acid containing an etch inhibitor, as described in U.S. Patent 2,283,171, granted May 19, 1942. A still further different type of coloring for this purpose is described in U.S. Patent 2,618,578.

The coating baths containing chromic acid combined with reducing agent can be stored for prolonged periods of time by adding to them a small amount of a soluble maganese compound as described in U.S. Patent 2,777,785. Some manganese compounds, such as potassium permanganate, will cause after a short period of time the development of a slight precipitate of manganese dioxide. This is not a sign of complete deterioration, however, since after another day or so the manganese dioxide precipitate will spontaneously dissolve. The presence of the precipitate will interfere with the coating operation, and if the bath is to be used before the precipitate redissolves, it should be filtered. After spontaneous dissolution the bath can generally be stored for several weeks before a chromium-containing precipitate forms, to indicate that the bath is no longer suitable.

The coatings of the present invention can also be applied to fabricated articles such as forgings, machinings, castings and the like. Brushing, dipping or spraying can be used for the application of the precursor solution and ovens or banks of heating lamps or gas burners for the curing. Small objects such as rivets, nails, screws, etc., can be wet with the precursor solution and then cured by heated air while continuously moved in

a tumbling barrel. Rods, plates, strips, coils and stamped articles can also be heated in at least one of the above-described ways.

The coatings of the present invention can also be changed in color by subjecting them to a buffing operation. For example, the coated metal of Example II, when buffed with a cloth buffing wheel six inches in diameter and rotating at a speed of 3400 r.p.m., will take on a somewhat gold color. The coating color appears to change to gold under the frictional treatment. A buffing compound may or may not be used in such an operation.

Another feature of the present invention is that the coatings behave as though they are electrically conductive. One example of such behavior is that electroplatings can be applied over the coatings. Chromium, for instance, can be readily deposited at room temperature from an aqueous solution of 400 grams of chromic acid and 4 grams H_2SO_4 per liter, the coated metal being connected as a cathode, and using a cathode current density of 50 amperes per square foot. The current density can range from 20 to 100 amperes per square foot, and the temperature can range from about 60 to 140° F. The chromium deposits as a dull layer that adheres to the oxide coating, but can be removed by electrolytic stripping, using the chromium plating as an anode in an aqueous solution of 5% sodium hydroxide. After stripping, the mixed chromium oxide coating of the present invention is found still adhering to the base metal.

Copper, nickel, zinc and the other metals can also be electroplated over the coating of the present invention, in place of or in addition to the chromium, and any or all of these metals can be so plated on the mixed chromium oxide coating regardless of the base metal which carries the coating.

Although as described in applicants' prior applications, Serial No. 592,552, filed June 20, 1956, now U.S. Patent No. 3,031,333, and Serial No. 615,755, filed October 15, 1956, now U.S. Patent No. 2,861,906, corrodible ferrous metals coated in accordance with the present invention show improved corrosion resistance if before the coating the ferrous metal is subjected to a grain boundary etch, this does not apply with the chromium-type stainless iron alloys.

Iron alloys containing insufficient chromium to be called stainless do show improved corrosion resistance when a grain boundary etch is used. A typical alloy of this low chromium kind would be Type AISI 8620 steel having the following composition (in addition to iron):

	Percent
Carbon	0.18 to 0.23
Chromium	0.4 to 0.6
Nickel	0.4 to 0.9
Manganese	0.7 to 0.9
Molybdenum	0.12 to 0.25

However, even with the above low chromium alloy the grain boundary etch can be omitted where the mixed chromium oxide coating of the present invention is not intended to remain permanently in place. For example, the above low chromium steel shows considerable scaling when subjected to a heat treatment as for the purpose of hardening or tempering. However, if the unetched metal is coated with the mixed chromium oxide coating of the present invention, a heat treatment at 1700 to 1800° F. for 20 minutes will produce very much less and uniform scaling. The scaling will be substantially completely eliminated if over the mixed chromium oxide there is placed a loose layer of clay about ¼ inch thick. Instead of the clay, a layer of borax, sodium silicate or sand can be used.

The greatly improved corrosion resistance of the present invention as described above is obtained with all of the chromium-type stainless steels whether the chromium content be as low as 10% or as high as 25%. Specifically included are AISI Types 403, 405, 406, 414, 416, 430F, 431, 442, 443 and 446 steel. Alloys that contain appreciable amounts of nickel usually have more inherent corrosion resistance and this resistance increases as the nickel content increases. However, a stainless steel having as much as 20% chromium and 11% nickel, such as Types AISI 301 and 302 ordinarily used in building panels, will still show some improvement when the coating of the present invention is applied thereover.

Coatings of the present invention are also made more protective by incorporating certain resins in the coating solution. For example, the addition to the chromic acid reducing agent solution of the butadiene-styrene resin described in Example 1 of U.S. Patent 2,772,254, granted November 27, 1956, dispersed in water to make a mixed bath having equal amounts of chromic acid and resin, gives a resin-chromium oxide coating that is much more resistant to salt spray and has much better adhesion than the resin-free chromium oxide coating, particularly with overall coating weights of less than 50 milligrams per square foot. Other butadiene-styrene resins both thermosetting or thermoplastic will also give the same improvement, as will polyvinyl chloride, polystyrene, and alkyd resins either unmodified or oil-modified as with tung oil. Other resins such as polyethylene seem to show only slight effects whereas the above-listed resins will increase the salt-spray corrosion resistance by about 50% or more.

In general, it is preferred to hold the maximum curing temperature down to not over 400° F. to keep from degrading the resin. As much as 90% resin can be used if desired, and the advantages of the resin are felt with as little as 25% of the resin. Best results are obtained, however, at 30 to 60%, particularly with adhesion under impact. All of the above resin concentrations are based on the weight of resin solids as compared with the total weight of chromic acid and resin solids present in the coating solution.

The following example shows the corrosion reduction obtained by the resin-chromic acid coating:

Example X

A pressure container drawn in one piece from SAE 1010 steel and having a wall thickness of 12 mils, is cleaned by solvent degreasing with trichloroethylene and ¼ minute dip in 5% aqueous Na_2HPO_4, then sprayed over its interior with an aqueous solution having 1% CrO_3, ⅓% sucrose and 1% (solids content) of the butadiene-styrene (30:70) copolymer made as in Example II of U.S. Patent 2,683,698, granted July 13, 1954. The container was then passed through a hot air furnace held at 400° F. for 3 minutes, the metal surface reaching a temperature of 375° F. Upon cooling, the container which on analysis showed a coating weight of 10 milligrams per square foot, was subjected to saturated salt spray at 120° F., and showed only slight corrosion after 50 hours.

The product of Example X, even though no preliminary nitric acid etch it used, is suitable for many commercial purposes such as pressure-type containers for solutions of self-lathering shaving cream as described in U.S. Patent 2,655,480, granted October 31, 1953. The presence of the resin not only improves the adhesion of paints, but it increases the corrosion resistance, particularly by acids such as are present in anionic detergents and in resin latices. Similar results are obtained with the above resin replaced by the alkyd resin emulsion of Example I in U.S. Patent 2,634,245, granted April 7, 1953, the polyvinyl chloride emulsion of Example I in U.S. Patent 2,689,242, granted September 14, 1954, or the polystyrene emulsion of Example I in U.S. Patent 2,635,086, granted April 14, 1953.

The above resin-containing coatings are very useful for application to containers for latex paints as well as

detergents, and can be so used with or without a covering paint or enamel layer. Without the etch and without the resin, the protection although poorer, is still effective for the shaving-cream container use. On other metals such as copper, and chromium type stainless iron alloys similar improvements are provided by the mixed chromium oxides themselves. Copper is also very effectively protected against sulfide blackening by the resin-free coating without any preliminary etch, as well as by the resin-containing coatings.

The resin-containing coating mixtures more readily wet metal surfaces, particularly where the surfaces have not yet been too scrupulously cleaned. A fairly short cleaning operation is accordingly all that need be used, and if the metal as received is free from gross contaminants, an extremely short dip in aqueous alkali such as trisodium phosphate is all that is needed. Also because of the physical characteristics of the coating dispersions when they contain resin in addition to the chromic acid and reducing agent, they can be more readily used to build up heavier coatings as by spraying. The coatings thus formed whether heavy or light also show better adhesion for paints that are applied over them.

The mixed chromium oxide coating of the present invention can also be prepared with a chromic acid solution that has an appreciable proportion of sucrose-containing resins. By way of example, the presence of the phenol-formaldehyde-aniline-sugar resins of U.S. Patent 2,666,037, granted January 12, 1954, or the phenol-formaldehyde-sucrose resins described in Chemical and Engineering issues of March 4, 1957, page 7, and March 25, 1957, page 27, can be added to the chromic acid solution so as to provide a solid resin content of from 10 to 50% of the total solids. The presence of such resins in dissolved form increases the amount of reducing agent apparently because the sugar proportions of the resin molecules can be oxidized by the CrO_3. It is accordingly preferred when these resins are used, to diminish the amount of separate reducing agent. In general, the decrease in amount of separate reducing agent is about one-half the amount by weight of sugar that is polymerized in the resin. For example, a coating solution containing 2% chromic acid and 1% of the resin of Example 1 of U.S. Patent 2,666,037, need only have sucrose separately added in an amount of ½% by weight to give the chromium conversion of 95%, corresponding to the conversion of a similar resin-free coating solution containing ⅔% sucrose when both solutions are used with curing temperatures of 390° F.

A feature of the present invention, particularly as applied to the resin-free mixed chromium oxide layer on chromium-type stainless steel alloys, is that the protective effect of the coating is retained even though the coated surface is buffed intensively enough to apparently remove all the coating. In other words, a buffing operation, as with an ordinary felt wheel 10 inches in diameter without the help of any buffing compound and with the wheel rotating at 3500 r.p.m., can remove the color ordinarily present when a mixed chromium oxide layer of about 10 milligrams per square foot is applied. Although the color is removed, the increased corrosion resistance of the coated stock remains substantially unaffected. Similar buffing of coatings having lower coating weights, even down to as low as 1 milligram per square foot, will likewise not detract from the corrosion resistance even though the buffing is severe enough to apparently completely remove the coating.

Referring now to the drawings, FIG. 1 shows a hub cap formed from Type 430 stainless steel that had been coated before forming in accordance with the process described in Example I. The coating is partly broken away in the figure to more clearly show it.

FIG. 2 illustrates a trim strip made of a sheet of Type 442 stainless steel and coated as in Example III after it was formed into the strip.

FIG. 3 is a building panel made of Type 410 stainless steel colored orange while in strip form according to the process of Example IX, and with the chromium oxide protective coating applied over the color. This panel is of the interlocking type that can be used both as external or internal wall facing.

The present application is in part a continuation of applications Serial No. 615,755, filed October 15, 1956, now U.S. Patent No. 2,861,906, and Serial No. 587,388, filed May 25, 1956, now U.S. Patent No. 2,911,332. The latter application is in turn a continuation-in-part of applications Serial No. 277,286, filed March 18, 1952, now U.S. Patent 2,768,103, granted October 23, 1956; Serial No. 278,481, filed March 25, 1952, now U.S. Patent 2,768,104, granted October 23, 1956; Serial No. 371,427, filed July 30 ,1953, now U.S. Patent 2,777,785, granted January 15, 1957; Serial No. 433,698, filed June 1, 1954, now U.S. Patent 2,773,623, granted December 11, 1956; and Serial No. 458,668, filed September 27, 1954, now abandoned.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

A method of reducing scale formation during the heat treatment of ferrous metal objects that normally form scale during such treatment at 1700 to 1800° F., said method being characterized by the steps of applying to the surface of the metal before the heat treatment an in situ formed coating of a combination of hydrated mixed chromium oxides, the coating having from 20 to 60% chromium by weight, about 40 to 95% of this chromium being trivalent and the coating weighing at least 1 milligram per square foot of coverage, and then carrying out the heat treatment.

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