

NC-96,346/347

PATENT

5 PROCESS FOR PREPARING CHROMIUM CONVERSION COATINGS FOR
 IRON AND IRON ALLOYS

ORIGIN OF INVENTION

 The invention described herein was made by employee(s) of the United States
10 Government and may be manufactured and used by or for the Government for
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CONTINUATION APPLICATION

15 This Application is a Continuation-In-Part of copending Application Serial No.
NC-96,347, Filed: , 2005.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

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 This invention relates to a process for preparing zirconium-chromium conversion
coatings on iron and iron alloys. The process comprises pretreating iron and its alloys
with effective amounts of an acidic aqueous solution containing trivalent chromium
compounds, at least one hexafluorozirconate and optionally, tetrafluoroborates and/or
25 hexafluorosilicates, zinc compounds, surfactants, wetting agents and/or thickeners.
More specifically, this invention relates to a process for pretreating iron and iron alloys to

improve the alloys adhesion bonding and corrosion resistant properties. The process comprises treating iron and its alloys with an acidic aqueous solution containing effective amounts of at least one water-soluble trivalent chromium compound, a water soluble alkali metal hexafluorozirconate, at least one water soluble alkali metal tetrafluoroborate and/or hexafluorosilicate, at least one water soluble divalent zinc compound, and effective amounts of water soluble thickeners and/or water soluble surfactants.

Current surface preparation of iron alloys such as steel include a variety of mechanical and chemical processes, depending on the application. Phosphate coatings have been used historically to improve the adhesion of various outer coatings such as paint and corrosion resistance of steel. For example, grit blasting has been used to improve the adhesion when phosphate coatings were not practical to apply. In this case, the desired paint primer is applied directly to the grit-blasted steel which is referred to as the "direct-to-metal" process. Many organizations rely on the direct-to-metal technique as the use of phosphate coatings decline due to their reliance on a hexavalent chromium "rinse" for optimum adhesion and corrosion resistance. While direct-to-metal coating is straightforward and does not rely on a chemically-produced coating, it does not, however, provide an optimum-performing coating system. The absence of a chemical pretreatment lowers the overall corrosion resistance of the system. This is partially due to the near ubiquitous use of non-chromated primers for painting iron alloys such as steel. In addition, while grit- blasting imparts a sound mechanical base for paint adhesion it is labor intensive and requires application of the grit over all the steel surface, generating large quantities of spent grit that must be collected and then recycled or disposed.

Further, where there is no corrosion-resistant conversion coating on the iron alloys such as steel there is the problem of "flash rusting" that occurs after the steel parts are

grit blasted or cleaned, but before the paint can be applied. The requirement to keep flash rust from occurring places a tremendous burden on scheduling and does not allow for components to sit for more than a few hours before being painted. This prevents the parts or components from being allowed to sit overnight or over the weekend and

5 therefore prevents the work from being completed by the end of a shift where the parts cannot be painted before the end of a particular shift. This renders production less productive than it ordinarily could be. In addition, parts or components that are processed, but not yet painted that need to be shipped or moved before painting requires an elaborate and costly protective coating that must then be subsequently stripped before

10 application of the paint. A chemical pretreatment for iron alloys e.g. steel that is analogous to an aluminum pretreatment is not available but would be desirable. Such a coating would impart good paint adhesion to the steel substrate without needing a grit-blasted surface and thereby increase the corrosion resistance of the painted steel. A pretreatment of the alloy would also serve to prevent flash-rusting and allow for expanded

15 handling times of the steel parts before they need to be painted. Such a pretreatment could be produced by merely immersing the components or steel parts in a tank of the pretreating solution, or by spraying the solution onto the alloy, or by wiping the solution on to the alloy.

20 SUMMARY OF THE INVENTION

This invention relates to a process for preparing conversion coatings on iron and its alloys at ambient temperatures or higher e.g. ranging up to about 120°F. More specifically, this invention relates to a process of preparing conversion coatings on iron

alloys such as steel to improve its corrosion resistance and adhesion bonding properties.

The trivalent chromium process (TCP) of this invention comprises an acidic aqueous solution having a pH ranging from about 2.5 to 5.5 and preferably 3.7 to 4.0, and per liter of said acidic solution, from about 0.01 to 22 grams of a water soluble trivalent chromium
5 compound, about 0.01 to 12 grams of an alkali metal hexafluorozirconate, from 0.0 to 12 grams of at least one fluorocompound selected from the group consisting of tetrafluoroborates, hexafluorosilicates and various combinations thereof in any ratio, from 0.0 to 10 grams of at least one water soluble divalent zinc compound, from 0.0 to 10 grams and preferable 0.5 to 1.5 grams of at least one water-soluble thickener, and/or from
10 0.0 to 10 and preferably 0.5 to 1.5 grams of at least one water soluble non-ionic, cationic or anionic surfactant or wetting agent.

It is therefore an object of this invention to provide an acidic aqueous solution comprising a trivalent chromium compound, hexafluorozirconates, and tetrafluoroborates and/or hexafluorosilicates for pretreating iron alloys to improve its adhesion and
15 corrosion-resistance properties.

It is another object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 2.5 to 5.5 which comprises a trivalent chromium salt and hexafluorozirconates for pretreating iron alloys such as steel.

It is another object of this invention to provide a pretreatment process for coating
20 steel that has a practical color change and imparts good adhesion without a grit-blasted surface. The pretreatment process of this invention also provides improved corrosion resistance of painted steel compared to steel that is painted by the direct-to-metal method.

It is a further object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 3.7 to 4.0 comprising a trivalent chromium compound

and hexafluorozirconates for treating iron alloys at about room temperature or higher wherein said acidic solution contains substantially no hexavalent chromium.

These and other object of the invention will become apparent by reference to the detailed description when considered in conjunction with the accompanying FIG's. 1-6,

5 (photos).

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photo of MIL-C-53022 primer on steel, with no grit blast.

10 Fig. 2 is a photo of MIL-C-53022 primer on steel with TCP-P coating, with no grit blast.

Fig. 3 is a photo of MIL-C-53022 primer on steel with Aqua Zen treatment, with no grit blast.

Fig. 4 is a photo of MIL-C-53022 primer on steel with grit blast treatment.

15 Fig. 5 is a photo of MIL-C-53022 primer on steel with TCP-P coating with grit blast treatment.

Fig. 6 is a photo of MIL-C-53022 primer on steel with Aqua Zen treatment with grit blast treatment.

20 DETAILED DESCRIPTION OF THE INVENTION

This invention relates to the process of using an acidic aqueous solution having a pH ranging from about 2.5 to 5.5, and preferably from about 2.5 to 4.5 or 3.7 to 4.0 for preparing a zirconium-chromium conversion coating on iron and its alloys such as steel to

improve adhesion bonding and the corrosion-resistance properties of the alloy. The process comprises preparing the pretreatment coating by using an acidic aqueous solution at temperatures ranging up to about 120°F or higher which comprises from about 0.01 to 22 grams and preferably from about 0.01 to 10 grams e.g. 5.0 to 7.0 grams of at least one water soluble trivalent chromium compound e.g. chromium sulfate, about 0.01 to 12 grams and preferably about 1.0 to 8.0 grams e.g. 6.0 to 8.0 grams of at least one alkali metal hexafluorozirconate, about 0.0 to 12 grams and preferably from about 0.01 to 1.2 grams e.g. 0.12 to 0.24 grams of at least one fluorocompound selected from the group consisting of alkali metal tetrafluoroborates, alkali metal hexafluorosilicates and various mixtures or combinations thereof in any ratio, and from about 0.0 to 10 grams and preferably 0.001 to 10 or 0.1 to 5.0 grams of at least one divalent zinc compound such as zinc sulfate.

After cleaning and deoxidizing or pickling the iron alloy e.g. steel substrate via conventional mechanical or chemical techniques, the solution is applied at about room temperature to the substrate via immersion, spray or wipe-on techniques similar to the process used for aluminum pretreatments. Solution dwell time ranges from about 1.0 to 10 minutes. With this solution, the 1.0 to 10 minute dwell time yields an optimum film for color change, paint adhesion, and corrosion resistance. More importantly for this invention, the 1.0 to 10 minute dwell time yields appreciable color change to the as-deposited coating that ranges from royal blue to blue-gray depending primarily on the chemical composition of the aqueous solution. The remaining unreacted solution is subsequently rinsed from the substrate with tap or deionized water. No additional post-treatments of the alloy are necessary. The pretreatment coating is allowed to dry thoroughly before subsequent painting.

In some processes, depending on the physical characteristics of the iron alloy i.e. steel substrate such as the physical size of the substrate, an unique feature is the addition of a thickener to the solution that aids in optimum film formation during spray and wipe-on applications by slowing down solution evaporation. This also mitigates the formation of powdery deposits that degrade paint adhesion. The addition of thickeners, also aids in proper film formation during large area applications and mitigates the diluent effect of rinse water that remains on the substrate during processing from previous steps. This feature of the process yields films that have no streaks and are an improvement in coloration and corrosion protection. Water-soluble thickeners such as the cellulose compounds are present in the acidic aqueous solution in amounts ranging from about 0.0 to 10 grams per liter and preferably 0.5 to 1.5 e.g., or about 1.0 gram per liter of the aqueous solution.

Further, depending on the characteristics of the iron alloy, an effective but small amount of at least one water-soluble surfactant or wetting agent can be added to the acidic solution in amounts ranging from about 0.0 to 10 grams and preferably from 0.5 to 1.5 grams e.g. 1.0 gram per liter of the acidic solution. There are many water soluble surfactants known in the prior art and therefore for purpose of this invention the surfactants can be selected from the group consisting of non-ionic, cationic and anionic surfactants.

The trivalent chromium is added to the solution as a water-soluble trivalent chromium compound, preferably as a trivalent chromium salt. Specifically, in formulating the acidic aqueous solutions of this invention, the chromium salt can be added conveniently to the solution in its water soluble form wherein the valence of the chromium is plus 3. For example, some of the preferred chromium compounds are

incorporated in the solution in the form of $\text{Cr}_2(\text{SO}_4)_3$, $(\text{NH}_4)\text{Cr}(\text{SO}_4)_2$ or $\text{KCr}(\text{SO}_4)_2$ and any mixtures of these compounds. A preferred trivalent chromium salt concentration is within the range of about 5.0 to 7.0 grams per liter of the aqueous solution. It has been found that particularly good results are obtained from these processes when the trivalent chromium compound is present in solution in the preferred ranges.

In some treatments, the alkali metal tetrafluoroborates and/or hexafluorosilicates can be added to the acidic solutions in amounts as low as 0.01 grams per liter up to the solubility limits of the compounds. For example, about 50% weight percent of the fluorosilicate is added based on the weight of the fluorozirconate. In other words, for 8.0 grams per liter of the fluorozirconate salt, about 4.0 grams per liter of fluorosilicate is added to the solution. An alternative is to add about 0.01 to 100 weight percent of the fluoroborate salt based on the weight of the fluorozirconate salt. For example, about 1.0 to 10 weight percent of the fluoroborate salt can be added based on the weight of the fluorozirconate salt. A specific example comprises from about 6.0 to 8.0 grams per liter of potassium hexafluorozirconate, about 5.0 to 7.0 grams per liter of chromium III sulfate basic, about 0.1 to 5.0 grams per liter of divalent zinc sulfate and about 0.12 to 0.24 grams per liter of potassium tetrafluoroborate and/or hexafluorosilicate. An important result of the addition of the stabilizing additives i.e. the fluoroborates and/or fluorosilicates is that the solution is stable while the pH is maintained between about 2.5 and 5.5. However, in some examples the solutions may require small adjustments to the pH by the addition of effective amounts of a dilute acid or base to maintain the pH in the range of about 2.5 to 5.5 and preferably from 2.5 to 4.5 or 3.7 to 4.0.

The solution may contain at least one divalent zinc compound to improve the color and corrosion protection of the alloy when compared to other treatment or

compositions that do not contain zinc. The amount of the zinc compounds can be varied to adjust the color imparted to the coating, from as little as about 0.001 grams per liter up to 10 grams per liter e.g. 0.1 to 5.0 grams of Zinc^{2+} cation. The divalent zinc can be supplied by any chemical compound e.g. salt that dissolves in water and is compatible with the other components in the acid solution. Divalent zinc compounds that are water soluble at the required concentrations preferably include, for example, zinc acetate, zinc telluride, zinc tetrafluoroborate, zinc molybdate, zinc hexafluorosilicate, zinc sulfate and the like or any combination thereof in any ratio.

The pretreatment of the iron alloys can be carried out at various temperatures including the temperature of the solution which ranges from ambient e.g. from about room temperature up to about 120°F or higher up to about 200°F. Room temperature is preferred, however, in that this eliminates the necessity for heating equipment. The coating may be air dried by any of the methods known in the art including, for example, oven drying, forced-air drying, exposure to infra-red lamps, and the like. For purposes of this invention, the term "iron alloys" includes any iron alloy such as steel containing small but effective amounts of various other metals and non-metals such as carbon.

The following Examples illustrate the stable solutions of this invention, and the method of using the solutions in providing color recognition, improved adhesion bonding and corrosion-resistant coatings for iron and its alloys.

EXAMPLE 1

A stable acidic aqueous solution having a pH ranging from about 3.4 to 4.0 for pretreating steel to provide a corrosion-resistant and a color recognized coating thereon

comprises, per liter of solution, about 3.0 grams of trivalent chromium sulfate basic, about 4.0 grams of potassium hexafluorozirconate and about 1.0 gram of zinc sulfate.

EXAMPLE 2

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A stable acidic aqueous solution for treating steel to form a corrosion-resistant coating thereon comprises, per liter of solution, about 3.0 grams of trivalent chromium sulfate basic, about 4.0 grams of potassium hexafluorozirconate, and from about 0.0 to 0.12 grams of potassium tetrafluoroborate.

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EXAMPLE 3

A stable acidic aqueous solution for treating steel to provide a corrosion-resistant and a color recognized coating thereon comprises, per liter of solution, about 3.0 grams of trivalent chromium sulfate basic, about 4.0 grams of potassium hexafluorozirconate, about 0.12 grams of potassium tetrafluoroborate and about 2.0 grams of divalent zinc sulfate.

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The following Examples and data in Tables 1 and 2 show the paint adhesion performance of coatings using Mil-P-53022 epoxy primer and 4130 steel test coupons. Mil-P-53022 primers are commonly used on steel in a variety of Department of Defense systems. It is evident from the data in the Tables that the coatings provide a substantial increase in paint adhesion compared to the control coatings. The compositions or solutions, though typically used at ambient conditions may be applied at elevated temperatures to increase the reaction rate.

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EXAMPLE A

Process data and Examples for TCP/TCP-CC as a Conversion Coating for iron Alloys. Conversion coatings were applied to 4130 steel as follows:

5 Test coupons made from 4130 steel were cleaned in a standard alkaline cleaner (Turco HTC) at 140-160°F for 10 minutes. Coupons were then rinsed and immersed directly into the test solution. The solution comprised an aqueous solution of about 6.0 grams per liter of chromium sulfate basic and 8.0 grams per liter of potassium hexafluorozirconate (TCP-P). Coupons were allowed to dwell in the the TCP-P for
10 approximately 10 minutes, removed, and then thoroughly rinsed in de-ionized water. Coupons were then allowed to dry in a rack at ambient conditions. The resulting coatings were a deep royal blue in color, easily visible from across the laboratory. This is a critical indication for quality control during processing so that the processors have a way of telling that the coating is complete.

15 In addition to the TCP-P coated 4130 steel, control sets of 4130 were prepared by cleaning (Turco HTC) in the above-identified solution. A subset of these steel panels or coupons were grit blasted with alumina grit media to produce an average profile of 1.0 to 1.5 mils, a standard for a direct-to-metal painting. These steel coupons were then painted with MIL-C-53022 primer to approximately 1.0 mil thick. One sub-set of coupons was
20 painted with Aqua Zen “wash primer” before the primer. The Aqua Zen is an industry standard coating used to promote adhesion and improve corrosion performance of the coating system. The painted coupons sat for 14 days at ambient conditions to allow the paint to cure. After curing, the coupons were subjected to painted adhesion and painted corrosion tests. Table 1 describes the paint adhesion results. Ratings of 4 and 5 are

considered passing, and 0 to 3 are failing. As shown by the data, TCP-P coating provides excellent paint adhesion to the 4130 steel whether or not the steel was grit blasted. The TCP-P coating also shows better overall performance in comparison to the two controls panels which are commonly used on DoD equipment. In this test, the TCP-P coating is a better alternative to the Aqua Zen treatment and shows excellent performance with the MIL-C-53022 primer without the grit blast, where paint adhesion is very poor with only the primer. Fig's. 1 through 6 (photos) show examples of 7-day wet-tape adhesion for each coating system described in Table 1.

TABLE 1

COATINGS AND PAINT ADHESION RESULTS

Grit Blast	Coating System	Paint Adhesion Results			
		Dry	1-day Wet	4-day Wet	7-day Wet
No	MIL-C-53022 primer only	4	4	0	0
No	Aqua Zen plus MIL-C-53022 primer	5	4	3	3
No	TCP-P plus MIL-C-53022 primer	5	4	4	4
Yes	MIL-C-53022 primer only	5	5	5	3
Yes	Aqua Zen plus MIL-C-53022 primer	4	4	3	1
Yes	TCP-P plus MIL-C-53022 primer	5	5	5	4

EXAMPLE B

Conversion coatings were applied to 4130 steel as follows:

Test coupons were prepared by the same process as in Example A. The

- 5 composition (TCP-CC) solution comprised 3.0 grams per liter of chromium sulfate basic, 6.0 grams per liter of potassium hexafluorozirconate, 0.18 grams per liter of potassium tetrafluoroborate, and 2.0 grams per liter of zinc sulfate.

Table 2 sets-forth the paint adhesion results from these coated coupons that are comparable to the results in Table 1. As seen from the data, the coatings formed from
10 this TCP i.e. color change composition (TCP-CC) performs as well as TCP-P as an adhesion promoter.

TABLE 2

15 PAINT ADHESION RESULTS FOR TCP-CC

<i>Grit Blast</i>	<i>Coating System</i>	<i>Paint Adhesion Results</i>			
		Dry	1-day Wet	4-day Wet	7-day Wet
No	TCP-CC plus MIL-C-53022 primer	5	5	4	NA
Yes	TCP-CC plus MIL-C-53022 primer	5	5	5	NA

In preparing the acidic solutions of this invention, the water soluble surfactants can be added to the trivalent chromium solutions in amounts ranging from about 0 to 10 grams per liter and preferably about 0.5 to 1.5 grams per liter. The surfactants are added

to the aqueous solution to provide better wetting properties by lowering the surface tension thereby insuring complete coverage, and a more uniform film on the iron alloy substrates. The surfactants include at least one water soluble compound selected from the group consisting of non-ionic, anionic, and cationic surfactants. Some of the better known water soluble surfactants include the monocarboxyl imidoazoline, alkylsulfate sodium salts (DUPONOL®), tridecyloxy poly(alkyleneoxy ethanol), ethoxylated or propoxylated alkylphenol (IGEPAL®), alkylsulfonamides, alkaryl sulfonates, palmiticalkanol amides (CENTROL®), octylphenyl polyethoxy ethanol (TRITON®), sorbitan monopalmitate (SPAN®), dodecylphenyl polyethyleneglycol ether (e.g. TERGITROL®), alkyl pyrrolidone, polyalkoxylated fatty acid esters, alkylbenzene sulfonates and mixtures thereof. Other known water soluble surfactants include the alkylphenol alkoxyates, preferably the nonylphenol ethoxylates, and adducts of ethylene oxide with fatty amines; also see the publication: "Surfactants and Detergent Systems", published by John Wiley & Sons in Kirk-Othmer's Encyclopedia of Chemical Technology, 3rd Ed.

When large surfaces do not permit immersion or where vertical surfaces are to be sprayed, thickening agents can be added to retain the aqueous solution on the surface for sufficient contact time. The thickeners employed are known inorganic and preferably the organic water soluble thickeners added to the trivalent chromium solutions in effective amounts e.g. at sufficient concentrations ranging from about 0 to 10 grams per liter and preferably 0.5 to 1.5 grams per liter of the acidic solution. Specific examples of some preferred thickeners include the cellulose compounds, e.g. hydroxypropyl cellulose (e.g. Klucel), ethyl cellulose, hydroxyethyl cellulose, hydroxymethyl cellulose, or methyl cellulose and mixtures thereof. Other water soluble inorganic thickeners include colloidal

silica, clays such as bentonite, starches, gum arabic, tragacanth, agar and various combinations.

After preparing the iron alloy surface to be coated via conventional techniques, the solution can be applied via immersion, spray or wipe-on techniques. The TCP solutions can be used at elevated temperatures ranging up to 65°C or higher and optimally applied via immersion to further improve the corrosion resistance of the coatings. Solution dwell time ranges from about 1 to 60 minutes, and preferably 5 to 15 minutes at about 80°F. After dwelling, the remaining solution is then thoroughly rinsed from the substrate with tap or deionized water. No additional chemical manipulations of the deposited films are necessary for excellent performance. However, an application of a strong oxidizing solution can yield a film having additional corrosion resistance. The additional corrosion resistance is presumed to be due to the formation of hexavalent chromium in the film derived from the trivalent chromium. The aqueous solutions may be sprayed from a spray tank apparatus designed to replace immersion tanks. This concept also reduces active chemical volume from about 1,000 gallons to about 30 to 50 gallons. Another feature of this invention is that this process provides coatings with corrosion resistance that is better or at least equivalent to other known coatings produced by sulfuric, chromic, or boric-sulfuric compositions.

While this invention has been described by a number of specific examples, it is obvious that there are other variations and modifications which can be made without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

THE INVENTION CLAIMED

1. Process for preparing zirconium-chromium conversion coatings on iron and iron alloys to improve the corrosion resistance and adhesive bonding strength which comprises treating iron and iron alloys with an acidic aqueous solution having a pH ranging from about 2.5 to 5.5; said acidic aqueous solution comprising, per liter of solution, from about 0.01 to 22 grams of a trivalent chromium compound, about 0.01 to 12 grams of a hexafluorozirconate, about 0.0 to 12 grams of at least one fluorocompound selected from the group consisting of tetrafluoroborate, hexafluorosilicate and mixtures thereof, from about 0.0 to 10 grams of at least one divalent zinc compound, from 0.0 to about 10 grams of at least one water soluble thickener and from 0.0 to about 10 grams of at least one water soluble surfactant.

2. The process of Claim 1 wherein the pH of the aqueous solution ranges from about 3.7 to 4.0 and the iron alloy is steel.

3. The process of Claim 1 wherein the trivalent chromium is a water soluble compound ranging from about 0.01 to 10 grams, the hexafluorozirconate is a water soluble compound ranging from about 0.01 to 8.0 grams, and the fluorocompounds are water soluble compounds ranging from about 0.01 to 1.2 grams.

4. The process of Claim 3 wherein the thickener ranges from about 0.5 to 1.5 grams and the surfactant ranges from about 0.5 to 1.5 grams.

5. Process for preparing zirconium-chromium conversion coatings on iron and iron alloys to improve corrosion resistance and adhesive bonding which comprises treating iron and iron alloys with an acidic aqueous solution having a pH ranging from about 3.7 to 4.0; said acidic aqueous solution comprising, per liter of solution, from about 0.01 to 10 grams of a trivalent chromium salt, about 0.01 to 8.0 grams of an alkali metal hexafluorozirconate, about 0.01 to 1.2 grams of at least one fluorocompound selected from the group consisting of alkali metal tetrafluoroborates, alkali metal hexafluorosilicates and mixtures thereof, from about 0.001 to 10 grams of at least one divalent zinc compound, from 0.5 to about 1.5 grams of at least one water soluble thickener and from 0.5 to about 1.5 grams of at least one water soluble surfactant.
6. The process of Claim 5 wherein the iron alloy is steel.
7. The process of Claim 6 wherein the thickener is a cellulose compound.
8. The process of Claim 7 wherein the chromium salt is trivalent chromium sulfate.
9. The process of Claim 8 wherein the alkali metal zirconate is potassium hexafluorozirconate.
10. The process of Claim 5 wherein the trivalent chromium salt ranges from about 5.0 to 7.0 grams, the hexafluorozirconate ranges from about 0.01 to 8.0 grams, and the tetrafluoroborate ranges from about 0.12 to 0.24 grams.

11. The process of Claim 10 wherein the thickener is a water soluble alkyl cellulose compound.
12. The process of Claim 11 wherein the zinc compound is zinc acetate.
13. The process of Claim 11 wherein the chromium salt is trivalent chromium sulfate and the divalent zinc compound is zinc sulfate.
14. The process of Claim 13 wherein the surfactant is selected from the group consisting of water soluble non-ionic, anionic and cationic surfactants.
15. The process of Claim 14 wherein the zinc sulfate is present in the aqueous solution in an amount ranging from about 0.001 to 10 grams.
16. The process of Claim 15 wherein the zinc compound is a divalent zinc sulfate ranging from about 0.1 to 5.0 grams.
17. The process of Claim 5 wherein the chromium salt is trivalent chromium sulfate present in the aqueous solution in an amount ranging from 5.0 to 7.0 grams, and the mixture of the alkali metal tetrafluoroborates and hexafluorosilicates are present in the aqueous solution in an amount ranging from about 0.5 to 1.5 grams.
18. The process of Claim 17 wherein the zinc compound is divalent zinc sulfate present in the aqueous solution in an amount ranging from about 0.001 to 10 grams.

19. Coated iron alloys obtained by the process of Claim 2.
20. Coated iron alloys obtained by the process of Claim 6.