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METHOD OF AND SOLUTION FOR IMPROVING CONVERSION COATED METALLIC SURFACES

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This invention relates to improvements in metal coating and more particularly relates to solutions for and a method of improving chemically formed coatings on metal surfaces as a base for paint, lacquer, varnish or other organic finishes.

In the art of preparing metal surfaces to receive paint, it is now widely understood that the application of a dilute chromic acid rinse to phosphate coatings and oxide coatings on the metal surface improves that coating as a base for paint, usually both with respect to corrosion resistance and humidity resistance of the painted surface. The use of such rinses is now quite conventional and widely used. Such use is not without difficulty, however, and one of the long standing problems has been the avoidance of uneven concentrations of the chromic acid on different areas of a rinsed metal surface. Such uneven concentrations produce blistering, peeling or other premature failure of the paint applied thereover. A number of solutions have been proposed to overcome this problem including the use of specially controlled and formulated rinses subsequent to the conventional chromic acid rinse, the application of the dilute chromic acid rinse by atomization on a hot bare or chemically coated surface, and the use of dried on coatings containing hexavalent chromium compounds, reduced hexavalent chromium compounds or mixtures thereof. While these proposals represent advances in this art and have utility in specific applications, they each have substantial drawbacks from the commercial standpoint. There is still an important need for an inexpensive, simple process which is adaptable for use in conventional apparatus in high speed production line operation to improve the corrosion and humidity resistance of conversion coatings on metal surfaces.

In commercial highspeed production line processing of metal parts for painting, the predominant processes apply the phosphate or other chemical coating from an aqueous bath and after water rinsing the formed chemical coating, it is subjected to an aqueous chromic acid rinse, either by spraying or dipping. In many of these processes, the chromic acid rinsed coating is thereafter water-rinsed to remove uneven concentrations of chromic acid on certain areas of the surface. It is well-known that the final water rinse dissolves a substantial portion of the applied chromic acid rinse and yet the final water rinse continues to be employed because non-uniform distribution of chromic acid on the surface causes more serious paint failure than results from the reduction in the chromic acid content in the final rinsing step. Moreover, the final water rinse has the advantage that it prepares the surface for use with all types of paints and painting systems, even including those which are susceptible to contamination by excess chromic acid in the coating, since the rinse eliminates any water soluble chromic acid.

This invention provides a process which includes the conventional steps which are predominantly employed in highspeed production line operations, namely, conventional cleaning, phosphate or other conversion coating forming steps and thereafter rinses the phosphate or conversion coating with the modified aqueous rinse solution of this invention, and finally employs the step of water

rinsing the rinsed conversion coating to insure the absence of uneven concentrations of rinse material on the surface.

This invention is based on the discovery that certain chromium-containing solutions are capable of forming water-insoluble chromium-containing complexes with certain integral chemical coatings on a metal surface by a simple rinsing step in a short time, which complexes remain on and in the coating during a subsequent water rinsing step. It was also found that the application of such rinse solutions, under the hereinbelow specified conditions, forms such water-insoluble chromium-containing complexes in unexpectedly large quantities as an integral part of the conversion coating. The evidence at hand clearly demonstrates that coatings such as phosphates, mixed phosphate-oxides, chromates, oxalates and arsenates on the surfaces of metals which are susceptible to corrosion such as iron, steel, zinc, aluminum and the like, after painting, show substantially better corrosion resistance, humidity resistance or paint adhesion, when they are rinsed in the solutions of this invention than when they are rinsed in the heretofore used dilute chromic acid solutions.

In accordance with this invention, it has been found that in order to control the reaction or interaction between the chemical conversion coating and the applied rinse solution which produces the water insoluble chromium complex in that coating the rinse solution should be a dilute aqueous solution containing chromium complexes which include an anion portion that is displaceable upon contact by an anion in the chemical coating. When such a chromium complex contacts the chemical coating, the complex is modified to contain the anion of the surface coating, and the chromium complex thus becomes attached to and an integral part of the coating. It has been found that in order to form dilute aqueous solutions which contain such a chromium complex, it is necessary to provide a solution containing at least about 0.001%, w./v., of the trivalent chromium ion and having a pH within the range of about 3.8 to about 6.0. As used herein and in the appended claims, concentrations are expressed as "percent w./v." or percent weight per unit volume of the solution, and pH refers to the numerical values obtained from solutions prepared with deionized water. The pH should be adjusted in the rinse solution prior to the application of the solution to the surface since the necessary chromium complex must be present in the rinse solution at the moment of contact of the chemical coating.

The chromium complex which becomes attached to the chemical coating is water insoluble and the entire complex remains in place through the subsequent water rinse step. When using the rinse solution of this invention it has been found that there is a substantial increase in the chromium concentration in the coating after water rinsing relative to that which is present in the coating after the use of the heretofore known dilute aqueous chromic acid solutions. It has also been found that the improvement in corrosion and humidity resistance after painting which is obtained correlates with the increase in the integral water insoluble chromium complex which is found in that coating. However, in order to form the needed chromium complexes in the solution to enable this interaction with the coating on the surface it has been found that the pH of the rinse solution containing at least about 0.001% tri-valent chromium ion must be adapted to within the range of about 3.8 to 6.0. When the pH of the rinse solution is below about 3.8 the tendency for the formation of the necessary complexes in the rinse solution is reduced and the use of such solutions produces no commercially significant improvement in corrosion or humidity resistance of painted surfaces treated with such rinse solutions relative to the results obtained from the use of conventional unmodified dilute chromic acid rinse solutions. When the pH of the rinse solution of this invention exceeds about 3.8, however, it is possible to detect a significant increase in the concentration of chromium which remains on the surface in a water insoluble form relative to that which remains on a similar surface treated with a conventional dilute chromic acid rinse solution containing an identical concentration of chromium, and the corrosion resistance to salt spray is measurably improved relative to the conventionally rinsed coatings. When the pH of the rinse solution of this invention exceeds about 6, there is a tendency for the complex to become insoluble. It has been observed, however, that the solubility of the complex varies not only with the numerical pH value but is also a function of the additional anions which are present in the solution, for example, oxalate or the like, and gelation or precipitation does not always occur precisely at a pH of 6. The upper limit of pH referred to in the claims as "about 6" means that value at which the chromium complex remains stable in the dilute aqueous solution.

As above indicated, the dilute aqueous rinse solutions of this invention should contain chromium complexes which include an anion that is displaceable by the anion portion of the coating to be rinsed. While the most commercially important coating of this type is a phosphate coating, it is to be understood that the coating may be of the phosphate-oxide type such as is obtained from the use of alkali metal dihydrogen phosphate solutions, e.g., sodium or potassium or ammonium dihydrogen phosphate solutions, or may be a chromate coating, an oxalate coating, or an arsenate coating. The method is adaptable for use in conjunction with such chemical coatings on the surfaces of any metal which is susceptible to corrosion in the atmosphere or under other corrosive conditions and particularly including iron, steel, zinc, aluminum, copper, brass, bronze, magnesium, titanium and the like. It has been found that the anion of phosphate coatings most effectively displaces from a chromium complex one or more of the anions nitrate, chloride or chromate. The PO_4 anion will displace other anions to a somewhat lesser degree, such as sulfate ion, the formate ion and the acetate ion. When the coating is other than phosphate, for example, one which contains the oxalate anion, the dilute rinse solution containing the chromium complex may satisfactorily be one which contains any one of the anions nitrate, chloride, sulfate, phosphate, formate, acetate or sulfite, and when the coating is chromate or arsenate, the preferred anions are nitrate and chloride or mixtures thereof. When rinsing any of the above specified surface coatings, the dilute chromium complex rinse solution may contain certain other anions as well as those above mentioned, such as the nitrite, phosphate, chromate, oxalate or chlorate anions, and it is to be understood that in any case the rinse solution may contain chromium complexes which are mixtures of complexes containing one or more of the above named anions. The presence of such other anions does not prevent the interaction between the chromium complex and the coating and in the case of the chromate anion the concentration may even exceed the chromium complex concentration and yet the benefits of the invention are still obtained, although the degree of insoluble complex formation in the coating does vary as the concentration of the other anion is increased or decreased, and ordinarily only relatively small amounts of such other anions should be present.

The rinse solutions of this invention may contain tri-valent chromium in concentrations within the range of about 0.001% w./v. up to the limit of solubility of the selected chromic salt. A preferred operating concentration is within the range of 0.01% to 0.25% and for typical commercial phosphate coating rinse applications no advantage has been found from the use of tri-valent chromium concentrations exceeding about 0.1% w./v.

The rinse solutions of this invention are those which are made by dissolving a tri-valent chromium salt preferably in deionized water and thereafter adjusting the pH of the solution to within the range of about 3.8 to about 6. The solutions may be made, however, with ordinary tap water or other water which does not contain relatively high concentrations of undesirable anions such as chlorides, sulfates, etc. The pH may be adjusted by adding any alkaline material which does not contain a cation, the presence of very small quantities of which in the rinsed coating cause a reduction in corrosion or humidity resistance and a wide range of alkaline materials have been found to be suitable for this purpose. For example, goods results have been obtained with sodium hydroxide, calcium hydroxide, lithium hydroxide, zinc carbonate, etc. In the absence of pH adjustment, deionized water solutions of tri-valent chromium salts produce solutions having a pH lower than about 3.7 and in order to obtain the improved rinse solutions of this invention it is necessary to add alkali or alkaline material to insure that the pH exceeds the minimum of about 3.8. For example, deionized water solutions of typically available tri-valent chromium salts, at a tri-valent chromium ion concentration of 0.01% are as follows:

Chromium nitrate	3.4
Chromium chloride	3.7
Chromium sulfate	3.3
Chromium acetate	3.7

As the concentration of each of these chromium salts is increased above about 0.01% the pH decreases numerically, that is, the solutions become more acid. At a concentration of 0.25% chromic nitrate gives a pH of 2.8, chromic chloride a pH of 3.15, chromic sulfate a pH of 2.7 and chromic acetate a pH of 3.2. As is shown in the examples which follow, rinse solutions having a pH value in these lower acid value ranges do not provide the degree of corrosion and humidity resistance which is characteristic of the rinse solutions of this invention.

In solutions within a range of pH of about 3.8 to about 6.0, the formation of the needed chromium complexes occurs fairly rapidly so that it is unnecessary to age the rinse solution for an extended period of time prior to use. For example, a solution prepared at normal room temperature and adjusted to within the above stated pH range will have formed sufficient chromium complexes to be effective as a rinse in the interval of time which is required to confirm that the pH is within the desired range.

The method of this invention simply comprises the application of the dilute rinse solution to the preliminarily formed chemical coating on the metal surface to be prepared to receive paint or other organic finish in a conventional manner such as by spraying, dipping, brushing or the like. After the rinse solution is permitted to drain from the treated chemically coated metal surface, the surface is subjected to a water rinse to insure the absence from uneven concentrations of primarily water-soluble chromium in and on the coating and after drying, the surface is ready to receive an organic finish coating. The after rinse solution is preferably deionized water and excellent results are obtained when it is applied in accordance with the method disclosed in Richards United States Patent No. 3,034,933. The benefits of the invention are obtained even though the final rinse is tap water or other water which is not contaminated with unusually high concentrations of undesirable anions such as chlorides, sulfates, etc. After the final water rinse the coating may be permitted to dry in air or, if desired, may be dried in an oven or with forced air where greater speed is necessary.

It has been found that when using the rinse solutions of this invention on a continuous basis that the rinse solutions tend to become more acid, and if the solutions are not adjusted periodically by the addition of alkaline material, the pH of the rinse solution will migrate below 3.8. It is necessary to check the pH of the solution during use and in order to obtain the improvements which characterize this invention to adjust the pH so that it is within the herein claimed range. It has also been observed that the chromium complex rinse solutions of this invention have the same tendency upon mere standing and if substantial periods of time occur subsequent to the preparation of a rinse solution it is important to check the pH of that rinse solution before it is used and, if necessary, to adjust it within the claimed range.

The following examples illustrate the invention in somewhat greater detail but it is to be understood that the specific compositions, conditions of treatment and products produced are given for purposes of illustration only and are not intended to set forth the definitive limits of the invention which have been given hereinabove.

Example I

An aqueous acidic zinc phosphate coating solution was prepared in a conventional manner and upon analysis was found to contain zinc 0.23%, PO_4 0.45%, calcium 0.56%, nitrate 2.48%, ferrous iron 0.17%, and to have a total acid of 15.1 and a free acid number of 1.0. The total acid was determined by titrating a 10 ml. sample of the solution with an N/10 sodium hydroxide solution to a phenolphthalein end point, the total acid number being the ml. of sodium hydroxide required to reach the end point. The free acid was determined by titrating a 10 ml. sample of the solution with N/10 sodium hydroxide to a brom phenol blue end point, and these determinations apply to all total acid and free acid numbers given herein unless otherwise specified.

A number of 4" x 12" cold rolled steel panels were conventionally cleaned and sprayed with the above phosphate solution at 177° F. for 60 seconds, thereafter cold water rinsed for 30 seconds. The panels thus treated had a conventional appearing adherent phosphate coating on the surface having an average weight of about 150 mg. per square ft. A series of such coated panels were then dipped into an aqueous chromic acid rinse solution containing .05% CrO_3 and having a pH of 3.4, and then withdrawn. The panels were then rinsed in deionized water by spraying for 10 seconds at room temperature and finally dried in an oven at 375° F. for 3 minutes.

A tri-valent chromium rinse solution was prepared by dissolving 15.5 grams of $Cr(NO_3)_3 \cdot 9H_2O$ in 4 liters of deionized water to thus form a solution containing 0.05% tri-valent chromium. The solution was then brought to boiling temperature and nitrogen gas was bubbled through the solution to insure the complete absence of oxygen therein. The solution was found to have a pH of 2.7. A separate portion of the same solution was adjusted in pH by adding a 20% solution of sodium hydroxide thereto until the pH reached 4.7.

A series of 5 panels were dipped for 30 seconds into the chromic nitrate rinse solution having a pH of 2.7 and another series of 5 panels were dipped for 30 seconds in the chromic nitrate rinse solution having a pH of 4.7, all panels removed, deionized water rinsed for 10 seconds by spraying at room temperature, and thereafter dried in an oven at 375° F. for 3 minutes.

All of the panels were then coated with a commercial two-coat white enamel, Dulux 707-6741, and after conventional preparation of one surface of two of the panels by diagonal scratches from corner to corner, the panels were then subjected to salt spray corrosion testing under the conditions specified in ASTM Method 117-61, which is the 5% sodium chloride fog test.

After 336 hours in the salt spray cabinet the panels rinsed in the dilute chromic acid rinse solution having a pH of 3.4, upon inspection, were found to have rusted between 3/16" and 1/4" from the scratched lines and to have widely spaced spots of corrosion over the entire surface. The panels which were rinsed in the dilute chromic nitrate solution having a pH of 2.7, upon inspection, were found to be peeled over 75% of their surface. The panels which were rinsed in the chromic nitrate solution, adjusted to a pH of 4.8, upon inspection, were found to have migration of the corrosion from the scratch marks of between 0 and 1/16" as an average along the lengths of the scratches. After 840 hours, the panels rinsed in the chromic nitrate rinse which was adjusted to a pH of 4.8, upon inspection, were substantially comparable to their 336 hour condition, except that spaced spots of corrosion were beginning to appear over the surfaces.

A rinse solution was prepared by dissolving in 4 liters of deionized water, 10.1 grams $CrCl_36H_2O$. The solution was then brought to boiling temperature and nitrogen was bubbled therethrough to displace air from the solution and thus avoid possible oxidation of trivalent chromium to the hexavalent state. The solution was found to have a pH of 2.5. A portion of this solution was adjusted with 20% sodium hydroxide to a pH of 4.85. Panels coated in the above described zinc phosphate coating solution were dipped in each of these rinse solutions, rinsed in deionized water by spraying for 10 seconds at room temperature, dried at 375° F. in an oven for 3 minutes and then painted in an identical manner to that described above and subjected to comparable salt spray testing. After 336 hours, an inspection of the panels rinsed in the solution having a pH of 2.5 were found to have corroded for distances between 9/16" and 3/4" from the scratch marks and the surface of the panels was approximately 20% peeled. The panels rinsed in the solution having a pH of 4.85, after 336 hours in the salt spray, upon inspection, were found to have no discernible corrosion along the scratch marks and one corrosion spot was found on the entire surface panel. After 504 hours, the panels rinsed in the 4.85 pH solution were again inspected and found to be free of corrosion and, similarly, after 840 hours, no discernible corrosion was detected and only one spot of corrosion appeared on the entire surface of the panels.

A rinse solution was prepared by dissolving in 4 liters of deionized water, 7.6 grams of anhydrous $Cr_2(SO_4)_3$. The solution was brought to boiling temperature and nitrogen gas was passed through the solution for about 15 minutes to insure the absence of oxygen. The pH was determined to be 2.7. A portion of the solution was adjusted in pH by the addition of 20% of sodium hydroxide to a final pH value of 4.7. A series of panels coated with zinc phosphate in the above described phosphate coating solution were dipped in the rinse solutions, withdrawn, rinsed in deionized water by 10-second spraying at room temperature and thereafter dried in an oven at 375° F. for 3 minutes, painted in a similar manner to that above described and subjected to the standard salt spray corrosion test. After 336 hours in the salt spray cabinet, the panels rinsed in the solution having a pH of 2.7 were inspected and found to have corroded an average of between 1/4" and 1/2" from the scratch marks and spotty corrosion to a maximum of 20% peeling on the surface of the panels. The panels rinsed in the solution having a pH of 4.7, after 336 hours in the salt spray, were found to have corroded an average of 1/8" to 3/16" from the scratch marks with no indication of spotty corrosion over the balance of the surface.

A rinse solution was prepared by dissolving in 4 liters of deionized water 14 grams of a 50% solution of $Cr(COOCH_3)_3$, thus forming a solution containing 0.05% tri-valent chromium and having a pH of 3.5. The solution was then brought to a boiling temperature and nitrogen gas passed through to free the solution from oxygen and a determination of pH indicated the solution to have a pH of 3.9. A portion of the solution was then adjusted by adding 20% sodium hydroxide to form a solution having a pH of 4.8. A series of panels coated with the phosphate solution above described were immersed in both rinse solutions for 30 seconds, withdrawn, rinsed in deionized water for 10 seconds by spraying at room temperature, dried in an oven at 375° F. for 3 minutes and, after painting in the manner above described, were subjected to the standard salt spray corrosion test. After 336 hours in the salt spray cabinet the panels rinsed in the rinse solution having a pH of 3.9 were found to have corroded an average of 1/4" to 5/16" from the scratch marks and to have a number of scattered spots of corrosion on their surfaces. The panels rinsed in the solution having a pH of 4.8, after 336 hours, upon inspection, were found to have corroded an average of about 1/4" along the scratch marks on their surfaces and to be free of spots on the balance of their surfaces.

All of the panels above described, when subjected to standard humidity tests and conventional bend, concave, convex and adhesion tests, were found to be satisfactory in all cases.

Example II

A series of 3" x 6" black plate panels and another series of 3" x 6" cold rolled steel panels were conventionally cleaned and coated by using the zinc phosphate composition and identical processing steps as those set forth above in Example I to produce thereon adherent gray phosphate coating having an average weight of about 150 milligrams per square ft. After conventional water rinsing, a number of the phosphate coated panels were rinsed by dipping in an aqueous chromic acid rinse solution containing 0.05% CrO_3 and having a pH of 3.4. The panels were withdrawn and water rinsed with deionized water by spraying for 10 seconds at room temperature, and dried in an oven for 3 minutes at 375° F.

A portion of the dilute chromic nitrate solution prepared in Example I was used for rinsing a number of the zinc phosphate coated panels by dipping those panels in the chromic nitrate solution, containing 0.05% trivalent chromium ion, pH 4.8, withdrawing and rinsing in deionized water by spraying for 10 seconds at room temperature, and thereafter drying by positioning in an oven for 3 minutes at 375° F.

The retained chromium in the coating on each of these series of panels was checked by both wet analytical procedures and the X-ray fluorescence method of chromium determination, and the average weight of chromium on the panels rinsed in the dilute chromic acid solution having a pH of 3.4 was an average of 0.04 milligram per square ft., whereas the panels coated in the dilute chromic nitrate solution adjusted in pH to 4.8 was an average of 0.19 milligram per square ft.

Example III

An aqueous alkali metal phosphate solution was prepared from sodium dihydrogen phosphate and sodium chlorate and upon analysis was found to contain PO_4—1%, ClO_3—0.5%, and to have a total acid of 10 points and a pH of 5.2.

A number of 4" x 12" cold rolled steel panels, conventionally cleaned, were phosphate coated in the alkali metal phosphate solution by spraying those panels for 60 seconds at 160° F., and cold water rinsing. The panels were coated with a uniform typical light gray phosphate-oxide coating having an average weight of about 30–40 milligrams per square ft.

A dilute aqueous chromic acid solution was prepared by dissolving chromic acid in water to form a concentration of 0.09% CrO_3, the solution having a pH of 2.2.

5 gallons of tri-valent chromium rinse solution were prepared by dissolving $Cr(NO_3).9H_2O$ in commercial tap water to form a solution containing 0.05% tri-valent chromium. The solution as prepared had a pH of 3.5.

Another tri-valent chromium rinse solution was prepared having the identical concentration of 0.05% tri-valent chromium and was adjusted in pH by adding 20% sodium hydroxide thereto until the pH was raised to 4.5.

A series of panels coated with the alkali metal phosphate solution above described were rinsed in each of the tri-valent chromium rinse solutions by spraying for 30 seconds at room temperature, and after draining, the rinsed panels were rinsed in deionized water by spraying for 10 seconds at room temperature and the panels were thereafter dried in an oven at 375° F. for 3 minutes.

All of the rinsed and dried panels were then painted with a commercial two-coat white enamel, Dulux 707–6741, and in conventional scratched form placed in the 5% sodium chloride corrosion test chamber.

After 600 hours in the salt spray cabinet, the panels rinsed in the dilute chromic acid solution having a pH of 2.2, upon inspection, were found to have peeled between about 50% and 80% of the total surface area. Panels which were rinsed in the dilute chromic rinse solution having a pH of 3.5, upon inspection, were found to have corroded an average of between 5/16" and 1/2" from the diagonal scratch marks and to have between 5% and 10% peelage on the balance of the surface of the panels. The panels which were rinsed in the chromic nitrate solution having a pH of 4.5, upon inspection, were found to have corroded an average of between 1/16" and 3/16" from the diagonal scratch marks and to have an average of 4 small spaced spots of corrosion on the balance of the surface of the panels.

Example IV

The dilute chromic nitrate solution described above in detail in Example I was modified to contain varying concentrations of nitrite and chlorate. One solution as modified contained 0.05% tri-valent chromium and 0.05% sodium nitrite and had a pH of 4.6. A second solution contained 0.05% tri-valent chromium and 0.1% sodium nitrite and had a pH of 4.8. A third solution contained 0.05% tri-valent chromium and 0.9% ClO_3, added as $NaClO_3$ and had a pH of 4.71.

These rinse solutions were employed to rinse steel panels coated with zinc phosphate coating of the type described in detail above in Example I by immersing the panels for 30 seconds in the solutions at room temperature, and thereafter deionized water rinsing the panels by spraying for 10 seconds at room temperature, and drying in an oven at 375° F. for 3 minutes. Another series of similar phosphate coated panels were rinsed in an aqueous chromic acid rinse solution containing 0.05% CrO_3 and having a pH of 3.4.

After the panels were painted with the two-coat enamel system described above and subjected to the standard salt spray corrosion test, an inspection of the panels rinsed in the chromic acid solution having a pH of 3.5, after 432 hours, showed the corrosion to have advanced along the scratch marks averaging 1/8" to 1/4" with 4–6 spots of corrosion appearing over the balance of the surface of the panels. The panels rinsed in the tri-valent chromium solution containing 0.05% $NaNO_2$, after 432 hours, showed corrosion along the scratch marks varying between 0 and 1/16" with from 1–3 spots of corrosion on the balance of the surface of the panel. The panels rinsed in the tri-valent chromium solution containing 0.1% $NaNO_2$, after 432 hours, showed the corrosion to have advanced from the scratch mark an average of 0–1/16" with a single spot of corrosion on the balance of the surface of the panels. The panels rinsed in the tri-valent chromium rinse solution containing 0.9% ClO_3, after 432 hours, upon inspection, showed that the corrosion had progressed from the scratch marks between 0 and 1/16" with a single spot of corrosion on the balance of the surface of the panels.

What is claimed is:

1. A method of preparing integral chemical coatings on a metal surface selected from the group consisting of phosphate, phosphate-oxide, chromate, oxalate and arse-

nate coating to receive an organic finish which comprises the steps of applying to said chemical coating a dilute aqueous solution containing at least about 0.001% tri-valent chromium in the form of a chromium complex, said complex containing an anion capable of being displaced by the anion portion of said chemical coating upon contact by the said solution with said coating, said solution having a pH in the range of about 3.8 to about 6, and thereafter water rinsing said surface.

2. A method of preparing integral chemical coatings on a metal surface selected from the group consisting of phosphate, phosphate-oxide, chromate, oxalate and arsenate coating to receive an organic finish which comprises the steps of applying to said chemical coating a dilute aqueous solution containing about 0.01% to about 0.25% tri-valent chromium in the form of a chromium complex, said complex containing an anion capable of being displaced by the anion portion of said chemical coating upon contact by the said solution with said coating, said solution having a pH in the range of about 3.8 to about 6, and thereafter water rinsing said surface.

3. A continuous method of treating integral chemical coatings on a metal surface selected from the group consisting of phosphate, phosphate-oxide, chromate, oxalate and arsenate coating which comprises the steps of applying to said chemical coating a dilute aqueous solution containing at least about 0.001% tri-valent chromium in the form of a chromium complex, and having a pH in the range of about 3.8 to about 6, and maintaining the pH of said solution in said range by periodically adding alkaline material thereto.

4. A method in accordance with claim **3** wherein said solution is sprayed on said chemical coatings.

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