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METHOD FOR FORMING IMPROVED COATING ON METAL

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ABSTRACT OF THE DISCLOSURE

A method for forming a protective coating on zinc-containing surfaces wherein a clean, zinciferous surface is coated with an aqueous acidic solution which contains hexavalent chromium ions, fluoride ions, and at least 0.01% by weight of the solution of an activator formed of at least one ion selected from the group consisting of tungsten, molybdenum, vanadium, and uranium. After the zinc metal surface has been contacted with this solution for a period sufficient to form the desired coating thereon, the thus-coated surface is then rinsed with an aqueous solution containing hexavalent chromium ions.

This invention relates to an improved process for coating metal surfaces and more particularly it relates to an improved process for chemically coating zinc-containing surfaces to provide a corrosion resistant and paint bonding coating on such surfaces.

Many compositions and processes have been heretofore proposed for the treatment of zinc-containing surfaces, i.e., surfaces of zinc and alloys which are predominantly zinc, to produce a chemical coating thereon. In many of these, and particularly those which have been the most successful commercially, hexavalent chromium has been employed as the principal coating material. Fluoride ions, as well as various other anions or cations to provide increased coating weight and coating efficiency, have also frequently been used in compositions of this type, with the hexavalent chromium. In all these processes, it has been attempted to provide a coating solution which is relatively simple to prepare and which is easily maintained in effective coating condition during use. Additionally, it has frequently been found desirable that the coating methods used are not only effective in coating zinc-containing surfaces but are also useful in treating various types of aluminum and aluminum alloys. In this way, the same method and composition can be effectively used on so-called "mixed production," without the necessity of interrupting the coating process to change solutions each time it is desired to coat a different type of metal. For the most part, however, the processes of the prior art have not been successful in achieving all of these objectives.

It is, therefore, an object of the present invention to provide an improved process for coating zinc-containing surfaces which process is also effective in coating other metals, such as aluminum.

Another object of the present invention is to provide an improved method for coating zinc-containing surfaces wherein the coating solution used is easily prepared and maintained in acceptable coating condition.

These and other objects of the invention will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a method for forming a coating on zinc-contain-

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ing surfaces which comprises contacting a clean zinc-containing surface with a coating composition which comprises an aqueous acidic solution, substantially free of silver ions, which contains hexavalent chromium ions, fluoride ions, and at least 0.01 percent of an activator formed of at least one ion selected from the group consisting of tungsten, molybdenum, vanadium, and uranium, the amounts of said ions being calculated as the respective metals, maintaining the solution in contact with the surface for a period of time sufficient to form the desired coating, removing the thus-coated surface from contact with the solution and, thereafter, contacting the thus-coated surface with a rinsing composition which comprises an aqueous solution containing hexavalent chromium ions.

More specifically, in the method of the practice of the present invention, the coating composition utilized is an aqueous acidic solution which is substantially free of silver ions. It has been found that not only do the silver ions not add any beneficial properties to the composition used, but, in many instances, are in fact detrimental to the operation and maintenance of the coating solution and to the protective coatings which are produced. Accordingly, it is desirable that the coating solutions utilized in the method of the present invention be substantially free of silver ions. By "substantially free" it is meant that the solutions used are free of at least amounts of silver ions which are detrimental to the solution or the coating produced. It is not necessarily intended, however, to exclude minor amounts of these ions which are not detrimental, such as amounts which may occur in the water used in making up the aqueous solutions, e.g., amounts less than about 0.01 percent by weight of the solution.

The aqueous acidic coating solution used in the method of the present invention contain hexavalent chromium ions in an amount sufficient to provide the desired chromium coating on the zinc surfaces which are treated therewith. Desirably, these solutions contain hexavalent chromium ions, calculated as CrO_3 , in an amount within the range of about 0.05 to about 1% by weight of the solution. The hexavalent chromium ions may be added to the solution in many suitable forms, such as chromic acid, or one or more of the water soluble or water dispersible salts of chromic acid. Exemplary of the salts which may be used are the alkali metal or ammonium salts, such as the alkali metal or ammonium chromates and dichromates, as well as mixtures thereof both with each other and/or with chromic acid.

The fluoride ion is present in the composition in an amount sufficient to cause attack of the zinc-containing surface to be coated and to effect formation of the resulting coating on this surface. Desirably, the fluoride ion is present in an amount within the range of about 0.05 to about 2.7% by weight of the solution. As with the hexavalent chromium ions, the fluoride ions may be added to the composition in many convenient forms, including various fluorine-containing compounds which are capable of ionizing in the aqueous acidic solutions to provide fluoride ions. Exemplary of such fluorine containing compounds which may be used are hydrofluoric acid, fluosilicic acid, fluoboric acid, as well as the various water soluble or water dispersible salts thereof, such as the alkali metal and ammonium salts.

As has been indicated hereinabove there is also included in the coating composition used in the method of the present invention at least 0.01 percent by weight of the solu-

tion of an activator formed of at least one ion selected from the group consisting of tungsten, molybdenum, vanadium, and uranium. Where more than one of these ions are present in the composition, it has been found to be desirable that at least one of the ions utilized is present in an amount of at least 0.005% by weight of the coating solution.

It has also been found that it may be desirable, in some instances, to include arsenic ions in the activator composition with one or more of the ions selected from the indicated group. When this is done, the arsenic ions are considered to be similar to the other ions, in that the activator composition is still present in an amount of at least 0.01% by weight and at least one of the ions is present in the activator composition in an amount of 0.005% by weight.

Although the maximum amount of these ions in the composition has not been found to be critical, amounts up to the maximum solubility of the ions in the solution giving satisfactory results, it has been found that when amounts of these ions substantially in excess of about 0.4% by weight of the solution are used, no appreciable additional improvements in coating weights and coating efficiencies are obtained. Accordingly, it has been found to be desirable that the activator composition used contains at least one ion selected from the group consisting of tungsten, molybdenum, vanadium, and uranium and that this composition is in the coating solution in an amount within the range of about 0.01 to about 0.4% by weight of the solution. These ions as well as the arsenic ions, when they are used, may be added to the solution in the form of various compounds which are ionizable in the coating solution, such as tungstic acid, molybdic acid, vanadic acid, uranic acid or arsenic acid as well as the various water soluble or water dispersible salts of these acids which will provide the desired metal ion when oxidized in the solution by the chromic acid or salts thereof. Exemplary of such salts which may be used are the alkali metal or ammonium salts of tungstic, molybdic, vanadic, uranic acid or arsenic acid.

Additionally, where the compositions used in the present method contain hydrogen fluoride, as the source of the fluoride ions, it may also be desirable to include in the composition a quantity of a buffering acid, such as boric acid or silicic acid, to act as a buffer for the fluoride ions. Where these acids are included in the coating solution, they are typically present in amounts within the range of about 0.1 percent by weight of the solution up to the maximum solubility of the acid in the solution. Desirably, however, these acids are present in the composition in amounts within the range of about 0.1 to about 0.2% by weight of the coating solution.

In addition to the above components, in many instances it has also been found desirable to include in the subject composition aluminum, preferably as an aluminum fluoride complex ion. Desirably, the aluminum is present in an amount within the range of about 0.01 to about 1% by weight of the coating solution, although amounts up to the maximum solubility of the aluminum compound added may be used. The preferred aluminum fluoride complex ion is expressed as $Al(F)_x$ because, when used, it is present in the operating solution as an equilibrium of $Al(F)$ ions which may contain from 1 to 6 fluoride atoms per aluminum atom. In the solutions of the present invention, it has been found that this equilibrium averages out to be approximately equivalent to the AlF_3 ion. Accordingly, as used in the specification and claims, the expression $Al(F)_x$ is intended to represent any aluminum fluoride ion and the quantities thereof refer to an amount of such ion equivalent to the AlF_3 ion. This aluminum fluoride complex ion, when used, may be incorporated in the present composition as such or it may be formed in the composition as a complex from free aluminum and fluoride ions. In the later instance, the fluoride may be present as hydrofluoric acid, fluoboric acid, fluosilicic acid,

or the like. Where the aluminum fluoride complex ion is added as such, it may be prepared by dissolving aluminum oxide (Al_2O_3) in water and hydrofluoric acid in appropriate proportions to obtain the requisite parts of AlF_3 for the composition.

Particularly preferred compositions for use in the present method are those falling within the following formulation:

Solution component:	Concentration in percent by wt.
Hexavalent chromium ions (calculated as CrO_3)	0.1 to 0.5
Fluoride ions	0.05 to 1.6
Activator composition	0.03 to 0.1
Buffering acid	Nil to 0.2
$Al(F)_x$ complex	Nil to 1.9

In carrying out the process of the present invention, the aqueous coating solutions as described hereinabove, are applied to a cleaned zinciferous surface. By a cleaned zinciferous surface is meant a zinc containing surface which is substantially free of foreign matter such as oil, grease, dirt, and the like. The cleaning of the zinciferous surface may be effected by contacting the surface with various alkaline cleaning solutions, such as aqueous solutions containing alkali metal hydroxides, alkali metal carbonates, alkali metal phosphates, alkali metal silicates, and the like. Exemplary of the alkali metal phosphates which may be used in the alkaline cleaning solution are the trialkali metal phosphates, the tetraalkali metal pyrophosphates, the alkali metal tripolyphosphates, and the like. It will be appreciated that as used in the specification and claims the term "alkali metal" is intended to refer to lithium, sodium, potassium, cesium, and rubidium. The preferred alkali metal is sodium, however, and primary reference will be made hereinafter to sodium compounds. This is not, however, to be taken as a limitation of the alkali metal compounds which may be used as other alkali metal compounds, and particularly potassium compounds, have been found to be suitable for use in the process of the present invention.

It has been found that in addition to cleaning the zinciferous surfaces, in some instances these alkaline solutions also have an activating effect on the surface which results in obtaining an improved paint bonding coating upon the subsequent application of the coating composition. Accordingly, although various alkaline material may be used in formulating the aqueous solution, such as the hydroxides and/or carbonates of sodium and potassium, trisodium, or tripotassium phosphate and the like, the preferred alkaline solution, in terms of the activation of the zinciferous surface, are those solutions which contain an alkali metal metasilicate, such as sodium metasilicate. Exemplary of typical alkaline solutions which may be used are those containing the alkaline material in an amount within the range of about 4 to about 28 grams per liter and having a pH within the range of about 9.5 to about 13.5. A particularly desirable composition for cleaning and activating the zinciferous surface is one having the following formulation:

	Percent by weight
Sodium metasilicate	50
Trisodium phosphate	50

This dry composition is formulated into an aqueous cleaning solution by admixing it with water in amounts within the range set forth above.

The aqueous alkaline solution may be applied to the zinciferous surface to be treated using various techniques, such as immersion, flooding, spraying, and the like, with spraying techniques generally being preferred. Desirably, the alkaline solution at the time of application to the zinciferous surface is at an elevated temperature, with temperatures within the range of about 45 to about 90 degrees centigrade being typical and temperatures within the range of about 65 to about 80 degrees centigrade

being preferred. The hot alkaline solution is maintained in contact with the surface to be treated for a period of time sufficient to effect cleaning and the desired activation of the zinciferous surface. Generally, contact times up to about 2 minutes are typical, with contact times of about 10 seconds to about 1 minute being preferred. After cleaning, the surface may be rinsed with water, preferably using a hot water spray, with the water at a temperature within the range of about 50–80 degrees centigrade.

After the cleaning and rinsing of the zinciferous surface has been accomplished, the coating solution, as described hereinabove, may be applied thereto using various coating techniques, such as dipping, brushing, spraying, flooding, roller coating or the like. Additionally, the coating solutions may be applied to the zinc containing surfaces by atomizing the solution on the surface in a heated condition, in accordance with the procedure set forth in a co-pending U.S. patent application Ser. No. 728,095, filed Apr. 14, 1958. Generally stated, this atomization application technique includes the step of preliminarily heating the zinc or zinc alloy surface to be coated to a temperature above about 65 degrees centigrade and atomizing on the heated surface a quantity of the coating solution sufficient to form the desired coating but insufficient to cause the droplets of atomized coating solution to coalesce or puddle on the surface. The coating on the zinc surface results from the substantially instantaneous flashing or volatilization of the liquid from the solution, so that each individual atomized particle droplet remains substantially in the locus of its original contact with the surface treated.

Although the coating process of the present invention may be carried out effectively and with good efficiency over a wide range of solution temperatures and solution acidities, it has been found that the rate of coating may be improved and the coating efficiency increased by the concurrent selection and control of the degree of the acidity of the solution and the temperature of application. With regard to the temperature, it has been found that as the temperature of the operating solution is increased from room temperature, i.e., about 20 degrees centigrade, up to about 50 degrees centigrade, the coating rate rapidly increases and in some instances it is possible to obtain an increase in the coating rate of from 2 to 5 times that obtained at room temperatures. At solution temperatures within the range of about 50 to about 70 degrees centigrade, the coating rate has been found to increase more slowly and, in many instances, has been found to be substantially uniform throughout this temperature range. It is, therefore, preferred to utilize the solutions in the present coating method at solution temperatures within the range of about 50 to about 70 degrees centigrade. Higher temperatures than 70 degrees centigrade may be employed, for example, temperatures of 80 degrees centigrade or even up to the solution boiling point, but no particular advantages in terms of increased coating rates are obtained by operating at such higher temperatures.

With regard to the pH of the operating solutions of the present invention, it has been found that these, as with the temperatures affect the coating rate and coating efficiency of the solution being applied to the zinc containing surface. Accordingly, it is desirable that the coating solution have a pH within the range of about 1.3 to about 3.2, and preferably in the range of about 1.7 to about 2.2. This pH range refers to measurements taken by using an electrical pH meter employing a glass electrode and a calomel electrode, by immersing the electrodes in fresh portions of the operating solution and observing the indicated values.

In addition to the pH of the operating solution, it is also desirable that this solution have a concentration within the range of about 2 to about 30 points and that once the concentration is established within this range, it is maintained within about ± 0.5 points of the estab-

lished value. The concentration of the operating solution in points is determined by the following procedure.

To a ten milliliter sample of the operating solution there are added 25 milliliters of 50% sulfuric acid and 2 drops of ortho-phenanthroline ferrous complex (ferroin) indicator. This solution is then titrated with 0.1 N ferrous sulfate in dilute sulfuric acid until the solution changes through blue to a reddish brown color. The concentration points of the operating solution are the number of milliliters of the 0.1 N titrating solution used. It is to be appreciated, that although the operating solution of the present invention is desirably used at a concentration within the range of about 4 to 30 points, operation of the solution at both high and lower point concentrations is not only possible, but in some instances, is preferred.

Following the application of the coating solution to the zinc-containing surfaces to be treated, the thus-coating surfaces are then desirably rinsed with water. Either spray or immersion techniques for the water rinse may be used, with rinsing times of about 3 to 5 seconds duration being typical.

Thereafter, the zinc containing surface is contacted with a rinsing composition, which composition comprises an aqueous solution containing hexavalent chromium ions. This rinsing composition is a water solution containing a source of hexavalent chromium, calculated as CrO_3 , in an amount within the range of about 0.03 to about 0.8 percent by weight of this solution and preferably in an amount within the range of about 0.07 to about 0.3 percent by weight of the solution. Various water-soluble or water dispersible sources of hexavalent chromium may be used in formulating this solution, provided the anions and cations introduced with the hexavalent chromium do not have a detrimental effect on either the solution itself or the coated zinc surfaces which are treated. Exemplary of hexavalent-chromium materials which may be used are chromic acid, the alkali metal and ammonium chromates, the alkali metal and ammonium dichromates, the heavy metal dichromates, such as the dichromates of Zn, Ca, Cr, Fe^{+3} , Mg, and Al, and the like. This rinsing composition may be applied to the coated zinc surface using various means, including roller, immersion, flooding, and spraying techniques, and the like, with spraying techniques being preferred. Additionally, if desired, after the application of the hexavalent chromium solution to the surface, the excess of this solution may be removed from the surface, preferably by wiping or squeegeeing. Generally, it is preferred that the aqueous hexavalent chromium containing solution is maintained at an elevated temperatures while it is in contact with the zinc surface to be treated. Temperatures within the range of about 35 to about 60 degrees centigrade and contact times of up to about 60 seconds are typical. After contacting the coated zinc-containing surface with the rinsing composition, and removing excess liquid from the surface by wiping or squeegeeing, the surface may be dried, temperatures within the range of about 100 to 125 degrees centigrade and times up to about 5 minutes being typical of those used in such a drying operation.

The coatings thus-produced on the zinc surfaces are slightly colored and vary in appearance from iridescent to light gold to yellow to brown. The color changes in the coating produced may be used as a general guide to the coating weights obtained, the darker colors being produced with higher coating weights and the lighter colors resulting from lower coating weights.

In formulating the operating coating solution for use in the present invention, a makeup composition, containing the components desired in the operating solution, is admixed with water in amounts suitable to provide concentrations of the components within the ranges as has been set forth hereinabove. Normally, in addition to the above indicated components, the makeup composition may also contain an inorganic mineral acid, such as nitric acid, sulfuric acid, hydrochloric acid or the like, in order to

provide the desired acidity or pH. Suitable makeup compositions are those falling within the following formulations:

Component:	Parts by weight
CrO ₃ -----	15 to 20
HF -----	4 to 7
Inorganic acid, such as nitric acid -----	1 to 5
Activator composition -----	2 to 5
Buffering acid -----	0 to 2
AlF _x complex -----	0 to 2

It will be appreciated that this is a single package makeup composition as compared to the prior art composition wherein separate packaging of some of the make-up components was often necessary.

In the operation of the process of the present invention, the components of the operating coating solution are depleted. Accordingly, in order to maintain these components in the operating solution within the preferred ranges heretofore given, it is desirable in order to obtain a continuous operation, to periodically replenish the operating solution. One advantage of the present composition is that, as in formulating the operating solution, this replenishing may be effected using a single package replenishing material, as opposed to many of the prior art compositions wherein separate addition of the components during replenishing is necessary. As with the make-up composition, in addition to the hexavalent chromium fluoride and activator components, it may also be desirable to include in the replenishing material an inorganic mineral acid such as nitric acid, sulfuric acid, hydrochloric acid or the like, so as to maintain the acidity or pH of the operating solution within the desired ranges as have been indicated hereinabove. Additionally, where the fluoride components is added as hydrogen fluoride rather than fluosilicic acid or fluoboric acid, it may also be desirable to include in the replenishing material a quantity of boric acid or silicic acid to act as a buffer for the fluoride ions.

A single package replenishing material suitable for use in maintaining the operating solution of the present invention in optimum coating forming conditions may contain the following components in the amounts indicated:

Component:	Parts by weight
Hexavalent chromium (calculated at CrO ₃) -----	15 to 20
HF -----	1 to 5
Inorganic mineral acid -----	2.0 to 20
Activator composition -----	2 to 10
Boric acid -----	0 to 2
AlF _x complex -----	0 to 5

A preferred replenishing material, having particular utility for use with a continuous strip line operation, is one containing the following components in the amounts indicated:

Component:	Parts by weight
CrO ₃ -----	18 to 20
HF -----	1 to 3
HNO ₃ -----	10 to 20
Sodium tungstate -----	4 to 6
Boric acid -----	0 to 2
AlF _x complex -----	0 to 5

A preferred replenishing material, particularly suitable for production operations in which the parts to be coated are moved through a spray installation on a mono-rail conveyor, is one having the following components in the amounts indicated:

Component:	Parts by weight
CrO ₃ -----	15 to 17
HF -----	2 to 4
HNO ₃ -----	8 to 16
Sodium tungstate -----	4 to 10
AlF _x complex -----	0 to 5
Boric acid -----	0 to 2

In some instances, it has been found to be advantageous to operate the solutions of the present invention in conjunction with cation exchange units. In this manner, the amount of mineral acid in the composition may be reduced and the consumption of fluoride ions may also be decreased.

It has further been found that in many instances, by the use of an activator composition made up of at least two ions selected from the group consisting of tungsten, molybdenum, arsenic, vanadium, and uranium, in an amount of at least 0.01% by weight of the coating solution and wherein at least one of the ions selected is present in an amount of at least 0.005% by weight of the coating solution and the sum of the amounts of the remaining ions selected are at least 0.005% by weight of the coating composition, a synergistic activation is obtained and high coating rates and coating efficiencies are consistently maintained during the use of such solutions. Accordingly, in some instances it may be desirable to utilize such a combined activator composition rather than the cation exchange apparatus.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. It is to be understood that these examples are presented for illustrative purposes only and are not intended to be taken as a limitation on the present invention. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and amounts are in percent by weight.

In the following examples, 1-14, panels of the hot dip galvanized steel were cleaned by immersion for 15-20 seconds in an aqueous, alkaline cleaning solution containing about 15 grams/liter of a 50-50 mixture of sodium metasilicate and trisodium phosphate. The cleaning solution was at a temperature of about 70° C. Thereafter, the cleaned panels were rinsed in a hot water spray, at about 65° C. The panels were then sprayed with the coating solutions indicated hereinbelow. These solutions were formulated by mixing the components in the quantities indicated with sufficient water to form about six liters of solution. The CrO₃ was added as chromic acid, the fluoride was added as fluoboric acid except in Example 6 where it was added as hydrofluoric acid, the NO₃ was added as nitric acid and the WO₃ and MoO₃ were added as sodium tungstate and sodium molybdate, respectively. The coating solutions were at a concentration level of about 11 points, a temperature of about 60° C. and the spraying time was about 15 seconds. Thereafter, the coated panels were rinsed in second hot water spray and were then sprayed with an aqueous rinsing solution containing about 0.1% by weight of CrO₃. The rinse solution was at a temperature of about 50° C. and the contact time was about 15 seconds. The excess liquid was removed from the panels with a squeegee and the panels were dried for 2 minutes at 110° C. Several panels from each example were then painted with a white vinyl paint and subjected to the standard 5% salt spray, 100% humidity, knife blade adhesion and physical deformation tests. In each instance high ratings were obtained, indicating the formation of an excellent protective and paint bonding coating on the panels under the paint. Additionally, all of the panels were weighed before cleaning and after drying. In all cases, the weight loss in these panels was less than about 15 milligrams/square foot as compared to control panels treated with the same coating solutions, but not containing the activator materials, which control panels all had at least a 50% greater weight loss. With regard to the weight loss, this is a measure of the effectiveness of the coating process, the lower the weight loss, the greater the amount of coating applied and the more effective the coating process. The difference in weight loss between the control panels and those treated with the activated compositions is not necessarily the coating weight applied. The actual coating weight applied

can not be easily determined because there is no satisfactory way of stripping the coating from the coated zinc panels.

Examples	Components in percent by weight of coating solution						pH
	CrO ₃	F	NO ₃	WO ₃	MoO ₃	H ₃ BO ₃	
1.....	0.33	0.14	0.08	0.05	0.05	-----	1.4
2.....	0.10	0.14	0.08	0.05	0.05	-----	1.4
3.....	1.00	0.14	0.08	0.05	0.05	-----	1.4
4.....	0.05	0.14	0.08	0.05	0.05	-----	1.4
5.....	0.33	0.05	0.08	0.05	0.05	-----	1.6
6.....	0.33	2.7	0.08	0.05	0.05	0.10	1.3
7.....	0.33	0.60	2.16	0.05	-----	-----	1.6
8.....	0.33	0.69	2.65	-----	0.05	-----	1.5
9.....	0.33	0.60	0.13	0.005	0.005	-----	1.6
10.....	0.33	0.69	0.18	0.40	-----	-----	1.5
11.....	0.33	0.14	2.85	0.05	0.05	-----	1.3
12.....	0.33	0.14	0.09	0.05	0.05	-----	3.2
13.....	0.33	0.14	0.08	0.05	0.03	-----	1.7
14.....	0.33	0.14	0.08	0.05	0.03	-----	2.2

Example 15.—The procedure of the preceding examples was repeated with the exception that a coating solution, aged for about 72 hours, was used. This solution, at a concentration of about 11 points, had a pH of 1.58. The solution in an amount of six liters, was formulated as in the previous examples and contained the following components in the amounts indicated:

Components:	Percent by weight of coating solution
CrO ₃	0.38
Zn ⁺²	0.39
Cr ⁺³	0.29
Al ⁺³	0.19
NO ₃ ⁻	1.76
F ⁻	0.55

The Zn⁺² and Cr⁺³ were added as the respective nitrates and the Al⁺³ was added as Al(OH)₃. To this solution there was then added 0.08% HF and hot dip galvanized panels were processed as in the previous examples, using this composition as the coating solution. The weight losses obtained were 17 milligrams/square foot. Thereafter, 3 grams of sodium arsenate and 6 grams of sodium tungstate were added and additional panels processed. The weight loss on these panels was about 10.7 milligrams/square foot. Upon adding 3 more grams of sodium arsenate to the solution, the panels processed had a weight loss of about 6.5 milligrams/square foot.

Example 16.—The procedure of Example 15 was repeated with the exception that sodium uranate and tungstate were added instead of arsenate and tungstate. Using this procedure, the accelerator added and the results obtained were as follows:

Accelerator added:	Losses in milligrams/ft. ²
None	23.80
Sodium uranate (2 g.)	18.90
Sodium uranate (1 g.)	18.75
Do	17.73
Do	17.07
Sodium tungstate (6 g.)	14.40
Sodium uranate (1 g.)	13.35

Example 17.—The procedure of Example 15 was repeated with the exception that the accelerator added was sodium vanadate. The amounts added and results obtained were as follows:

Accelerator added:	Losses in milligrams/ft. ²
None	22.0
Sodium vanadate (1 g.)	15.7
Sodium vanadate (2 g.)	6.7
Sodium vanadate (1 g.)	6.4
Do	4.0
Do	3.9

It is to be appreciated that the solutions used in the preceding three examples were formulated with zinc and Cr⁺³ as components so as to approximate an aged solution which had been used on both aluminum and galva-

nized stock, i.e., "mixed production." From the results obtained, as compared to those in Examples 1-14, it is seen that the solutions of the present invention are equally good whether made up fresh or aged and that use on mixed aluminum and zinc production does not have an adverse effect on the solution.

Example 18.—A coating solution was formulated as in the preceding examples, which solution contained the following components in the amounts indicated:

Components:	Percent by weight of coating solution
CrO ₃	0.25
Zn ⁺²	1.35
Cr ⁺³	0.44
Al ⁺³	0.07
NO ₃ ⁻	2.85
F ⁻	0.77
WO ₃	0.06
MoO ₃	0.04

The pH of this solution was 2.0. Hot dip galvanized stock was coated with this solution as in the previous examples. The coating obtained was a very good paint base and when painted provided excellent corrosion resistance. During the time the stock was coated with the above solution, the coating solution was periodically replenished, as required, to maintain the desired amounts of the various components, with a replenishing material having the following composition:

Components:	Percent by weight
CrO ₃	4.80
HF	0.40
HNO ₃	2.10
Sodium tungstate	0.44
Sodium molybdate	0.38
AlF ₃ complex	1.20
Water	Balance

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is intended to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A method of forming a protective coating on zinc-containing surfaces which comprises contacting a clean, zinciferous surface with a coating composition which consists essentially of an aqueous acidic solution which contains an effective coating amount of hexavalent chromium ions, fluoride ions in an amount effective to attack the surface being treated and from at least 0.01% by weight of the coating composition up to its maximum solubility in the solution of an activator formed of at least one ion selected from the group consisting of tungsten, molybdenum, vanadium and uranium, the amounts of said ions being calculated as the respective metals, maintaining said solution in contact with the surface for a period sufficient to form the desired coating thereon, removing the thus-coated surface from contact with the solution and, thereafter, contacting the thus-coated surface with a rinsing composition which comprises an aqueous solution containing hexavalent chromium ions.

2. The method as claimed in claim 1 wherein the coating composition contains 0.05 to 1% by weight hexavalent chromium ions, calculated as CrO₃, 0.05 to 2.7% fluoride ions, and 0.01 to 0.4% of the activator composition.

3. The method as claimed in claim 2 wherein the coating composition also contains 0.1 to 0.2% by weight of

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a buffering acid, effective in buffering the fluoride ions in the composition.

4. The method as claimed in claim 3 wherein the buffering acid is boric acid.

5. The method as claimed in claim 3 wherein the coating solution also contains aluminum in an amount within the range of about 0.01 to about 1.0% by weight.

6. The method as claimed in claim 5 wherein the amounts of the components of the coating solution are maintained within the indicated ranges by periodically replenishing the solution with an aqueous composition comprising the following components in the amounts indicated:

Components:	Parts by weight
Hexavalent chromium (calculated as CrO_3)	15-20
HF	1-5
Inorganic mineral acid	2-20
Activator composition	2-10
Boric acid	0-2
AlF_x complex	0-5

7. A method for treating a zinc-containing surface which comprises contacting a zinciferous surface with an aqueous alkaline solution, maintaining the alkaline solution in contact with the surface for a period sufficient to effect cleaning of the surface, contacting the thus-cleaned zinciferous surface with a coating composition which consists essentially of an aqueous acidic solution which contains an effective coating amount of hexavalent chromium ions, fluoride ions in an amount effective to attack the surface being treated, and from at least 0.01% by weight of the coating solution up to its maximum solubility in the coating solution of an activator composition containing at least one ion selected from the group consisting of tungsten, molybdenum, vanadium and uranium, the amounts of said ions being calculated as the respective metals, maintaining said coating solution in contact with the surface for a period sufficient to form the desired coating thereon, removing the thus-coated surface from contact with the solution and, thereafter, contacting the thus-coated surface with a rinsing composition which comprises an aqueous solution containing hexavalent chromium ions.

8. The method as claimed in claim 7 wherein the aqueous acidic coating solution contains from about 0.05 to about 1% by weight of hexavalent chromium ions, calculated as CrO_3 , from about 0.05 to about 2.7% by weight

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fluoride ions, and from about 0.01 to about 0.4% by weight of the activator composition.

9. The method as claimed in claim 8 wherein the aqueous acidic coating solution also contains from about 0.1 to about 0.2% by weight of a buffering acid, effective in buffering the fluoride ions in the composition.

10. The method as claimed in claim 9 wherein the buffering acid is boric acid.

11. The method as claimed in claim 9 wherein the aqueous alkaline solution with which the zinciferous surface is first contacted is an aqueous solution of an alkali metal metasilicate.

12. The method as claimed in claim 9 wherein the coating solution also contains aluminum in an amount within the range of about 0.01 to about 1.0% by weight.

13. The method as claimed in claim 12 wherein the amounts of the components of the coating solution are maintained within the indicated ranges by periodically replenishing the solution with an aqueous composition comprising the following components in the amounts indicated:

Components:	Parts by weight
Hexavalent chromium (calculated as CrO_3)	15-20
HF	1-5
Inorganic mineral acid	2-20
Activator composition	2-10
Boric acid	0-2
AlF_x complex	0-5

14. The method as claimed in claim 7 wherein the aqueous alkaline solution with which the zinciferous surface is first contacted is an aqueous solution of an alkali metal metasilicate.

15. A zinc surface having a coating thereon produced in accordance with the method as claimed in claim 1.

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