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**COMPOSITION AND METHOD FOR PRODUCING CORROSION RESISTANT PROTECTIVE COATING ON ALUMINUM AND ALUMINUM ALLOYS**

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This invention relates to the treatment of aluminum and alloys wherein aluminum is a principal constituent, to provide the same with a corrosion resistant coating. The coating formed is also one which forms an improved bond for organic finishes, such as paints, lacquers and the like, and which may be suitably dyed when desired.

The invention comprises an aqueous solution of a chromic compound selected from the group consisting of chromic acid and water-soluble salts thereof and ferricyanic or ferrocyanic acid and water-soluble salts thereof and mixtures of the same.

The attainment of a corrosion resistant coating on aluminum and alloys thereof is desirable in order to prolong the life of the object being coated. Coatings utilized heretofore suffered from various disadvantages which the present coating composition is specifically designed to eliminate.

For example, the aluminum protective coatings known heretofore generally have necessitated the use of electric current, heated or cooled solutions, venting and the like, and the coating baths utilized to attain the same necessitate very long immersion times in order to impart a coating of any practical use.

The coating composition comprising the present development is designed to obviate these disadvantages. The coatings produced by use of our compositions exhibit greatly improved corrosion resistance and the coating operation can be conducted with the solution at room temperature as a simple dip treatment without need of venting. In addition, shorter immersion times in the bath can be realized.

Further, as will be pointed out hereinafter, by carefully controlling the operating conditions surrounding the utilization of our coating baths, we can realize coloring in situ ranging from clear to yellow, brown and blue. For example, by adding a ferric compound such as ferric chloride to the basic composition noted heretofore, a blue coating results with enhanced corrosion resistance as noted above.

In the case of yellow and brown coatings, for example, these can, if desired, be bleached by dipping in hot water to a clear colorless appearance. In addition, they may be readily dyed, if required.

Accordingly, a principal object of this invention is the provision of a novel coating bath that will produce a coating on aluminum and aluminum alloys of greatly enhanced corrosion resistance and far more advantageous physical and operational characteristics, as recited above, than did those previously utilized.

Further objects include:

1. The provision of a novel coating composition which, when dissolved in water, will yield a coating bath that produces improved corrosion resistant coatings on aluminum and alloys thereof, and can be applied by dip, brush or spray, as distinguished from complicated electrolytic operations.

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2. A further object of this invention is to provide a dry powder mixture for use in aqueous solutions to impart a corrosion resistant coating to aluminum and alloys thereof, comprising a chromic compound selected from the group consisting of chromic acid and water-soluble salts thereof and ferricyanic or ferrocyanic acid and water-soluble salts thereof and mixtures of the same.

3. An additional object of this invention is to provide a composition for use in aqueous solutions to impart a corrosion resistant coating to aluminum and alloys thereof, comprising chromic acid and potassium ferricyanide wherein said chromic acid concentration is from .5 g./l. to 50 g./l. and the potassium ferricyanide concentration can vary from .1 g./l. to 50 g./l.

4. Still another object of this invention is to provide a composition as described heretofore including hydrofluoric acid and salts of hydrofluoric acid, such as barium, sodium, potassium, and ammonium fluoride, fluosilicic acid and salts thereof, notably barium, sodium, and potassium fluosilicates, and fluoboric acid and salts thereof, such as sodium, potassium and ammonium fluoborate, to increase the protective value of the corrosion resistant coating, as well as to decrease the time necessary for applications of such coating. Other soluble fluo compounds which will act in the same manner as those recited may be used.

5. An additional object of this invention is to provide the composition of this invention including a fluo compound as described heretofore wherein, for example, the hydrofluoric acid concentration can vary from 0.05 to 5 g./l., the fluosilicic acid concentration from 0.075 to 8 g./l., and the fluoboric acid concentration from 3.3 to 33 g./l. Salts of these three acids may be used in amounts chemically equivalent to the stated amounts of acid, in each instance.

6. Another and further object of this invention is to provide a composition including a fluo compound listed heretofore wherein said fluo compound is of limited solubility thereby being maintained, through self-replenishment, at a constant desired value, i. e., the concentration of the semi-soluble fluo compound is maintained at a constant desired value by virtue of the fact that the dipping bath is saturated with respect thereto.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

These objects can be accomplished, according to the invention, by the dissolution in water of a composition including at least a chromic compound selected from the group consisting of chromic acid and water-soluble salts thereof and ferricyanic or ferrocyanic acid and water-soluble salts thereof and mixtures of the same. In addition, this composition may include fluo compounds as recited above and a mineral acid, such as sulfuric, nitric or hydrochloric acid. These additional compounds are added in the proportions and under the conditions which will be hereinafter set forth in detail.

The composition of the present invention may also be supplied to the coating plant as a dry mixture and made up into a suitable bath by the addition of water, or it may be supplied to the coating plant as a concentrated aqueous solution which may be diluted by the consumer to provide the necessary coating bath.

We have discovered that it is possible to effectively protect aluminum surfaces by a dip, brush or spray with

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a solution containing compounds as heretofore set forth. Not only is an improved protective coating deposited on the aluminum surface, but such coating has excellent bonding power for subsequent organic finishing, e. g., with paints and lacquers, and, in some cases, where desired, can be dyed readily with various colors. In addition, the coating operation can be modified to produce, in situ, protective coatings of many and varied desired colors by reason of the composition of the coating bath and the operational procedure used.

The aluminum or aluminum alloy articles to be coated are first preferably cleaned by conventional methods which remove organic matter and metallic oxides. The articles are then subjected to a dipping, brushing or spraying step in an aqueous solution comprising the compositions of our invention.

As heretofore noted, the coatings realized by utilization of our invention exhibit greatly enhanced corrosion resistant characteristics. It is believed that when an aluminum or aluminum alloy surface is subjected to solutions of the character comprehended by this invention, a chemical reaction takes place between the particular solution and the aluminum surface. The nature of this chemical reaction cannot specifically be described but the final coating, after drying, is tightly adherent to the aluminum surface and, as a matter of fact, appears to be integral therewith.

A more complete understanding of the procedure of this invention may be had by reference to the following illustrative examples of actual operations in accordance with the invention.

## EXAMPLE I

Chromic acid.....	g./l.	25
Potassium ferricyanide.....	g./l.	5
Temperature.....	° F.	70
pH.....		0.8
Immersion time.....	minutes	5

The above composition is considered a typical formulation of chemical ingredients which, when made into an aqueous solution, produced protective coatings as heretofore described. Generally, the concentration of the ingredients can be varied to from .5 g./l. to 50 g./l. of chromic acid and from .1 g./l. to 50 g./l. potassium ferricyanide. In addition, other chromic compounds, such as potassium or sodium bichromate, can be substituted for the chromic acid. The operating temperature in Example I can be between 32° to 160° F. which constitutes the temperature range generally contemplated in our invention. In addition, an immersion time of from five seconds to ten minutes has been found to be the preferred time range within which the compositions of our invention is operable. The exact immersion time is dependent upon the degree of corrosion resistance desired and, further, whether it is desired to produce a color in situ rather than to utilize a later dyeing step.

With respect to this latter point, it should be noted that a clear coating will be obtained by the utilization of the composition of Example I if an immersion time of from one to three minutes is used. A yellow coating can be realized with a three to ten minute immersion time.

The pH may be varied within a range of about 0.1 to 2.5 measured by an electrometric pH meter, and this pH variation may also be utilized to control color.

A salt spray test on 24 S. T. aluminum (an aluminum alloy containing up to about 4½% copper) having a yellow coating imparted by the composition of Example I exhibited less than 1% white corrosion after 766 hours exposure.

By the addition of a fluo compound, such as a salt of fluosilicic acid to the formulation of Example I, equivalent or better coatings can be obtained with much shorter immersion times. An example of this modified dipping bath follows:

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## EXAMPLE II

Chromic acid.....	g./l.	50
Potassium ferricyanide.....	g./l.	5
Sodium fluosilicate.....	g./l.	5
Temperature.....	° F.	70
Immersion time.....	seconds	60
pH.....		0.4

As previously indicated, the general temperature range of 32° to 160° F. is applicable to the above composition. A temperature range of 70° F. to 90° F. is preferred. We should state that the immersion time can preferably vary from five seconds to about five minutes or over, depending upon the color or thickness of coating desired to be attained. It should be noted that, upon the addition of the fluosilicate, heavier coatings can be realized with shorter immersion times.

Using the formulation of Example II under the conditions described, a coating was produced which, on 24 S. T. aluminum, showed less than 1% white corrosion after 1000 hours in a salt spray. It can be appreciated that the sodium fluosilicate significantly decreased the immersion time required to produce a coating possessing corrosion resistance substantially equivalent or better to that obtained by utilization of the basic formulation of Example I. This effect of the sodium fluosilicate can best be explained by stating that this compound accelerates film formation.

As we stated heretofore, the color imparted by the formulations of either Example I or II or subsequent examples may be varied by controlling the immersion time. However, a variety of colored finishes can also be obtained ranging from clear through yellow to dark brown by adjusting the pH of the dipping solutions between below pH 0.1 and pH 3.0. Any of the known pH controlling agents can be used in Examples I and II.

Examples of the use of various chromic, ferricyanide, ferrocyanide and fluo compounds are hereinafter set forth.

## EXAMPLE III

Chromic acid.....	g./l.	5
Potassium ferricyanide.....	g./l.	2.5
Sodium ferrocyanide.....	g./l.	2.5
Sodium fluoborate.....	g./l.	5
pH.....		1.5
Immersion time.....	minutes	5
Temperature.....	° F.	70

The above formulation yielded a yellow-brown coating which, on 24 S. T. aluminum, showed less than 1% corrosion after 1000 hours in salt spray.

## EXAMPLE IV

Sodium bichromate.....	g./l.	7.5
Potassium ferricyanide.....	g./l.	5
Sodium fluoride.....	g./l.	1
Nitric acid (42° Bé).....	ml./l.	3
pH.....		1.5
Immersion time.....	minutes	5
Temperature.....	° F.	80

The above formulation yielded results similar to those described heretofore and is of particular interest since it illustrates the use of a mineral acid to adjust the pH of the bath.

## EXAMPLE V

To the formulation of Example I can be added 1 to 10 ml. of sulfuric acid. We added 8 ml. of sulfuric acid to lower the pH to about 1.2 and the coating that resulted had a dark clear reflective color under what were otherwise the same operating conditions of Example I.

As noted heretofore, the concentration of the basic formulation, typified by chromic acid and potassium ferricyanide, varied from .1 g./l. and .5 g./l. respectively to 50 g./l. for both of these compounds. Different concentration ranges would be applicable to the use of salts

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of chromic acid, or ferricyanic or ferrocyanic acid or salts thereof as well as mixtures of the same. These different concentration ranges can be calculated using the .1 g./l. and .5 g./l. respectively to 50 g./l. ranges noted heretofore. In other words, the calculations should be such that the same amount of hexavalent chromium and ferricyanide or ferrocyanide is realized in the mixture being formed. On this latter point, it should be noted that the ferricyanic and ferrocyanic radicals do not differ in structure but merely in valence.

The same type of calculation can be utilized to determine the concentration range of the various fluo compounds, that can be substituted for the fluo acids whose concentration ranges were noted heretofore. For example, the fluosilicic acid range was given as from 0.075 to 8 g./l. from such figures, the sodium fluosilicate concentration range, if such salt was substituted for fluosilicic acid, is calculated at about 0.1 to 10 g./l.

As previously indicated, the desired chromic compound can be obtained from a number of compounds. For example, chromic acid, sodium or potassium bichromate, or sodium or potassium chromate can be utilized. Chromic acid or sodium or potassium bichromate is preferred for economical reasons.

## EXAMPLE VI

Chromic acid	5 g./l.
Potassium ferricyanide	5 g./l.
Barium fluosilicate	2.0 g./l.
Temperature	Room temperature (80° F.).
pH	1.5

A yellow corrosion resistant coating was produced by utilizing the above formulation.

This formulation illustrates the use of a fluo compound of limited solubility in order to impart a partial self-replenishment to the dipping bath. Barium fluosilicate is of such solubility in water as to provide a solution of fixed concentration with respect to the fluo compound, i. e., the excess undissolved barium fluosilicate automatically maintains the fluo concentration at a constant desired value. Other examples of such a feature would include the use of potassium fluosilicate, barium fluoride, aluminum fluoride or magnesium fluoride.

## EXAMPLE VII

Chromic acid	5 g./l.
Sodium ferrocyanide	1.5 g./l.
Barium fluosilicate	2.0 g./l.
pH	1.5.
Operating temperature	Room or above.
Immersion time	5 minutes.

## EXAMPLE VIII

Chromic acid	5 g./l.
Ammonium ferrocyanide	1.0 g./l.
Barium fluosilicate	2.0 g./l.
pH	1.5.
Operating temperature	Room or above.
Immersion time	5 minutes.

## EXAMPLE IX—DRY POWDER MIX

	Percent by weight
Chromic acid	54
Potassium ferricyanide	11
Barium nitrate	20.5
Sodium fluosilicate	14.5

## EXAMPLE X

Chromic acid	5 g./l.
Potassium ferricyanide	1 g./l.
Barium nitrate	1.9 g./l.
Sodium fluosilicate	1.35 g./l.
pH	1.5.
Operating temperature	Room temperature (about 80° F.).
Immersion time	About ½ minute.

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In this formulation the use of barium nitrate and sodium fluosilicate in aqueous solution results effectively in the formation of barium fluosilicate and has the same effect as if barium fluosilicate alone were used. The choice of ingredients in this case is made for practical economical reasons.

The temperature may vary between 32° and 160° F., the preferred range being 65° to 80° F. The time may vary between 1 second to ten minutes, the preferred range being about ½ minute to six minutes.

It can be appreciated that Examples VI-X represent formulations that exhibit and produce preferred effects. In other words, the basic chromic and ferri- or ferrocyanide compositions are enhanced by the fluosilicate compound addition in that immersion time is decreased and a heavier, more even coating is produced. Add to this the fact that a self-replenishing feature is imparted by the barium fluosilicate, as heretofore set forth, and the fact that a preferred overall dipping composition is realized has been made evident.

Referring to Example IX, from about .1 ounce to 5 ounces of the powder mix of Example IX per gallon of water are useful as in Example X.

## Conclusions

The present invention provides a new coating composition for use in aqueous solutions to impart a corrosion resistant coating to aluminum and alloys thereof. The new composition provides better corrosion resistance, an excellent bond for paint and varnishes, a clearer coating and shorter immersion times at room temperature (80° F.). In addition, by varying the ingredients and controlling the pH of the dipping solution and immersion times of the articles being coated, various colors in situ can be realized.

The novel principles of this invention are broader than the specific embodiments recited above, and rather than unduly extend this disclosure by attempting to list all the numerous modifications which have been conceived and reduced to practice during the course of this development, these novel features are substantially defined in the following claims.

This application is a continuation-in-part of application Serial No. 400,774, filed December 28, 1953, now abandoned.

## We claim:

1. A composition for use in the art of applying a chemically bonded coating on metal surfaces, said composition consisting essentially of hexavalent chromium, a fluorine-bearing compound and a soluble cyanide selected from the group consisting of ferricyanide and ferrocyanide in proportions which are capable of coating aluminum.

2. A composition for use in aqueous solution to impart a corrosion-resistant coating of aluminum and alloys thereof consisting essentially of at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one cyanide selected from the group consisting of ferricyanic acid, ferrocyanic acid, and salts thereof and mixtures of these acids and salts and including a ferric salt.

3. A composition as claimed in claim 1 including at least one fluo compound selected from the group consisting of hydrofluoric acid and salts thereof, fluosilicic acid and salts thereof, and fluoboric acid and salts thereof.

4. A composition as claimed in claim 3 wherein said fluo compound is in amount equivalent to from about 0.05 to 5 grams of hydrofluoric acid per liter of solution for the hydrofluoric acid and salts thereof, in amount equivalent to from about 0.075 to 8 grams of fluosilicic acid per liter of solution for the fluosilicic acid and salts thereof, and in amount equivalent to from about 3.3 to 33 grams of fluoboric acid per liter of solution for the fluoboric acid and salts thereof.

5. An aqueous solution to impart a corrosion-resistant-

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coating to aluminum and alloys thereof consisting essentially of water, at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one cyanide selected from the group consisting of ferricyanic acid, ferrocyanic acid, and salts thereof and mixtures of these acids and salts, and at least one fluo compound selected from the group consisting of hydrofluoric acid and salts thereof, fluosilicic acid and salts thereof, and fluoboric acid and salts thereof.

6. An aqueous solution as claimed in claim 5 wherein said fluo compound is in amount equivalent to from about 0.05 to 5 grams of hydrofluoric acid per liter of solution for the hydrofluoric acid and salts thereof, in amount equivalent to from about 0.075 to 8 grams of fluosilicic acid per liter of solution for the fluosilicic acid and salts thereof, and in amount equivalent to from about 3.3 to 33 grams of fluoboric acid per liter of solution for the fluoboric acid and salts thereof.

7. An aqueous solution as claimed in claim 5 wherein said fluo compound is of limited solubility to thereby provide a solution of continuously fixed concentration with respect to the fluo compound.

8. An aqueous solution as claimed in claim 7 wherein said fluo compound is selected from the group consisting of potassium fluosilicate, aluminum fluoride and magnesium fluoride.

9. An aqueous solution as claimed in claim 5 including a mineral acid and having pH range from about 0.1 to pH 3.0.

10. A method for imparting a corrosion-resistant coating to aluminum and alloys thereof which comprises subjecting the latter to an aqueous acidic solution comprising water, at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof and at least one cyanide selected from the group consisting of ferricyanic acid, ferrocyanic acid, and salts thereof and mixtures of these acids and salts.

11. A method as claimed in claim 10 wherein said chromic compound is in amount equivalent to from about 0.5 to 50 grams of chromic acid per liter of solution, and wherein said cyanide salt is in amount equivalent to from about 0.1 to 50 grams of potassium ferricyanide per liter of solution.

12. A method as claimed in claim 10 wherein the pH of the solution is from about pH 0.1 to 3.0.

13. A method as claimed in claim 10 wherein the ob-

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ject being coated is subjected to the said solution for a period of from 5 seconds to 10 minutes and wherein the temperature of the solution is from about 32° F. to 160° F.

14. A method as claimed in claim 10 wherein the aqueous acidic solution includes at least one fluo compound selected from the group consisting of hydrofluoric acid and salts thereof, fluosilicic acid and salts thereof, and fluoboric acid and salts thereof.

15. A method as claimed in claim 14 wherein said fluo compound is in amount equivalent to from about 0.05 to 5 grams of hydrofluoric acid per liter of solution for the hydrofluoric acid and salts thereof, in amount equivalent to from about 0.075 to 8 grams of fluosilicic acid per liter of solution for the fluosilicic acid and salts thereof, and in amount equivalent to from about 3.3 to 33 grams of fluoboric acid per liter of solution for the fluoboric acid and salts thereof.

16. In the method of producing a corrosion-resistant chemically bonded coating on an aluminum surface wherein the surface is treated with an aqueous acid coating solution the essential coating-producing ingredients of which are hexavalent chromium and fluorine, the step which includes dissolving a complex cyanide in such solution as an addition agent and then treating the metal surface therewith.

17. A composition for use in preparing an aqueous acid metal coating solution of the type in which the principal and essential coating-producing ingredients are hexavalent chromium, a fluorine-bearing compound and a soluble ferricyanide in proportions capable of coating aluminum.

18. An aqueous solution as claimed in claim 5 including a mineral acid and having pH range from about 0.1 to pH 2.5.

19. A method as claimed in claim 10 wherein the pH of the solution is from about pH 0.1 to 2.5.

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