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3,364,080

**METHOD OF IMPROVING THE CORROSION
RESISTANCE OF CHROMATE CONVERSION
COATED ALUMINUM SURFACE**Wilbur S. Hall, Plymouth Meeting, Pa., assignor to
Amchem Products, Inc., Ambler, Pa., a corporation
of DelawareNo Drawing. Filed Oct. 22, 1964, Ser. No. 405,854
6 Claims. (Cl. 148-6.2)

This invention relates to the art of improving the corrosion resistance of aluminum surfaces and is more particularly concerned with improving the corrosion resistance of aluminum surfaces which will be subjected to relatively high temperatures, i.e. temperatures above what may be considered usual or normal for most purposes.

At this time it should be noted that the word "aluminum" as used herein and in the appended claims is to be understood as applying to alloys thereof wherein aluminum is the principal or dominant ingredient as well as to essentially pure aluminum.

Before proceeding to a detailed description of the invention it is desired to refer to certain practices of the prior art because this will be of assistance in appreciating the contribution made by the present invention.

During the past decade or so numerous processes have been developed for providing corrosion resistant coatings on aluminum surfaces. Probably the most important of these are those which provide the aluminum surface with an integral, amorphous, chemically applied chromate conversion coating. Typical examples of this type of coating technique are disclosed in the following United States patents: 2,276,353; 2,507,956; 2,796,956; 2,796,370; 2,796,371; 2,825,697; 2,843,513; 2,851,385; 2,859,144; 2,868,679; 2,988,465; 3,009,842 and 3,113,051.

While such integral, amorphous, chemically applied chromate conversion coatings, such as typified by the processes of the patents mentioned above, have been eminently satisfactory for most situations where the aluminum is subjected to what might be termed normal usage, i.e., where the aluminum is never subjected to more than usual or average living temperatures, they have been found to be considerably less than adequate and have even failed completely to provide adequate corrosion protection under conditions where the surfaces may be exposed to elevated temperatures, that is, to temperatures of 100° C. or higher. This problem is particularly acute in the aircraft industry where aluminum can be subjected to temperatures well in excess of 100° C., under which conditions it has been found that, after exposure to such elevated temperatures, aluminum surfaces bearing the integral, amorphous, chemically applied chromate conversion coatings of the prior art, corrode at a much faster rate (or even fail completely) than they would had they been exposed only to relatively low or what might be termed ordinary ambient or living temperatures.

With the foregoing in mind the principal object of the present invention may be stated as residing in the provision of a process for enhancing or increasing the corrosion resistance of aluminum surfaces which already carry an integral, amorphous, chemically applied chromate conversion coating of the type familiar to the art.

The present invention is based upon the discovery that if an aluminum surface, which already carries a chromate conversion coating of the character familiar to the prior art, is subjected to the action of an aqueous alkaline solution having dissolved therein from 15 to 100 g./l. of a soluble hexavalent chromium-containing compound, calculated as $\text{Na}_2\text{Cr}_2\text{O}_7$, where such solution is maintained at a pH value between 8 and 12 and where the surface is treated with such a solution at a temperature of at least

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65° C. and for a period of at least 4 minutes, the corrosion resistance of the said coated aluminum will be markedly improved even under conditions where the surface may have been subjected to relatively high temperatures for extended periods of time and particularly to temperatures in excess of 100° C.

In order to realize the benefits of this invention the aluminum surface must first have applied thereto an integral, amorphous, chromate conversion coating such as typified by the patents referred to above. Known processes for producing such chromate conversion coatings utilize acidic solutions which contain, inter alia, soluble hexavalent chromium ions and halogenated accelerating agents such, for example, as a fluorine bearing compound. Other additives which have been employed frequently include ferro- or ferricyanide ions, salts of complex heteropoly- molybdates, or barium, antimony or tin ions. The important consideration is that before the process of the present invention is carried out the aluminum surface to be treated should carry some form of integral, amorphous, chemically applied chromate conversion coating such as is now familiar to those skilled in this art.

As noted above the alkaline hexavalent chromium treating solution of this invention must contain from about 15 to about 100 g./l. of a soluble hexavalent chromium-containing compound calculated as $\text{Na}_2\text{Cr}_2\text{O}_7$. Where less than the minimum amount of chromium-containing compound is utilized little or no corrosion resistance after high temperature exposure will be retained by the treated aluminum surfaces. Conversely, where more than 100 g./l. of hexavalent chromium-containing compound is utilized a definite reduction in corrosion resistance following exposure to high temperatures is noticed with the reduction becoming more pronounced as the amount of hexavalent chromium compound is increased above a maximum of about 100 g./l.

It should also be noted that my experience has indicated that best results are secured from the treating solutions utilized in accordance with this invention where such solutions contain from about 20 to 80 g./l. of hexavalent chromium-containing compound (calculated as $\text{Na}_2\text{Cr}_2\text{O}_7$).

Within this range it has been found that optimum high temperature corrosion resistance is realized with ease and economy of operation.

The hexavalent chromium-containing compound may be supplied from one or more of the sodium, potassium, lithium or ammonium salts of chromic acid, or simply from chromic acid itself (CrO_3). Where the latter is employed, and also where certain less basic salts of chromic acid are utilized, it will be necessary to add an alkaline agent for the purpose of obtaining the required solution pH. Preferred hexavalent chromium-containing agents are the alkali metal or ammonium dichromate salts, since solutions of these salts provide a ready source of the desired alkalinity and are easily adjusted to the desired pH range by the addition of some excess of caustic solution.

It should be noted that the pH of the aluminum treating solution is critical and must be maintained between 8 and 12 if the improvements of this invention are to be fully realized. Where the pH value is permitted to fall below 8.0 the outstanding corrosion protection afforded by this invention will not be realized and severe corrosion will occur where the treated articles have been exposed to temperatures above 100° C. Conversely, where the pH value is permitted to rise above 12.0 there will be an abnormally high rate of dissolution of the metal surface, and certain aluminum alloys will exhibit an undesirable smut on their surfaces if they are subjected to treatments at these high pH values. Adjustments in pH, as indicated above, may be made with conventional alkaline

agents, such, for example, as aqueous sodium hydroxide solutions.

In utilizing the present invention the treating solution should be maintained at a temperature of at least 65° C. If lower temperatures are utilized it will be found that the surface will fail to develop the desired increase in corrosion resistance, especially where the aluminum is subjected to temperatures above 100° C. While good results are secured where the treating solution is at temperatures of at least 65° C. I have found that unusually excellent and consistently high levels of corrosion protection can be secured where the temperature of the treating solution lies between 93° C. and the boiling point of the treating solution. For this reason the preferred operating temperature should be not less than 93° C.

The time of treatment should be long enough to insure a reaction between the coated aluminum articles and the alkaline chromate treating solution which is sufficient to improve the corrosion resistance of the surface and this, of course, may vary depending in part at least upon such considerations as the concentration of the hexavalent chromium compound in the treating solution or its pH within the specified range and the temperature at which it is employed. As a general rule, I have found that the treatment should be continued for at least 4 minutes although this is not an absolute requirement in all instances because the advantages of the invention may sometimes be at least partially realized where the treatment time is somewhat less than 4 minutes. On the other hand, much longer treating times may be employed as, for example, one hour or more, without adversely affecting the improved results which are obtained by the process of this invention. As a general guide it may be said that where the quantity of the hexavalent chromium-containing compound in the treating solution is within the upper half of the permissible concentration range the treating times may be of shorter duration. Conversely, as the quantity of hexavalent chromium-containing compound decreases to somewhere in the lower half of the permissible concentration range the time of the treating cycle may be increased somewhat so as to insure obtaining the improved results of this invention.

If desired, a water rinse may be utilized after the treatment with the solution of this invention although such a water rinse is not essential to realization of the advantages of the invention.

In order to illustrate the effects of the process of the present invention upon variously pre-treated aluminum surfaces there is presented below in tabular form a series of tests and the results secured thereby. However, these tests are to be considered merely as illustrative and should not be construed as limitations upon the scope of this invention.

EXAMPLE I

A group of Type 2024 aluminum alloy panels were prepared according to the teachings of United States Patent 2,796,370 employing a chromate conversion coating solution according to Example I of the said patent. These panels were found to have incorporated thereon an integral, amorphous, chromate conversion coating weighing from 35 to 40 mg./ft.². A series of separate aqueous solutions each containing 40 g./l. of Na₂Cr₂O₇·2H₂O was prepared so that these different solutions had pH values ranging from 0.75 to 12 according to Table I below. Each of the solutions in Table I was then utilized to treat one panel from the group which had been prepared according to the teachings of the said United States patent. Each treatment was conducted for five minutes at the boiling point of the solution. All panels were then water rinsed and then subjected to a temperature of 130° C. for ten minutes, following which they were evaluated in a standard salt spray corrosion test in accordance with ASTM B-368-61T using a 5% concentration of sodium chloride. After 114 hours the results in each instance are shown in Table I below.

TABLE I

Solution No.	pH	ASTM B-368-61T Corrosion Results
Control.....	(1)	Failed.
1.....	0.75	Do.
2.....	2	Do.
3.....	3	Do.
4.....	4	Do.
5.....	5	Do.
6.....	6	Do.
7.....	7	Do.
8.....	8	Passed.
9.....	9.5	Do.
10.....	11.5	Do.
11.....	12	Do.

¹ No treatment in alkaline Na₂Cr₂O₇.

As will be seen upon analysis of Table I, the foregoing tests clearly demonstrate the fact that the pH must be maintained between 8 and 12 in order to obtain the advantages of the invention. The first seven panels in the table following the control definitely failed the salt spray corrosion test and all of these involved use of a treating solution having a pH less than 8. However, when the pH was maintained at from 8 to 12 the panels clearly passed the specified salt spray corrosion test.

EXAMPLE II

A group of Type 2024 aluminum alloy panels were prepared according to the teachings of United States Patent 2,851,385 employing a chromate conversion coating solution according to Formula No. 2 of said patent. These panels were found to have incorporated thereon an integral, amorphous, chromate conversion coating weighing from 20 to 25 mg./ft.². A series of separate aqueous solutions containing from 15 to 250 g./l. of Na₂Cr₂O₇ was prepared so that these different solutions had concentrations of Na₂Cr₂O₇ as specified in Table II below. The pH value of each solution was adjusted with aqueous NaOH solution to lie within a range of from 11.1 to 11.5 as indicated in Table II. Each of the solutions in Table II was then utilized to treat one panel from the group which had been prepared according to the teachings of the said United States Patent 2,851,385. Each treatment was conducted at a temperature of 95° C. and for a treating time of five minutes. All the panels were then water rinsed, following which they were subjected to a temperature of 191° C. for thirty minutes and then they were subjected to the same salt spray corrosion test described in connection with Example I above except that the test was continued for 479 hours. Careful inspection showed the following results as reported in Table II below.

TABLE II

Solution No.	Grams/liter Na ₂ Cr ₂ O ₇	pH	ASTM B-368-61T Corrosion Results
Control.....	(1)	-----	Failed.
12.....	15	11.2	Passed.
13.....	40	11.5	Do.
14.....	80	11.4	Do.
15.....	100	11.2	Do.
16.....	120	11.1	Failed.
17.....	160	11.1	Do.
18.....	200	11.1	Do.
19.....	250	11.1	Do.

¹ No treatment in alkaline Na₂Cr₂O₇.

As will be seen from analysis of Table II, the foregoing tests clearly demonstrate that where no treatment with alkaline Na₂Cr₂O₇ was employed as per the control the coating failed, but where alkaline Na₂Cr₂O₇ solution having concentrations from 15 to 100 g./l. was applied the panels successfully passed the salt spray corrosion test. However, when the concentration of the treating solution was greater than 100 g./l. the panels failed to pass the salt spray corrosion test as shown by Table II.

EXAMPLE III

Another group of Type 2024 aluminum alloy panels was prepared according to the teachings of United States Patent 2,825,697 employing a chromate conversion coating solution according to Example I of said patent. A series of separate aqueous solutions containing 35 g./l. of $K_2Cr_2O_7$ at a pH of 11.6 was then prepared. Each of the solutions in Table III below was then utilized to treat one panel from the group which had been prepared according to the United States patent mentioned, namely 2,825,697. Each panel was first water rinsed before being subjected to the treatment. Each treatment was conducted for a period of 15 minutes at temperatures ranging from room temperature (21° C.) to boiling, as per Table III below. Each of the panels so treated was then water rinsed and subjected to a temperature of 191° C. for 30 minutes, following which they were subjected to the salt spray corrosion testing procedure described in Example I above. Periodic inspection of these panels at 18, 41, 136 and 240 hours showed the results as indicated in Table III below.

TABLE III

Solution No.	Treating Temp., °C.	ASTM B-368-61T Corrosion results in hours			
		18	41	136	240
Control.....		Failed..			
20.....	21	do.....			
21.....	38	Passed..	Failed..		
22.....	52	do.....	Passed..	Failed..	
23.....	65	do.....	do.....	do.....	
24.....	79	do.....	do.....	Passed..	Failed..
25.....	93	do.....	do.....	do.....	Passed..
26.....	Boiling..	do.....	do.....	do.....	Do.....

From the foregoing test and the results obtained thereby it is clearly apparent that the effectiveness of the present invention in improving the corrosion resistance of aluminum surfaces which carry an integral, amorphous, chemically applied chromate conversion coating progressively increases as the treating temperature goes up. The control, of course, failed after 18 hours and probably before. Where the temperature of the alkaline treating solution was 21° C. the panel also failed after 18 hours, but where the temperature was 38° C. the panel passed the 18-hour test although it failed the 41-hour test. When the treating solution was employed at 52° C. the panel passed the 41-hour test but failed by the 136-hour inspection period. This was true also of the 65° temperature, but when 79° C. was reached the 136-hour test was also passed. And, finally, at 93° C. and at boiling the panels passed the 240-hour test.

EXAMPLE IV

In order to still further illustrate the degree to which aluminum surfaces of the kind here involved, when treated by the process of this invention, will resist corrosion following high temperature conditions, a series of Type 2014 aluminum alloy panels was prepared according to the teachings of United States Patent 2,796,370 employing a chromate conversion coating solution according to Example I thereof. A series of these panels as so prepared were then treated for 5 minutes in an alkaline solution of $Li_2Cr_2O_7$ at a temperature of 93° C. and at a pH of 11.2. The alkaline solution contained 25 g./l. of $Li_2Cr_2O_7$. Following the treatment the panels were water rinsed and then

individual panels were subjected to varying temperatures lying between 260° C. and 315° C. Salt spray corrosion tests were then applied in accordance with the technique described in Example I and no panel showed corrosion after 24 hours in the salt spray and only very light corrosion after as much as 143 hours of salt spray testing.

It is apparent from all of the foregoing test results that my invention makes it possible to impart a very high level of corrosion resistance to aluminum surfaces which carry an integral, amorphous, chemically applied chromate conversion coating even when the surfaces are subjected to unusually high temperatures, as high, in fact, as 100° C. and even very much higher as shown by the foregoing examples.

In conclusion, I wish to emphasize that the foregoing examples of chemical formed integral, amorphous, chromate conversion coatings which were subjected to the technique of the present invention are simply typical of the improvement which I have been able to secure on all types of such chromate conversion coated aluminum surfaces. Indeed, I have tested in a similar way all of the coatings described in the list of United States patents referred to at the beginning of this specification and in every instance the results showed a marked improvement in corrosion resistance even after the chromate conversion coated surfaces were subjected to exceptionally high temperatures.

I claim:

1. In the art of improving the corrosion resistance of aluminum surfaces having thereon an integral, amorphous, chemically applied, chromate conversion coating; the method which comprises treating the said coated surface with an aqueous alkaline solution consisting essentially of from 15 to 100 grams per liter of a soluble hexavalent chromium-containing compound, calculated as $Na_2Cr_2O_7$, maintaining the pH of the solution, as may be required, at from 8 to 12 and its temperature at not less than 65° C., and continuing the treatment until the solution reacts with the said coating sufficiently to increase its corrosion resistance.

2. The method of claim 1 wherein the treatment is continued for a period of not less than four minutes.

3. The method of claim 2 wherein the temperature of the treating solution is not less than 93° C.

4. The method of claim 1 wherein the temperature of the treating solution is not less than 93° C.

5. The method of claim 1 wherein the concentration of the alkaline hexavalent chromium-containing compound is from 20 to 80 grams per liter.

6. The method of claim 1 wherein the hexavalent chromium-containing compound is chosen from the class consisting of chromic acid and the sodium, potassium, lithium and ammonium salts of chromic acid, and wherein the said pH of the treating solution is maintained, if necessary, by adding an alkaline agent as may be required.

References Cited

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