United States Patent Office

3,493,441
Patented Feb. 3, 1970

3,493,441

DETOXIFICATION OF HEXAVALENT CHROMIUM CONTAINING COATING ON A METAL SURFACE

Werner Rausch, Stierstadt, Taunus, Hans Hansen, Bergen-Enkheim, and Hans-Jurgen Schulz, Frankfurt am Main, Germany, assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

No Drawing. Filed Aug. 25, 1967, Ser. No. 663,213
Int. Cl. C23f *7/00, 7/14, 7/26*
U.S. Cl. 148—6.21 5 Claims

ABSTRACT OF THE DISCLOSURE

A process for treating metal surfaces particularly aluminum and aluminum alloys, wherein the surface is treated with an aqueous acid solution containing phosphate ions, fluoride ions, and hexavalent chromium ions, to produce a coating layer on the metal surface. Thereafter, the coated surfaces are treated with an aqueous acid solution which contains sulfur-oxygen compounds, capable of reducing hexavalent chromium, which solutions also contain at least one element selected from the group consisting of beryllium, calcium, boron, aluminum, cerium, and thorium. The treatment with the latter solution effects a detoxification of the hexavalent chromium in the coating layer on the metal surface, thus avoiding the accumulation of toxic, chromic acid-containing waste solutions. Desirably, the metal ions added to the acid treating solutions are present in amounts within the range of about 5 to 50 milliequivalents per liter of the treating solutions.

This invention relates to a process for treating metal surfaces and more particularly it relates to the treatment of aluminum and aluminum alloy surfaces with a hexavalent chromium containing treating solution, wherein detoxification of the hexavalent chromium in the coating produced is effected.

In the chemical surface treatment of metals, particularly alumium and aluminum alloys, utilizing treating solutions which contain hexavalent chromium, rinse water is produced which contains appreciable quantities of chromic acid. In view of the extreme toxicity of chromic acid, it must be rendered innocuous in this rinse water before disposal thereof can be effected. Heretofore, this has been carried out by reducing the hexavalent chromium in the waste water to appreciably less toxic trivalent chromium salts, which salts may then, if desired, be precipitated and removed from the water before it is disposed. Typical reducing agents which have been used are sulfur dioxide, sodium sulfite, sodium bisulfite, sodium metabisulfite, and the like.

Moreover, processes involving so-called "direct detoxification" are also known, wherein the accumulation of any appreciable amount of chromic acid-containing waste water is avoided. In these processes, the workpieces, which have been coated with the solutions containing hexavalent chromium, are not rinsed with clean water but rather, are rinced directly, by spray or immersion, in a detoxification solution which contains a suitable reducing agent for the hexavalent chromium, such as sulfurous acid or sodium bisulfite. In this manner, the coating solution adhering to the workpieces is uniformly detoxified and the workpieces are thereafter rinsed in clean, flowing water. Inasmuch as this latter rinsing removes only innocuous solution residues from the surface of the workpieces, the resulting discharged rinse water is substantially poison-free. Generally, in such a process, it is preferable if the workpiece which is withdrawn from the coating solution treatment bath is permitted to drain prior to contacting it with the detoxification solution. Additionally, if desired, an intermediate rinse in non-flowing water may be carried out prior to the application of the detoxification solution. This non-flowing or static rinse water can then be used for replenishing the coating solutions. When the detoxification solution is consumed, it may then be discharged, preferably after neutralization.

Although such processes of "direct detoxification" have proved to be a particularly advantageous solution to the problem of toxic rinse waters from metal coatings containing hexavalent chromium, it has been found that in many instances, the use of such processes have a disadvantageous affect on the chromate coating produced on the metal. In particular, it has been found that the use of the acid detoxification solutions containing sulfur-oxygen compounds capable of reducing hexavalent chromium, such as sodium bisulfite, result in a decrease of the adherent strength of the so-called "green chromate" coatings produced on the metal, as the metal surfaces are processed through the detoxification bath. Thus, the previously dark-green colored coating layers become, at least partially, light green in color after use of the detoxification solution and upon drying, the light green areas become powdery. Frequently, these powdery deposits can be easily wiped off the metal, down to the metal base. This, of course, greatly reduces the effectiveness of these materials as protective and/or paint-base coatings.

It is, therefore, an object of the present invention to provide an improved method for the direct detoxification of hexavalent chromium-containing coatings on metal surfaces, which method may be carried out without adverse affect on the coating.

A further object of the present invention is to provide an improved method for coating metal surfaces with a hexavalent chromium-containing material, wherein direct-detoxification of the coating formed may be effected without adverse affect on the coating.

These and other objects 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 process for the direct detoxification of a metal surface coated with a hexavalent chromium-containing coating which comprises contacting said coated surface with an aqueous acid treating solution containing at least one sulfur-oxygen compound capable of reducing hexavalent chromium and ions of at least one material selected from the group consisting of beryllium, calcium, boron, aluminum, cerium, and thorium, and maintaining said treating solution in contact with the coated metal surface for a period sufficient to effect detoxification of the coating. In this manner, direct detoxification of the hexavalent chromium in the coating on the metal surfaces is obtained with no deleterious affect on the coating itself.

More particularly, in the practice of the present invention the detoxification treating solution used are aqueous acidic solutions containing at least one sulfur-oxygen compound which is capable of reducing hexavalent chromium. Exemplary of such compounds which may be used are sulfurous acid, hydrogen sulfite, as well as various water-soluble sulfites, disulfites, hydrosulfites (dithionites) and hyposulfites (thiosulfates), the various alkali metal compounds, of these, such as the sodium compounds, being particularly suitable. Desirably, the sulfur-oxygen compounds contained in the detoxification treating solution are present in amounts within the range of about 0.5 to 3 grams per liter, calculated as $NaHSO_3$. It will, of course, be appreciated that in many instances, amounts of the sulfur-oxygen compounds which are outside of this preferred range may also be used to obtain satisfactory results, the only requirement being that the amounts of these compounds used are sufficient to effect the desired detoxification of the coating on the metal surface without adverse affect on the coating itself.

In addition to the sulfur-oxygen compounds, the detoxification treating solutions also contain one ion selected from the group consisting of beryllium, calcium, boron, aluminum, cerium, and thorium. Desirably, the concentration of these ions in the solution is within the range of about 5 to 50 milliequivalents per liter, with amounts within the range of about 8 to 30 milliequivalents per liter being preferred. These ions may be introduced into the treating solution in the form of various suitable compounds which are soluble in the treating solution. Typical of the compounds which may be used are nitrates, sulfates, hydroxides, and the like. In many instances, treating solutions which contain aluminum ions have been found to be particularly suitable, so that the addition of such ions, desirably in the form of aluminum sulfate, is often preferred, because of the particularly good activity obtained with the aluminum ions and the low cost and ready availability of the aluminum salts, such as aluminum sulfate.

Inasmuch as the rate at which the hexavalent chromium is reduced by the treating solution decreases greatly as the solution pH is raised above about 6, it has been found to be desirable if the detoxification treating solution is utilized at a pH which is below about 6. Appropriate additions, as with acids or the like, may be made as are necessary to adjust the pH into the desired operating range. Additionally, if desired, the treating solution may also contain a suitable surface active agent to aid in the drainage of the detoxification treating solution from the metal workpieces, thus minimizing the amount of the solution which is carried out with the workpieces.

In processing the hexavalent chromium coated metal surfaces with the detoxification treating solution, the coated metal surfaces are contacted with the solution using any suitable application technique, although contact by spraying with the treating solution or by immersing the workpieces in the solution are preferred. The coated metal surfaces are maintained in contact with the treating solution for a period sufficient to effect the desired reduction of the hexavalent chromium in the coating. Typically, these contact times may be from a few seconds up to several minutes. Thereafter, if desired, the treated surfaces may be rinsed in fresh water and then dried.

In the overall process for coating metal surfaces, utilizing the direct detoxification treatment of the metal, the metal surface, such as aluminum or aluminum alloys, are coated with a hexavalent chromium containing coating solution. As is known in the art, the metal surfaces may be subjected to various pretreatments, such as alkaline cleaning, etching, acidic passivation, and the like, prior to the application of the hexavalent chromium containing coating.

Various suitable hexavalent chromium solutions may be used, although the present direct detoxification process has been found to be particularly applicable on the so-called "green chromate" coatings. The coating solutions for producing such coatings generally contain phosphate ions, fluoride ions, and hexavalent chromium ions. Typical coating solutions of this type are described in U.S. Patent 2,928,763 and may contain from about 5 to 150 grams per liter of phosphate ions, from about 2.5 to 62 grams per liter of CrO_3, from about 2.5 to 123 grams per liter of fluoride ions. These coating solutions may be applied in any convenient manner, as is known to those in the art. Typically, the coatings are produced by contacting the metal surface for periods of time from several seconds up to five or more minutes, with coating weights within the range of about 10 to 1000 milligrams per square foot being typical of those produced, depending upon the particular coating conditions used.

Once the desired hexavalent chromium containing coating has been produced on the aluminum or aluminum alloy surface, the coated surface is then contacted with the detoxification treating solution, in the manner as has been described hereinabove. Rinsing of these surfaces, following the treatment with the detoxification solutions, is found to produce rinse water which is substantially free of toxic hexavalent chromium ions. Additionally, the coatings on the metal surface are found to be substantially unaffected by the detoxification solution, having good adhesion, with little or no lightening of the coating color being evidenced.

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. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and parts and percents are by weight. It is to be appreciated, however, that these examples are merely exemplary of the present invention and the manner in which it may be practiced and are not to be taken as a limitation thereof.

EXAMPLE 1

An aqueous chromating solution was prepared containing the following components in the amounts indicated:

Components:	Grams per liter
P_2O_5	21.1
CrO_3	10.0
HF	2.72

Aluminum plates were degreased in a mildly alkaline cleaner, etched for 2.5 minutes in a 5% aqueous sodium hydroxide solution at 50 degrees centigrade and rinsed with water. These plates were then passivated at room temperature in a 15% aqueous nitric acid solution and again water rinsed. The plates were then immersed for 2.5 minutes in the above formulated chromating solution, which solution was maintained at a temperature of 45 degrees centigrade. After their removal from the chromating solution, some of the coated plates were rinsed with clean water while other plates were rinsed with various aqueous detoxification solutions, the rinsing being effected by immersing the plates for 30 seconds in the solutions, which were at a temperature of 20 degrees centigrade. The aqueous detoxification solutions used contained 1 gram per liter of $NaHSO_3$ and a 60 milliliters per liter of the aqueous chromating bath, as formulated above, to simulate an aged detoxification solution. Additionally, these solutions also contained various additives, indicated hereinafter, the amounts of the additives given corresponding to 8 milliequivalents of the additives per liter of the detoxification solution. Following the rinsing of the plates, with either the clean water or the detoxification solution, the plates were all again rinsed in water, allowed to drain and then dried for 8 minutes at 85° C. The adhesive strength of the chromate layer on the plates was then determined by wiping the plates with a linen rag, using light pressure. The results thus obtained were reported as "very low," indicating a removal from 1 to 10% of the original layer thickness; "low," indicating a removal of from 11 to 30% of the original layer thickness; "average," indicating a removal of from 31 to 70% of the original layer thickness; "strong," indicating a removal of 71 to 90% of the original layer thickness; and "very strong," indicating a removal of 91 to 100% of the original layer thickness. Using the above procedure, the detoxification solutions used and the results obtained were as follows:

Additive	Amount in g./l.	pH value	Wipe off of the coating
None		2.4	Very strong.
$Ca(NO_3)_2.4H_2O$	0.95	2.4	Average.
$Be(NO_3)_2.3H_2O$	0.75	2.2	Low.
$Al_2(SO_4)_3.18H_2O$	0.89	2.1	Very low.
$Ce(NO_2)_3.6H_2O$	1.16	2.1	Low.
$Th(NO_3)_4.6H_2O$	1.18	2.1	Very low.
$B(OH)_3$	0.17	2.4	Low.

By way of comparison, the plates which had been rinsed only with clean water had a green-colored coating, the weight of which was about 5 grams per square meter.

The adhesive strength of this coating layer was good, the wipe off being "very low." Additionally, it was found that the rinse water from these plates was quite high in the toxic CrO_3 while the rinse water from the plates which had been rinsed with the various detoxification solutions contained substantially no CrO_3.

EXAMPLE 2

The procedure of Example 1 was repeated with the exception that the additives in the aqueous detoxification solution were as indicated below. Using this procedure, the following results were obtained:

Additive	Amount in g./l.	Concentration in mVal./l.	Wipe off of the coating
None			Very strong.
$Ca(NO_3).4H_2O$	0.35	3	Do.
$Ca(NO_3).4H_2O$	0.59	5	Strong.
$Ca(NO_3).4H_2O$	0.95	8	Average.
$Ca(NO_3).4H_2O$	3.54	30	Very low.
$Al_2(SO_4)_3.18H_2O$	0.33	3	Average.
$Al_2(SO_4)_3.18H_2O$	0.56	5	Low.
$Al_2(SO_4)_3.18H_2O$	0.89	8	Very low.
$Al_2(SO_4)_3.18H_2O$	3.34	30	Do.

As with the preceding example, although the adhesive strength of the chromate layer which had been washed only with water was good, with the wipe off being rated as "very low," the water rinse solution obtained from this coating contained appreciable quantities of the toxic CrO_3. In contrast, the water rinse solution from the panels which had first been rinsed with the detoxification solution contained substantially no CrO_3.

EXAMPLE 3

The procedure of Example 1 was repeated with the exception that that additives for the detoxification solutions were as indicated hereinbelow. Using this procedure, the following results were obtained:

Additive	pH value	Wipe off of the coating
None	2.4	Very strong.
0.75 g./l. $Be(NO_3)_2.3H_2O$ plus 0.95 g./l. $Ca(NO_3)_2.4H_2O$.	2.5	Very low.
0.95 g./l. $Ca(NO_3)_2.4H_2O$ plus 0.89 g./l. $Al_2(SO_4)_3.18H_2O$.	2.2	Do.
0.17 g./l. $B(OH)_3$ plus 0.89 g./l. $Al_2(SO_4)_3.18H_2O$	2.2	Do.

As with the preceding two examples, the chromate coating which had been rinsed only with water showed good adhesive strength with a wipe off rating of "very low." The rinse water obtained from the panel was, however, highly contaminated with appreciable quantities of CrO_3 as compared to the substantial complete absence of CrO_3 in the rinse water obtained from the panels which had been first rinsed with the detoxification solution.

What is claimed is:

1. A method for treating metal surfaces which comprises contacting a metal surface coated with a hexavalent chromium containing coating with an aqueous acid treating solution containing at least one sulfur-oxygen compound which is capable of reducing hexavalent chromium in an amount within the range of about 0.05 to 3 grams per liter, calculated as $NaHSO_3$, and ions of at least one material selected from the group consisting of beryllium, calcium, boron, aluminum, cerium, and thorium, in an amount within the range of about 5 to 50 milliequivalents per liter of treating solution, and maintaining said aqueous acid treating solution in contact with the coated surface for a period sufficient to effect substantial reduction of the hexavalent chromium in the coating on said surface.

2. The method as claimed in claim **1** wherein the metal ion selected from the indicated group are aluminum ions.

3. A method of treating metal surfaces which comprises contacting the metal surface to be treated with a hexavalent chromium containing coating solution, maintaining said coating solution in contact with the metal surface for a period sufficient to form the desired hexavalent chromium containing coating thereon, containing at least one sulfur-oxygen compound capable of reducing hexavalent chromium in an amount within the range of about 0.05 to 3 grams per liter, calculated as $NaHSO_3$, and ions of at least one material selected from the group consisting of beryllium, calcium, boron, aluminum, cerium, and thorium, in an amount within the range of about 5 to 50 milliequivalents per liter of treating solution, and maintaining said treating solution in contact with the coated metal surface for a period sufficient to effect substantial reduction of the hexavalent chromium in the coating on the metal surface.

4. The method as claimed in claim **3** wherein the hexavalent chromium containing solution is an aqueous acid solution containing phosphate ions, fluoride ions, and hexavalent chromium ions.

5. The method as claimed in claim **3** wherein the ions selected from the indicated group in the treating solution are aluminum ions.

References Cited

UNITED STATES PATENTS

3,391,032	7/1968	Hansen	148—6.16
2,976,193	3/1961	Pimbley	148—6.21
2,854,371	9/1958	Schidderup	148—6.21

ALFRED L. LEAVITT, Primary Examiner

M. F. ESPOSITO, Assistant Examiner

U.S. Cl. X.R.

148—6.16, 6.2