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3,391,032

ALKALINE RINSE FOR CHROMATIZED ALUMINUM

Hans Hansen, Gergen-Enkheim, and Wolfgang Mann, Frankfurt am Main, Germany, assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

No Drawing. Filed June 26, 1964, Ser. No. 378,422

Claims priority, application Germany, June 27, 1963, M 57,327

13 Claims. (Cl. 148—6.16)

ABSTRACT OF THE DISCLOSURE

A process for providing a protective coating on aluminum and aluminum alloy surfaces wherein the surface to be coated is contacted with a chromatizing solution containing hexavalent chromium ions, phosphate ions and fluoride ions and, thereafter, the thus-coated surface is rinsed with an aqueous alkaline solution having a pH within the range of about 9 to 13. Preferred alkaline rinsing solutions are aqueous solutions containing sodium hydroxide, sodium carbonate, or sodium silicate.

This invention relates to improvements in methods for coating metal surfaces, and more particularly relates to improvements in processes for producing chromium-containing coatings on surfaces of aluminum and alloys thereof in which aluminum is the principal ingredient.

It is known that coatings can be formed on surfaces of aluminum and its alloys by treatment of these metal surfaces with an aqueous acid solution containing phosphate ions, fluoride ions, and chromate ions. The coatings produced by these processes frequently are colored green or impart to the metal surfaces an iridescent green appearance, and hence are often referred to as "green chromate layers or coatings." Such coatings have been found to be useful in providing a decorative effect on the metal surfaces coated, for providing increased protection for the metal surfaces against corrosion and/or as a foundation or base for paint or similar coating materials.

Frequently, after the "green chromate coatings or layers" have been formed they have been treated or rinsed with aqueous solutions. Generally, the solutions used have been dilute aqueous acid solutions, such as solutions of chromic acid or solutions of chromic acids and phosphoric acid. In some instances, these acid rinse solutions have also contained other additives, as, for example, fluorine compounds, cerium compounds, nitrates, and the like. In other instances, the "green chromate coatings" have been rinsed with water only, rather than with acid solutions. In both instances, after rinsing, the coated surfaces are dried. Such after-treatments, i.e., rinsing and drying, are designed to provide the coating with an increased resistance to corrosion. Frequently, however, the adhesive strengths of the coatings thus produced and their resistances to wiping have not always been satisfactory.

It is, therefore, an object of the present invention to provide "green chromate layers" on metallic surfaces which are aluminum or alloys made up predominantly of aluminum.

Another object of the present invention is to provide improved chromate coatings for aluminum surfaces, which coatings have improved adhesive strength and resistance to wiping as compared to coatings which have been produced by prior art processes.

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

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Pursuant to the above objects, the present invention includes an improvement in the process for applying chromatizing solutions containing hexavalent chromium ions, phosphate ions, and fluoride ions to the surfaces of aluminum and aluminum alloys, which comprises treating the surfaces after they have been in contacts with the chromatizing solution with a solution having a pH within the range of about 9 to 13. In this manner, it has been found that the coatings produced have a much better resistance to corrosion and have improved adhesive strength and resistance to wiping, as compared to coatings which have been processed in a known manner, i.e., treated with an acidic rinse or substantially neutral water rinse after application of the chromatizing solution.

As has been indicated hereinabove, the after rinse or treating solution has a pH of from about 9 to 13. It has been found that where after rinse solutions are used having a pH appreciably above 13, a partial detaching or loosening of the chromate covering layer may take place. Additionally, when rinsing solutions having a pH value appreciably below 9 are used, the advantages in terms of improved corrosion resistance, resistance to wiping, and adhesion strength may not be obtained. For this reason, it is important that the after rinse solution have a pH within the range of about 9 to 13, with pH values within the range of about 10.5 to about 12.5 being preferred.

As has been heretofore indicated, the chromatizing solutions used are those containing hexavalent chromium ions, phosphate ions, and fluoride ions. Exemplary of such solutions are those described in U.S. Patents 2,928,763 and 2,967,791. These and other "green chromatizing solutions," as is known to those in the art, can be applied in many convenient ways, as, for example, by spraying, immersion, roll-on, flooding, or the like. The method of applying the chromatizing solution may differ from one application to another, depending upon the particular conditions, provided that, whatever application techniques are used, sufficient contact between the coating solution and the aluminum surface to be treated is effected to obtain the desired "green chromate coating" on the surface. Generally, after the application of the chromate coating, in order to avoid carry-over of the acid chromatizing solution into the alkaline after-treatment solution, it has been found to be desirable to rinse the coated surfaces with water.

The after-treating or rinsing solutions having a pH of from about 9 to 13, for use in the method of the present invention, are desirably aqueous solutions which may be formed by dissolving an alkaline-reacting material in water. Exemplary of compounds which may be used are alkaline compounds, such as the alkali metal hydroxides, alkali metal carbonates, alkali metal silicates, including both ortho silicates and condensed silicates, alkali metal compounds having a complex anion, such as the alkali metal aluminates, alkali metal stannates, alkali metal zincates, and the like. Additionally, ammonia, similar ammonium compounds, as well as similar compounds of the alkaline earth metals, may also be used where aqueous solutions of these compounds may be formed having the desired alkalinity. Additionally, alkaline-reacting compounds, such as the alkali metal, ammonium and alkaline earth metal condensed phosphates, may also be used. These and other alkaline materials may be used either alone or in various combinations to produce alkaline rinsing solutions having the desired pH within the range of about 9 to 13. The only restriction on the compounds which may be used, and in particular on combinations of compounds is that they should not have a significant adverse effect on the coated metal surface, or each other, as for example, by reacting to form insoluble products.

It is to be appreciated that by the term "alkali metal" is intended to refer to the compounds of sodium, potassium, lithium, rubidium and cesium. Moreover, it is to be understood that in referring to the term "alkaline earth metal" it is intended to mean the compounds of calcium, barium, strontium, manganese and radium.

In addition to the alkaline material, in many instances, it has been found to be advantageous to include a surface active agent in the rinsing solution. In this manner, there is obtained a better contacting on the surfaces being treated with the alkaline solution and solution losses caused by the solution being carried out of the rinse by the work pieces are reduced. Suitable surface active agents which may be used are those which are stable in alkaline solutions, such as the non-cationic surface active agents, in which are included the anionic and non-ionic surface active agents.

Exemplary of the anionic surface active agents which may be used are the sulfated and sulfonated organic surface active compounds, especially those having about 8 to 26 carbon atoms in a molecule. These include the alkyl aromatic sulfonates and aliphatic sulfates and sulfonates of about 8 to 26 carbon atoms. The alkyl aromatic sulfonates may be mono- or polynuclear in structure, i.e., the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresol, phenolic ethers, naphthalene, phenanthrene, and the like. The alkyl group may be straight or branched and may be radicals such as dodecyl, pentadecyl, octadecyl, octyl, nonyl, decyl, keryl, mixed alkyls derived from fatty materials, cracked paraffin wax olefins, polymers of monoolefins and so forth. These compounds include the sulfonated alkylated benzene compounds wherein the alkyl group contains from about 10 to about 18 carbon atoms, and in particular the alkali metal and amine salts of these compounds. Exemplary of specific compounds in this group are sodium tetrapropylene benzene sulfonate, sodium octylbenzene sulfonate, sodium dodecylbenzenesulfonate, sodium dodecyltoluenesulfonate, the like.

Other suitable anionic surface active agents are sulfated and sulfonated aliphatic compounds, particularly those having alkyl groups of about 12 to about 22 carbon atoms. Included within this group are the sulfuric acid esters of polyhydric alcohols incompletely esterified by higher fatty acids, e.g., coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; the long chain alcohol sulfates, e.g., lauryl sulfate, cetyl sulfate; the fatty acid esters of a sulfonic acid, e.g., oleic acid ester of isothionic acid; the fatty acid alkanolamide sulfates; the fatty acid amides of amine alkyl sulfonic acids, e.g., lauric acid amide of taurine; as well as the alkali metal and amide salts of these, and the like.

Similarly, non-ionic surface active agents which may be used are usually those organic compounds having an oxygenated side chain, for example, a polyoxyethylene side chain. Included in these are the essentially straight chain polymerized alkylene oxide condensates having more than five alkylene oxide groups in straight line configuration, e.g., higher fatty acid esters of polyoxyethylene alcohols, ethylene oxide-propylene oxide block copolymers of molecular weight between about 1,000 to about 20,000 and so forth. More specifically, these include the ditertiary acetylenic glycols, ethylene oxide nonylphenol, polyethylene glycol tertiary dodecyl thiourea ethers, fatty acid esters of higher polyglycols and the like.

These and other anionic and non-ionic surface active agents may be present in amount sufficient to provide the desired wetting or surface contacting, amounts of 0.01 to 0.3 percent of the solution being typical.

The alkaline rinsing solutions of the present invention, having a pH within the range of about 9 to about 13, may be applied to the "green chromate" coated surfaces in various convenient ways, for example, by spraying, flooding, immersion, or roller coating techniques. As with the application of the chromating solutions, the particular

application technique used will usually be that which best meets the conditions for each case. Similarly, the duration of the treatment with the alkaline rinse solutions, i.e., the length of time that the solution is in contact with the chromate coated surfaces may also be varied widely, with contact times of about ½ to 1 minute being typical. However, both shorter and longer treatment time may be used to obtain excellent results. Generally, the minimum contact time will be that which will provide the desired improvements in adhesion and resistances to corrosion and wiping, with the exact minimum time being dependent upon the various operating conditions involved.

For the most part, the temperature at which the alkaline rinsing treatment is carried out has not been found to be critical and temperatures over a wide range, from room temperature, 15 to 20 degrees centigrade, up to the boiling point of the solution may be used. In some instances, it has been found to be desirable to utilize temperatures within the range of about 50 to about 75 degrees centigrade, since such temperatures have been found contributory in imparting to the chromate coating excellent resistance to corrosion. Moreover, the use of such higher treating temperatures may be further advantageous because a separate drying of the rinsed pieces may often be omitted. Surprisingly, it has been found that when using such hot alkaline solutions, there is no adverse effect on the coatings with respect to their resistance to wiping. In contrast, however, such adverse effects frequently occur when the "green chromate" coatings are treated with either hot acid solutions or hot water solutions.

After treatment with the alkaline solutions of the present invention, the chromated aluminum or aluminum alloy surfaces may be used as such, without further treatment. Where, however, the chromate coating is to serve as a base for paints, varnishes, or similar protective coatings, it has been found to be desirable to rinse the alkaline treated coating with water in order to remove any adhering alkaline solution from the surface. Where such water rinses are used, they have not been found to impair the adhesion of the chromate coatings, or their resistance to wiping and corrosion.

So that those skilled in the art may readily understand the present invention and the manner in which it may be practiced, the following specific examples are given. In the examples, unless otherwise indicated, the temperatures are given in degrees centigrade and parts are by weight.

Example 1

A series of sheets of aluminum and aluminum alloys was degreased in a mildly alkaline cleaner and rinsed with water. Thereafter the sheets were treated by immersing in a solution containing 7.8 grams per liter CrO_3 (introduced as chromic acid), 17.0 grams per liter P_2O_5 (introduced as H_3PO_4) and 1.5 grams fluorine (introduced as hydrofluoric acid) for a period of three minutes at a temperature of 50 degrees centigrade. The thus-treated sheets were then rinsed with water at room temperature. These sheets were found to have coatings of a green color with a coating weight of about 3 grams per square meter. The sheets were then immersed for one minute, at 70 degrees centigrade, in water or solutions of various alkaline compounds having a pH within the range of about 8.0 to about 13.2. The thus-treated sheets were then dried in air. After 24 hours the sheets were examined to determine the resistance of the coatings to wiping and to corrosion. In determining the resistance to wiping, the surfaces were wiped with a linen cloth. The corrosion resistance was determined according to the American Society of Testing Materials Test (ASTM-B117-54T) which is a salt spray test using continuous spraying of a 5 percent sodium chloride at 35 degrees centigrade. Using this procedure, the following results were obtained:

TABLE 1

pH value of the solution	pH adjustment with—	Resistance of the coating to wiping	Sheets Al 99 F 14		Sheets AlCuMg F 28	
			Resistance to corrosion Evaluation after—		Resistance to corrosion Evaluation after—	
			24 hrs.	168 hrs.	24 hrs.	168 hrs.
7.0.....		Very bad....	4	6	8	14
8.0.....	Na ₂ P ₂ O ₇	do.....			11	14
8.5.....	NaOH	Bad.....	4	5	9	12
9.0.....	Na ₂ HPO ₄	Medium.....			7	11
10.5.....	Na ₃ PO ₄	do.....			4	8
11.5.....	Na ₄ SiO ₄	Good.....			3	8
12.0.....	NaOH	do.....	10	1	10	9
12.5.....	NaOH	do.....			1	8
13.2.....	NaOH	Very bad ² ...	7	11	14	15

¹ 0=no corrosion.

Corrosion.....	Weak	Medium	Intensive
Up to 20% of the surface.....	1	6	11
20-40% of the surface.....	2	7	12
40-60% of the surface.....	3	8	13
60-80% of the surface.....	4	9	14
80-100% of the surface.....	5	10	15

² Layer partially detached.

Example 2

A series of aluminum alloy sheets AlCuMg F 28 and sheets of pure aluminum Al 99 F 14 were degreased, chromatized and rinsed with water at room temperature as in Example 1. One-half the number of these sheets was then treated for one minute at 70 degrees centigrade with a dilute solution of chromic acid and phosphoric acid, which solution had a pH of 2.5. The second half of the number of sheets was then treated in accordance with the present invention for one minute at 70 degrees centigrade with an aqueous solution containing 3 parts sodium carbonate and one part sodium silicate and having a pH value of 11.1. All of the sheets were dried in air and after 24 hours were evaluated as to resistance to corrosion and resistance to wiping, using the procedures described in Example 1. Using this procedure, the alloy sheets rinsed with the acid solution had corrosion resistance ratings of 9 and 11 after 168 hours of testing and the pure aluminum sheets had bad resistance to wiping. In contrast, the alloy sheets treated with the alkaline solutions of the present invention had corresponding corrosion resistance values of 3 and 7 and the pure aluminum sheets had good resistance to wiping.

Example 3

To illustrate the effect of the preferred temperatures of the alkaline treating solution, a series of aluminum alloy sheets AlCuMg F 28 were degreased, chromatized and water rinsed as in Example 1. Thereafter, the sheets were rinsed with a sodium silicate solution having a pH of 11.7 for 1 minute, using various rinsing temperatures. Using the procedure described in Example 1, the sheets were then evaluated as to their resistance to corrosion and the following results were obtained:

TABLE 2

Treatment Temperature, °C.:	Resistance to corrosion Evaluation after—	
	24 hours	216 hours
25.....	9	13
70.....	3	8
98.....	9	72

Example 4

Aluminum and aluminum alloy sheets as described in Example 1 were degreased, chromatized and water rinsed, as in Example 1. These sheets were then treated for one minute at 70 degrees centigrade with an aqueous solution of sodium carbonate having a pH of 11.2. Half of the number of these sheets was then thoroughly rinsed in cold water and air dried while the other half was air dried

without water rinsing. The corrosion resistance of these sheets was then evaluated in the manner set forth in Example 1 and the following results were obtained:

TABLE 3

	Resistance to corrosion Evaluation after—			
	24 hours		168 hours	
	Al 99	AlCuMg	Al 99	AlCuMg
Without an after-rinse with water...	0	3	1	6
With an after-rinse.....	0	3	1	6

The procedure of the preceding examples are repeated using other alkaline solutions having a pH within the range of about 9 to 13, including solutions of sodium aluminate, sodium stannate, sodium zincate, ammonium hydroxide, calcium hydroxide, and the like, and also with alkaline solutions having a pH within the range of about 9 to 13 which contain non-cationic surface active agents, including sodium tetrapropylenebenzene sulfonate, sodium octylbenzene sulfonate, sodium dodecylbenzene sulfonate, sodium dodecyltoluene sulfonate, coconut oil monoglyceride monosulfate, lauryl sulfate, cetyl sulfate, oleic acid ester of isothionic acid, ethylene oxide nonyl phenol, and the like. In each instance, comparable results are obtained.

While there have been described various embodiments of the invention, the composition and methods described are not intended to be understood as limiting the scope of the invention as it is realized that changes there within are possible and it is further intended that each element recited in any of the following claims is 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. In the process for coating metal surfaces of aluminum or aluminum alloys, whereby the metal surface to be coated is contacted with a chromatizing solution which contains hexavalent chromium ions, phosphate ions, and fluoride ions, for a period of time sufficient to effect the desired coating, the improvement which comprises contacting the thus-coated surface with an aqueous alkaline rinse solution having a pH within the range of about 9 to 13, the components of said solution being materials which will not form insoluble products upon reaction with each or the coating on the metal surface.

2. The process of claim 1 wherein the alkaline rinse solution contains at least one material selected from the group consisting of sodium hydroxide, sodium carbonate, and sodium silicate.

3. The process of claim 2 wherein the alkaline rinse solution also contains a surface active agent selected from the group consisting of anionic and non-ionic surface active agents.

4. The process of claim 3 wherein the aqueous alkaline rinse solution is applied to the coated metal surface at a temperature within the range of about 50 to about 75 degrees centigrade.

5. A process as claimed in claim 4 wherein the aqueous alkaline rinse solution has a pH within the range of about 10.5 to about 12.5.

6. The process as claimed in claim 5 wherein following the application of the aqueous alkaline rinse solution, the thus-treated coating is rinsed with water.

7. A process for coating metal surface in which aluminum is the predominate metal, which comprises contacting the metal surfaces with a chromatizing solution which contains hexavalent chromium ions, phosphate ions, and fluoride ions, maintaining the solution in contact with the metal surface for a period of time sufficient to effect the desired coating of the surface, and contacting the thus-coated surface with an aqueous alkaline rinse solution having a pH within the range of about 9 to 13, the com-

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ponents of said rinse solution being materials which will not form insoluble products upon reaction with each other or the coating on the metal surface.

8. The process as claimed in claim 7 wherein the alkaline rinse solution contains at least one material selected from the group consisting of sodium hydroxide, sodium carbonate, and sodium silicate.

9. The process as claimed in claim 8 wherein the aqueous alkaline rinse solution also contains a surface active agent selected from the group consisting of anionic and non-ionic surface active agents.

10. The process as claimed in claim 9 wherein the coated metal surface is contacted with the aqueous alkaline rinse solution at a temperature within the range of about 50 to about 75 degrees centigrade.

11. The process as claimed in claim 10 wherein the aqueous alkaline rinse solution contains a pH within the range of about 10.5 to about 12.5.

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12. The process as claimed in claim 11 wherein after the application of the aqueous alkaline rinse solution, the thus-treated metal surface is rinsed with water.

13. A coated metal article as produced by the process of claim 7.

References Cited

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RALPH S. KENDALL, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,391,032

July 2, 1968

Hans Hansen et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 31, "formd" should read -- formed --. Column 2, line 6, "contacts" should read -- contact --; line 18, "above 13" should read -- above about 13 --. Column 13, line 69, "0.3 percent" should read -- 3.0 percent --. Column 4, line 74, "chloride at" should read -- chloride solution at --. Column 5, line 6, "72" should read -- 12 --. Column 6, line 67, "metal surface" should read -- metal surfaces --.

Signed and sealed this 31st day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents