



US 20090242081A1

(19) **United States**

(12) **Patent Application Publication**
Bauer et al.

(10) **Pub. No.: US 2009/0242081 A1**

(43) **Pub. Date: Oct. 1, 2009**

(54) **ALUMINUM TREATMENT COMPOSITION**

Publication Classification

(76) Inventors: **Richard Bauer**, Howell, MI (US);
Michael Malik, Livonia, MI (US)

(51) **Int. Cl.**
C23C 22/30 (2006.01)
C23C 22/44 (2006.01)
(52) **U.S. Cl. 148/267; 148/22; 148/243; 148/275**

Correspondence Address:
ARTHUR G. SCHAIER
CARMODY & TORRANCE LLP
50 LEAVENWORTH STREET, P.O. BOX 1110
WATERBURY, CT 06721 (US)

(57) **ABSTRACT**

An aqueous conversion coating composition for treating metal substrates such as aluminum, aluminum alloys, zinc, zinc alloys, magnesium, magnesium alloys and steel to provide a conversion coating thereon. The conversion coating composition comprises a) a source of aluminum ions; b) a fluoro compound; c) at least one pH adjuster; d) a source of Group VIB metal ions selected from the group consisting of tungstate ions and trivalent chromium ions; and e) optionally, a preservative. The conversion coating composition provides a corrosion resistant coating on the metal surface and improves the adhesion of subsequently applied layers.

(21) Appl. No.: **12/055,539**

(22) Filed: **Mar. 26, 2008**

ALUMINUM TREATMENT COMPOSITION

FIELD OF THE INVENTION

[0001] The present invention relates generally to compositions and methods for the formation of protective, corrosion-inhibiting coatings on metals, or other materials coated with metals.

BACKGROUND OF THE INVENTION

[0002] Metals such as aluminum, zinc, magnesium, titanium, cadmium, silver, copper, tin, lead, cobalt, zirconium, beryllium, or indium, their alloys, and items coated with these metals, tend to corrode rapidly in the presence of water due to their low oxidation-reduction (redox) potentials or ease of oxide formation. Non-alloyed specimens of these metals typically form a natural oxide film that will protect them somewhat and reduce their overall rate of corrosion. However, alloys of these metals are particularly sensitive to corrosive attack. In addition, these materials can also have a significant problem with paint adhesion, because the as-formed metal surfaces are typically very smooth, and tend to form weakly bound surface oxides, which do not normally provide a robust base on which subsequent applied paints can anchor themselves.

[0003] One method of enhancing the corrosion resistance of metal alloys is through the use of a conversion coating, which is a self-healing, corrosion-inhibiting layer formed during intentional exposure of the metal or metal alloy to a chemically reactive solution. Conversion coatings are particularly useful in surface treatment of metals such as steel, zinc, aluminum and magnesium. The conversion coating process forms an adherent surface containing an integral corrosion inhibitor that can provide protection to coating breaches. The metal is exposed to a compound that chemically alters the surface and forms a coating that provides a high degree of corrosion resistance. Thus, a chemical conversion coating applied to the surface of a less-noble alloy can reduce the extent and severity of aqueous corrosion, provide long-term property stability, and extend the useful life of the object of manufacture.

[0004] A critical feature of effective conversion coatings is their ability to provide corrosion protection to the base metal in the presence of a coating breach. Conversion coatings grow an oxide coating on the metal without an externally applied electrical potential. The protective film is produced by a chemical redox reaction between the metal surface and the conversion coating solution. The film is composed both of an oxide and integral corrosion inhibitor species formed during exposure to the conversion coating solution.

[0005] It has previously been common to apply these conversion or pretreatment coatings using hexavalent chromium-containing solutions. While these coatings provide good corrosion resistance, attempts have been made to provide more acceptable non-chromate derived coatings or coatings derived from trivalent chromium because of concern regarding the occupational, safety, health and environmental effects of hexavalent chromium, which is highly toxic and is a known carcinogen. Various efforts have been made to develop such coating and examples of these coatings can be found for example in U.S. Pat. No. 7,294,362 to Tanaka et al. in U.S. Pat. Nos. 6,375,726, 6,521,029 and 6,669,764 to Matzdorf et

al., and in U.S. Pat. No. 7,294,211 to Sturgill et al., the subject matter of each of which is herein incorporated by reference in its entirety.

[0006] The conversion-coated surface may be left bare or afforded further protection by the application of additional films or coatings. Conversion coatings need to adhere to the substrate and should also result in a surface that will promote the formation of a strong bond with subsequently applied coatings. Bonding with subsequently applied coatings is a function of the morphology and chemical composition of the conversion coating. Adhesion promoting surface treatments may exhibit corrosion inhibiting characteristics. Depending on the intended application, a conversion coating, as described herein, may also be considered to be an "adhesion promoter" and vice versa.

[0007] Conversion coatings are usually formed by the application of a conversion coating solution to the metal surface. The solution can be applied by immersion, spray, fogging, wiping, or other similar means depending on the complexity of the surface of the substrate being treated.

[0008] While various conversion coating chemistries have been proposed, the inventors of the present invention have determined that additional further improvement are still needed to approach the protection level of hexavalent chromium conversion coatings.

SUMMARY OF THE INVENTION

[0009] It is an object of the present invention to provide an improved conversion coating composition that does not contain toxic hexavalent chromium but affords improved corrosion protection of the metal surface.

[0010] It is another object of the present invention to provide an improved conversion coating composition that provides improved corrosion protection for aluminum, aluminum alloys, zinc, zinc alloys, magnesium, magnesium alloys and steel.

[0011] It is still another object of the present invention to provide a conversion coating composition that contains a stable solution for the treatment of metal substrates.

[0012] To that end, the present invention relates generally to an aqueous conversion coating composition comprising:

[0013] a) a source of aluminum ions;

[0014] b) a fluoro compound;

[0015] c) at least one pH adjuster;

[0016] d) a source of Group VIB metal ions selected from the group consisting of tungstate ions and trivalent chromium ions; and

[0017] e) optionally, a preservative.

[0018] The present invention also relates to a method of using the aqueous conversion coating composition of the invention to treat metal substrates such as aluminum and aluminum alloy substrates to provide an improved conversion coating thereon. In one embodiment, the aqueous conversion coating composition of the invention is substantially free of phosphorous and/or chromium.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] In one embodiment, the present invention relates generally to acidic aqueous conversion coatings for the pretreatment of metals, such as aluminum and aluminum alloys, zinc, zinc alloys, magnesium and magnesium alloys and steel,

and to a process for improving the corrosion resistant properties of such metal substrates.

[0020] In one embodiment, the present invention relates generally to compositions for pretreating aluminum and aluminum alloy substrates and to a process of pretreating aluminum and aluminum alloy substrates at temperatures ranging from ambient temperatures up to about 200° F. These pretreatment compositions typically comprise an acidic aqueous solution having a pH in the range of about 0.5 to about 6 and preferably from about 3 to 5.

[0021] The pretreatment composition of the invention is an aqueous solution that typically comprises:

[0022] a) a source of aluminum ions;

[0023] b) a fluoro compound;

[0024] c) at least one pH adjuster;

[0025] d) a source of at least one Group VIB metal ion selected from the group consisting of tungstate ions and trivalent chromium ions; and

[0026] e) optionally, a preservative.

[0027] In one preferred embodiment, the source of aluminum ions is ammonium hexafluoride aluminate. Although ammonium hexafluoride aluminate is typically preferred, alkali hexafluoride aluminates such as sodium hexafluoride aluminate may also be used in the practice of the present invention. In another preferred embodiment, the source of aluminum ions is pure aluminum powder which is used in combination with hexafluorotitanic acid, whereby the aluminum powder is thus dissolved in the solution by the acidity of the hexafluorotitanic acid.

[0028] Fluoro compounds usable in the practice of the invention include for example ammonium hexafluoride aluminate and hexafluorotitanic acid. Other similar fluoro compounds may also be used. The potassium, lithium, sodium, and ammonium salts of hexafluorotitanic acid works especially well for this application, with ammonium performing the best. Other complex fluorides, including, but not restricted to, fluoroaluminates (e.g., AlF_6^{-3} or AlF_4^{-1}), fluoroborates (e.g., BF_4^{-1}), fluorogallates (e.g., GaF_4^{-1}), fluoroindates (e.g., InF_4^{-1}), fluorogermanates (e.g., GeF_6^{-2}), fluorostannates (e.g., SnF_6^{-2}), fluorophosphates (e.g., PF_6^{-1}), fluoroarsenates (e.g., AsF_6^{-1}), fluoroantimonates (e.g., SbF_6^{-1}), fluorobismuthates (e.g., BiF_6^{-1}), fluorosulfates (e.g., SF_6^{-2}), fluoroselenates (e.g., SeF_6^{-2}), fluorotellurates (e.g., TeF_6^{-2} or TeOF_5^{-1}), fluorocuprates (e.g., CuF_3^{-1} or CuF_4^{-2}), fluoroargentates (e.g., AgF_3^{-1} or AgF_4^{-2}), fluorozincates (e.g., ZnF_4^{-2}), fluorohafnates (e.g., HfF_6^{-2}), fluorovanadates (e.g., VF_7^{-2}), fluoroniobates (e.g., NbF_7^{-2}), fluorotantalates (e.g., TaF_7^{-2}), fluoromolybdates (e.g., MoF_6^{-3}), fluorotungstates (e.g., WF_6^{-1}), fluoroyttrates (e.g., YF_6^{-3}), fluorolanthanates (e.g., LaF_6^{-3}), fluorocerates (e.g., CeF_6^{-3} or CeF_6^{-2}), fluoromanganates (e.g., MnF_6^{-2}), fluoroferrates (e.g., FeF_6^{-3}), fluoronickelates (e.g., NiF_6^{-2}), and fluorocobaltates (e.g., CoF_6^{-2}) are also suitable fluoride sources, with fluoroaluminates being preferred. Water-soluble potassium, sodium, lithium, or ammonium salts of these anions are typical, with ammonium salts of these anions being preferred. One particularly preferred compound for use in compositions of the invention is ammonium hexafluoride aluminate.

[0029] The pH adjuster, which may include one or more organic acids, inorganic acids, complex fluorides, alkali metal salts, ammonia or a salt thereof, can be added to adjust the pH. Examples of these additives include, without limitation, acetic acid, benzoic acid, citric acid, lactic acid, malic acid, propionic acid, succinic acid, tartaric acid, adipic acid,

1,2,3,4-butanetetracarboxylic acid, fluoboric acid, sulfuric acid, sulfonic acid, methane sulfonic acid, methane disulfonic acid, nitric acid, silicic acid, hydrosilicofluoric acid, hydrofluoric acid, phosphoric acid, fluoro-zirconic acid, fluoro-titanic acid, sodium hydroxide, ammonia, ammonium bicarbonate, ammonium carbonate, sodium carbonate, and sodium bicarbonate and combinations of one or more of the foregoing. Other compounds would also be known to those skilled in the art. In one preferred embodiment of the invention, the pH adjusters include an organic acid and ammonium bicarbonate and/or ammonium carbonate. In a preferred embodiment, the organic acid is benzoic acid.

[0030] The composition of the invention also includes at least one Group VIB metal compound which is selected from the group consisting of tungstate compounds and trivalent chromium compounds.

[0031] In one embodiment of the invention, the Group VIB metal compound is chromium, in particular trivalent chromium, which may be added to the solution as any water-soluble trivalent chromium compound, preferably as a trivalent chromium salt. A preferred trivalent chromium compound usable in the compositions of the invention comprises basic chromium(III)sulfate (chrometan), which has the formula $\text{CrOHSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ and contains about 17.2 percent of chromium. Other trivalent chromium compounds that may be usable in the practice of the invention include for example chromium(III)thiocyanate complexes as described in U.S. Pat. No. 4,062,737 to Barclay et al.; trivalent chromium ions in a solution with a low pH as described in U.S. Pat. No. 4,612,091 to Tardyt et al.; trivalent chromium chloride salts as described in U.S. Pat. No. 4,804,446 to Lashmore et al.; and the chromium complexes described in U.S. Pat. No. 4,460,438 to Benaben et al., the subject matter of each of which is herein incorporated by reference in its entirety. Other specific trivalent chromium salts usable in the practice of the invention include chromium (III) formate, chromium (III) acetate, chromium (III) bromide hexahydrate, chromium (III) chloride hexahydrate, chromium (III) iodate, hydrate, chromium (III) nitrate, chromium (III) oxalate, chromium (III) orthophosphate, chromium (III) sulfate, hexamine chromium (III) chloride, hexaurea chromium (III) fluosilicate, chromium (III) fluoride tetrahydrate, chromium (III) iodide nonahydrate, chromium (III) nitrate hexammonate, chromium (III) potassium oxalate, various art known equivalents thereof, and combinations of one or more of the foregoing.

[0032] In another embodiment, the Group VIB metal is tungsten. The tungsten is typically added to the composition as a source of tungstate ions. The source of tungstate ions includes all tungstates but most specifically all ortho-tungstates, meta-tungstates and para-tungstates, polytungstates, hetero-polytungstates, isopolytungstates, peroxytungstates, and combinations thereof. A source of meta- or para-tungstate is preferred. Suitable sources of tungstate ions include sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen and ammonium tungstate salts, such as ammonium metatungstate, potassium metatungstate, sodium metatungstate, tungstic acid, sodium tungstate, potassium tungstate and ammonium tungstate.

[0033] Another optional ingredient that may beneficially be included in some formulations prepared in accordance with the present invention is a preservative. One preferred preservative is hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, sold under the tradename Surcide P (available from

Surety Laboratories, Cranford, N.J.). Other similar preservatives would also be known to those skilled in the art.

[0034] A first formulation (Formula A) that has been determined to provide improved corrosion protection of metal substrates, such as aluminum, aluminum alloys, zinc, zinc alloys, magnesium, magnesium alloys and steel prepared in accordance with the present invention comprises:

- [0035]** a) an organic acid;
- [0036]** b) ammonium bicarbonate;
- [0037]** c) a preservative;
- [0038]** d) ammonium hexafluoride aluminate;
- [0039]** e) methanesulfonic acid;
- [0040]** f) a trivalent chromium compound; and
- [0041]** g) balance of water.

[0042] Table 1 sets forth one preferred composition for Formula A prepared in accordance with the present invention.

TABLE 1

Composition of Formula A		
Component	Percent	Grams/liter
Benzoic acid	0.1	1.03
Ammonium bicarbonate	1.1	11.32
Surcide P	0.2	2.06
Ammonium hexafluoride aluminate	0.4	4.12
Methanesulfonic acid	1.4	14.41
Basic chrome sulfate solution	8.2	84.38
Water	88.6	911.7

[0043] Table 2 sets forth examples various alternate use concentrations for the Formula A solution prepared in accordance with the present invention.

TABLE 2

Component	Use Concentration of Formula A		
	Formula A		
	A Grams/liter	B Grams/liter	C Grams/liter
Benzoic acid	0.021	0.103	0.00103
Ammonium bicarbonate	0.226	1.132	0.0132
Surcide P	0.041	0.206	0.00206
Ammonium hexafluoride aluminate	0.082	0.412	0.00412
Methanesulfonic acid	0.288	1.441	0.01441
Basic chrome sulfate solution	1.688	8.438	0.08438
Deionized water	Balance	Balance	Balance

[0044] Another formulation (Formula B) that has been determined to provide improved corrosion protection of metal substrates, including aluminum, aluminum alloys, zinc, zinc alloys, magnesium, magnesium alloys and steel prepared in accordance with the present invention comprises:

- [0045]** a) hexafluorotitanic acid (50%);
- [0046]** b) pure aluminum powder;
- [0047]** c) ammonium bicarbonate;
- [0048]** d) ammonium metatungstate; and
- [0049]** e) balance of water.

[0050] Table 3 sets forth one preferred composition for Formula B prepared in accordance with the present invention.

TABLE 3

Composition of Formula B		
Component	Percent	Grams/liter
Hexafluorotitanic acid (50%)	4.0	41.5
Aluminum	0.04	0.42
Ammonium bicarbonate	1.37	14.22
Ammonium meta tungstate	3.0	31.14
Water	91.59	950.7

[0051] Finally, Table 4 sets forth examples of various alternate use concentrations for the Formula B solution prepared in accordance with the present invention.

TABLE 4

Component	Use Composition of Formula B		
	Formula B		
	A Grams/liter	B Grams/liter	C Grams/liter
Hexafluorotitanic acid (50%)	1.66	8.3	0.083
Aluminum	0.168	0.084	0.00084
Ammonium bicarbonate	0.569	2.844	0.02844
Ammonium meta tungstate	1.246	6.228	0.06228
Water	Balance	Balance	Balance

[0052] The metal substrate for use in the process of the present invention may be any substrate at least having a metal surface. Examples of usable substrates include those having a surface made of iron, aluminum, magnesium, zinc, copper, tin or an alloy containing any of these metals. Particularly preferred are steel sheet substrates and aluminum or aluminum alloy substrates.

[0053] Examples of steel sheet substrates include hot-dip galvanized steel sheets, electrogalvanized steel sheets, iron-zinc alloy plated steel sheets, nickel-zinc alloy plated steel sheets, aluminum-zinc alloy plated steel sheets and the like. Also usable as steel sheet substrates are zinc-based metal plated steel sheets that have been subjected to chemical conversion treatment such as chromate treatment, zinc phosphate treatment or composite oxide film treatment. Further, a steel sheet assembly can be employed as a steel sheet substrate.

[0054] The coating composition of the present invention can be applied to a metal substrate by any known process, such as dip coating, shower coating, spray coating, roll coating and electrocoating. The duration of contact ranges from about 30 seconds to about 5 minutes, but longer contact may be required if the solution is weak or if the temperature of the solution is relatively low. The aqueous solution temperature is normally below 100° C., for example in the range of 15° to 75° C., and more preferably at about ambient temperature (e.g. about 25° C.).

[0055] It is generally preferable that the composition be dried for about 2 seconds to about 30 minutes by heating under such conditions that the substrate reaches a maximum temperature of about 60 to 250° C.

[0056] Prior to performing the trivalent chromium pretreatment, the substrates may be treated by cleaning and/or activating as is generally well known in the art. The substrates may then be contacted with the composition of the invention for a sufficient period of time to form a conversion coating layer on the surface of the substrate and then allowed to dry.

[0057] The compositions of the present invention can also be used to improve the adhesion and corrosion resistant properties of metal coated substrates, as suggested for example in U.S. Pat. Nos. 6,511,532, 6,527,841, and 6,663,700 to Matzdorf et al., the subject matter of each of which is herein incorporated by reference in its entirety. These “post-treatment” coatings are typically contacted with the metal being treated after formation of the initial coating and therefore the post-treatments normally have no direct contact with the underlying substrate, except possibly through some pores in the metal coating.

[0058] While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications, and variations can be made without departing from the inventive concept disclosed here. Accordingly, it is intended to embrace all such changes, modifications, and variations that fall within the spirit and broad scope of the appended claims. All patent applications, patents, and other publications cited herein are incorporated by reference in their entirety.

1. An aqueous conversion coating composition comprising:

- (a) a source of aluminum ions;
- (b) a fluoro compound;
- (c) at least one pH adjuster;
- (d) a source of at least one Group VIB metal ion selected from the group consisting of tungstate ions and trivalent chromium ions; and (e) optionally, a preservative;

wherein the composition has a pH of 0.5 to 6 and the source of aluminum ions is selected from the group consisting of (i) ammonium hexafluoride aluminate, (ii) alkali metal hexafluoride aluminates, and (iii) aluminum powder in combination with hexafluoro titanic acid.

2. The aqueous conversion coating composition according to claim 1, wherein the conversion coating composition does not contain chromium or phosphorus.

3. The aqueous conversion coating composition according to claim 1, wherein: the fluoro compound comprises hexafluorotitanic acid; the source of aluminum ions comprises aluminum metal; and the Group VIB metal ion comprises a source of tungstate ions.

4. The aqueous conversion coating composition according to claim 1, wherein the one or more pH adjusters comprises ammonium bicarbonate or ammonium carbonate.

5. The aqueous conversion coating composition according to claim 1, wherein the Group VIB metal ion is selected from the group consisting of ortho-tungstates, meta-tungstates and para-tungstates, polytungstates, hetero-polytungstates, isopolytungstates, peroxytungstates, and combinations thereof.

6. The aqueous conversion coating composition according to claim 5, wherein the Group VIB metal ion is selected from the group consisting of sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen and ammonium tungstate salts.

7. The aqueous conversion coating composition according to claim 6, wherein the Group VIB metal ion is selected from the group consisting of ammonium metatungstate, potassium metatungstate, sodium metatungstate, tungstic acid, sodium tungstate, potassium tungstate and ammonium tungstate.

8. The aqueous conversion coating composition according to claim 7, wherein the Group VIB metal ion comprises ammonium metatungstate.

9. The aqueous conversion coating composition according to claim 1, wherein:

the source of aluminum ions and the source of fluoro ions comprises ammonium hexafluoride aluminate; the composition contains a preservative; and the group VIB metal ion comprises a source of trivalent chromium ions.

10. The aqueous conversion coating composition according to claim 9, wherein the at least one pH adjuster comprises a material selected from the group consisting of organic acid, and ammonium bicarbonate.

11. The aqueous conversion coating composition according to claim 10, wherein the organic acid comprises benzoic acid.

12. The aqueous conversion coating composition according to claim 9, wherein the preservative comprises hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine.

13. The aqueous conversion coating composition according to claim 9, wherein the source of trivalent chromium ions comprises basic chrome sulfate.

14. A method of treating a metal substrate to form a conversion coating thereon, the method comprising the steps of (a) contacting the metal substrate with a composition comprising:

- i) a source of aluminum ions;
- ii) a fluoro compound;
- iii) at least one pH adjuster;
- iv) a source of at least one Group VIB metal ion selected from the group consisting of tungstate ions and trivalent chromium ions; and
- v) optionally, a preservative; and

(b) thereafter drying the treated metal surface;

wherein the composition has a pH of 0.5 to 6 and the source of aluminum ions is selected from the group consisting of (i) ammonium hexafluoride aluminate, (ii) alkali metal hexafluoride aluminates, and (iii) aluminum powder in combination with hexafluoro titanic acid.

15. The method according to claim 14, wherein the metal substrate is selected from the group consisting of aluminum, aluminum alloys, magnesium, magnesium alloys, zinc, zinc alloys, steel, and combinations of one or more of the foregoing.

16. The method according to claim 14, wherein the conversion coating composition does not contain chromium or phosphorus.

17. The method according to claim 16, wherein:

the fluoro compound comprises hexafluorotitanic acid; the source of aluminum ions comprises aluminum metal; and the group VIB metal ion comprises a source of tungstate ions.

18. The method according to claim 14, wherein the one or more pH adjusters comprises ammonium bicarbonate or ammonium carbonate.

19. The method according to claim 14, wherein the Group VIB metal ion is selected from the group consisting of ortho-tungstates, meta-tungstates and para-tungstates, polytungstates, hetero-polytungstates, isopolytungstates, peroxytungstates, and combinations thereof.

20. The method according to claim 19, wherein the Group VIB metal ion selected from the group consisting of sodium, potassium, lithium, calcium, cerium, barium, magnesium, strontium, hydrogen and ammonium tungstate salts.

21. The method according to claim 20, wherein the Group VIB metal ion is selected from the group consisting of ammonium metatungstate, potassium metatungstate, sodium meta-

tungstate, tungstic acid, sodium tungstate, potassium tungstate and ammonium tungstate.

22. The method according to claim **21**, wherein the Group VIB metal ion comprises ammonium metatungstate.

23. The method according to claim **14**, wherein the source of aluminum ions and the source of fluoro ions comprises ammonium hexafluoride aluminate;

the composition contains a preservative; and

the group VIB metal ion comprises a source of trivalent chromium ions.

24. The method according to claim **23**, wherein the at least one pH adjuster comprises a material selected from the group consisting of organic acid and, and ammonium bicarbonate.

25. The method according to claim **24**, wherein the organic acid comprises benzoic acid.

26. The method according to claim **23**, wherein the preservative comprises hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine.

27. The method according to claim **23**, wherein the source of trivalent chromium ions comprises basic chrome sulfate.

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