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(54) Title: CHROME FREE CONVERSION COATING FOR ALUMINIUM

(57) Abstract: A chromate free conversion coating for Al based metals and methods of use. The compositions comprise (a) water soluble fluoacids of Group IVB metals, (b) fluoboric acid, (c) boric acid, (d) gluconic acid and, optionally (e) an aminosilane adhesion promoter or an organophosphonate corrosion inhibitor. In the method, the requisite metal part is contacted by the composition such as by immersion or spraying or the like.

CHROME FREE TREATMENT FOR ALUMINUM

FIELD OF THE INVENTION

The invention relates generally to non-chromate coatings for aluminum and aluminum based alloys that improve the adhesion of siccative coatings to the aluminum surfaces and provides corrosion protection, while maintaining the bright appearance of the metal.

BACKGROUND OF THE INVENTION

The current practice for treating aluminum and aluminum alloy surfaces, such as automotive wheel surfaces, requires a chromate based process to effect good paint adhesion and corrosion resistance. These chromate based treatments result in an aesthetically pleasing appearance as the machined aluminum wheel surface maintains its bright, metallic luster. However, as is well known, chromate solutions are carcinogenic and represent an environmental liability and safety concern to those who handle these solutions. Moreover, the costs associated with disposal of spent chromate baths and chromate laden rinse waters are high.

Non-chromate alternatives have been provided to enhance the adherence of paints, lacquers, inks, varnishes, resins, etc. (hereinafter "siccative" coatings) and to provide corrosion inhibition. However, many of these treatments are not suitable in the aluminum wheel market as they result in a dulling or discoloration of the substrate metal and are unacceptable, especially when the wheels are coated with the now popular clear coat paints.

SUMMARY OF THE INVENTION

The inventors have endeavored to discover a chromate free conversion coating composition and method that provides corrosion protection and siccative coating adherence comparable to conventional chromate based systems.

In accordance with the invention, an acidic aqueous treatment solution comprising (a) a water soluble fluoacid of a Group IVB metal or mixtures of such acids (b) fluoboric

acid (c) boric acid and (d) gluconic acid or salt thereof is provided. The metal surface is contacted with this treatment solution and, optionally, with a topping agent (e) that is selected to provide enhanced adhesion of siccative coatings (i) and/or enhanced corrosion resistance (ii).

Typically, an aminosilane may be used as component (e)(i) and an organophosphonate may serve as the component (e)(ii). Despite the low pH of the treatment solutions, the incorporation of the fluoboric acid and boric acid components help to minimize aluminum etch, thereby maintaining the bright appearance of machined and polished metal surfaces.

In a typical treatment scenario, the aluminum or aluminum alloy part is first cleaned in a mild alkaline cleaning solution, such as those conventional in the art, to remove surface contaminants and to assure that the metal is receptive to the coating. Care must be taken in cleaning the part so as not to dull or discolor the metal.

Also, as is known in the art, after cleaning, the metal part is rinsed with water and then treated with a chemical deoxidizer to remove excess aluminum oxide and to remove alloying elements from the metal surface. This deoxidizer can be a strong acid solution typically comprising sulfuric or nitric acid combined with an oxidizing species such as ferric ion. The parts are again rinsed before treatment with the non-chromate conversion coating treatment of the invention.

After treatment with the inventive compositions and methods, the parts are typically rinsed to prevent puddling and the like. The quality of the water used for the conversion coating treatment and subsequent rinse must be good to avoid undesirable accumulation of soluble salts on the metal surface.

The parts are then dried and coated with the desired siccative coating such as paint, lacquer, varnish, ink, etc.

DETAILED DESCRIPTION

In accordance with the invention, a concentrated aqueous solution of: (1) water soluble fluoacid of a Group IVB metal or metals or mixtures of such fluoacids; (2) fluoboric acid; (3) boric acid; (4) gluconic acid or salt thereof and (5) pH regulators such as nitric acid and ammonium hydroxide is prepared. This concentrate is then diluted to make an aqueous solution comprising about 1-10 %v/v of the concentrate. To this bath is optionally added the desired adhesion promoter, preferably an aminosilane, an amount of about 50 to 500 ppm. In addition to or in lieu of the adhesion promoter, a corrosion inhibitor enhancer, such as an organophosphonate may be added. Alternatively, these latter components may be added directly to the concentrate.

The thus formed conversion coating solution can be applied to the requisite aluminum surface by any suitable method. For example, the surface can be immersed in the solution, or the coating solution can be applied via spray techniques. Additionally, flow-coating techniques can be employed where convenient. Typically, the treatment temperature ranges from about 70°F to about 170°F.

Preferably, the temperature of the coating solution can be adjusted to above about 100°F, and the contact time for the treatment solution to the metal substrate is normally between about 15 seconds to 2 minutes. As above stated, the thus coated substrate is rinsed with water and then dried, typically in an oven having forced circulation of hot air. After drying, the desired siccative coating is applied.

With regard to the fluoacid of a Group IVB metal, fluozirconic acid H_2ZrF_6 , and fluotitanic acid H_2TiF_6 are preferred. A combination of H_2ZrF_6 and H_2TiF_6 is preferred. These acids may be present in a molar amount of 1:3 to 3:1 of $H_2ZrF_6:H_2TiF_6$. Presently, a 1:1 molar ratio is preferred.

Fluoboric acid and boric acid are also added, as necessary to minimize etching of the aluminum. To maintain the bright appearance of aluminum articles such as wheels, it is required that aluminum etch be minimized.

Overall, after dilution of the concentrate and addition of the aminosilane adhesion promoter and/or organophosphate corrosion inhibitor, the pH of the diluted, working solutions will be on the order of about 0.5-5 with a range of about 1-3 even more preferred.

As to the aminosilane compounds that may be used, it is desirable to use gamma-aminopropyltriethoxysilane (γ -APS) due to its efficacy and commercial availability. However, other alkoxyated aminoalkylsilanes such as aminopropyltrimethoxy silane, etc., can also be mentioned. U.S. Patent 6,203,854 can be reviewed for a more complete listing of the alkoxyated aminoalkylsilanes.

With regard to the organophosphonates that may be employed, amino tri (methylene phosphonic acid) (ATMP) is presently preferred due to commercial availability, but other organophosphonates such as 1-hydroxy-1,1-diphosphonic acid; ethylene diamine tetra (methylene phosphonic acid); hexamethylene diamine tetra (methylene phosphonic acid) and diethylenetriamine penta (methylene phosphonic acid) can be mentioned.

Concentrate compositions in accordance with the invention include the following:

	Exemplary	Preferred
Fluoacid of Group IVB metal		
or mixtures of such acids	1-15	4-12
HNO ₃	0.1-10	4-8
NH ₄ OH	0.1-10	2-6
Fluoboric acid	1-10	1-6
Boric Acid	0.1-5	1-3
Gluconic Acid	1-10	1-3
H ₂ O	remainder	remainder

At present, the concentrate preferred for use is

100 wt% total

H ₂ ZrF ₆ (45%)	5.2 %w/w
H ₂ TiF ₆ (60%)	3.2
HNO ₃ (42°Be)	6.0
NH ₄ OH (26°Be)	3.2
Fluoboric acid (48%)	4.0
Boric acid	2.0
Gluconic Acid (50%)	2.4
deionized water	remainder

As stated above, the concentrates are diluted in deionized, distilled, reverse osmosis, or other suitably high purity water to about 0.5-10%v/v solutions, preferably about 1-2%v/v of the concentrate (concentrate/total solution). To this, the aminosilane may be added in small amounts. For instance, \square APS is added in an amount of about 5 to 500 ppm into the diluted working solution.

The organophosponate may be added in amounts similar to those of the addition levels of the aminosilane.

The bath, or working solution, that is used to contact the aluminum part thus includes the following active components given in terms of ppm.

	Exemplary	Preferred
Group IV metal fluoacid	20 - 9000 ppm	200 - 1400 ppm
HNO ₃	5 - 7000 ppm	300 - 1200 ppm
NH ₄ OH	2 - 2000 ppm	60 - 340 ppm
Fluoboric Acid	25 - 5000 ppm	50 - 600 ppm
Boric Acid	5 - 5000 ppm	100 - 600 ppm
Gluconic Acid	25 - 5000 ppm	50 - 300 ppm

Examples

[0023] The invention will be further described in conjunction with the following examples which are included for illustrative purposes and should not be viewed to limit the invention.

Protocols Used

1. Wheel Section Preparations Sections of cast aluminum wheels (supplied by various wheel manufacturers) are treated per the following process sequence:

preclean: hot water rinse, 30 s

clean: mild alkaline cleaner, 60 s spray at 15 psi and 130°F

rinse: tap water spray for 60 s

deox: acid deoxidizer, 90 s spray at 100°F

rinse: tap water for 30 s, followed by DI water for 30 s

treat: various treatments spray or dip applied for 90 s at 100-120°F

rinse: DI water spray for 60 s

shake off excess water

warm air dry: conveyor oven at 150°F air temperature, 8 min duration

Treated sections are allowed to cool overnight and then powder painted. The wheel sections are baked in accordance with the paint manufacturers' recommendations. Typical powder curing conditions include a metal temperature of 320°F for 17 min (typically 30-40 min in oven set at 360°F). Dry film thickness is 2.5 mils on average.

Painted wheel sections are allowed to "age" for at least three days prior to any performance testing.

2. Filiform Corrosion Resistance

The procedure is similar to GM 9682P.

Wheel sections are scribed using a carbide tip scribe as prescribed in ASTM D 1654. The scribe is made with the aid of a straight edge and using a moderate, even pressure over the length of the ~10 cm scribe. The scribe is made perpendicular to the machining marks. Wheel sections are placed into the CAASS chamber within 30 minutes of being scribed.

Vertically scribed wheel sections are placed so that the scribe is ~30° from vertical. A Singleton corrosion test chamber (Model # Q-FOG/SP1100), is used, running under CAASS condition as specified by ASTM B 368-97. The wheel sections are exposed to this test for 6.0 ± 0.3 hours.

Upon removal from the CAASS chamber, the sections are rinsed by immersion in deionized water. The wheel section is immersed straight into the water, rotated a quarter turn right and then a half turn left and pulled from the water; the total dip time taking ~3 s.

The wheel sections are then placed in a humidity chamber. A Blue M Model # FRS 09C maintained at 140°F and 80% RH is used. The sections are placed in the chamber with an orientation similar to that of the CAASS exposure. Wheel sections are exposed in a chamber for at least two weeks, more typically three weeks. Filiform is rated by recording the maximum filament length (to the nearest 0.5 mm), and the quantity of visible filaments along the scribe. For sections providing better performance, we further rate the wheel section by developing a histogram of the quantity of filaments in 0.5 mm length increments and by noting any design flaws.

Copper Accelerated Acid Salt Spray

This test is run in accordance with ASTM B 368-97.

Scribing and exposure conditions are the same as described in the corrosion inoculation portion of the filiform test. The duration of the test is 168 ± 3 hours. After rinsing the wheel sections in deionized water, we rate the average and maximum blister size along the scribe and along design edges.

Thermal Shock

This test is run in accordance with GM 9525P.

This procedure is used to determine the resistance to coating adhesion loss of coated surfaces of aluminum when subjected to a wet steam blast similar to that produced by vehicle wash equipment. The test consists of cooling the wheel part to minus 29°C for three hours, then scribing the painted part with an X scribe and subjecting this area to a steam blast. Paint loss, or paint blushing (whitening, loss of gloss) and the average distance of paint adhesion loss from the scribe line is reported.

Test Solutions

The following treatment baths were used in evaluating performance of powder painted aluminum wheels.

	A	B	C	D	E	F
fluozirconic acid (45%)	11.6	6.1	12.8	0.0	0.7	5.0
fluotitanic acid (60%)	7.0	3.2	0.0	1.6	0.8	0.0
nitric acid (42 Be)	6.6	7.1	7.5	1.5	1.5	0.0
ammonium hydroxide (26 Be)	3.5	3.7	3.9	0.8	0.8	3.4
fluoboric acid (48%)	8.8	4.7	5.8	1.0	1.0	0.0
boric acid	0.0	2.3	2.5	0.5	0.5	0.0
gluconic acid (50%)	2.7	2.8	3.0	0.6	0.6	0.0
chromic acid	0.0	0.0	0.0	0.0	0.0	4.0
Water	59.8	70.1	64.5	94.0	94.1	67.6

Example 1

Formulations A, B, and C were diluted to 1%v/v in deionized water, pH adjusted to 3.0 using ammonium hydroxide or left at native solution pH of 2.0, and further modified by the addition of 150, 300, or 450 ppm \square -APS. These solutions were used to treat aluminum wheels as set forth under Protocol #1 above. Treated wheels were painted with a clear coat acrylic powder from PPG and performance tested by CAASS and filiform test conditions.

solution				paint performance evaluation			
				filiform corrosion resistance** (max / # along scribe / # design failures)			CAASS** * (max / avg)
1	F	(chrome controls)		2.5 / 7.8 / 1	3.0 / 9.9 / 0	-	1.0 / 0.5
		pH	□-APS (ppm)				
2	B	2	150	2.0 / 5.9 / 2	2.5 / 6.0 / 1	4.5 / 8.1 / 0	1.0 / 0.5
3		2	450	2.0 / 6.0 / 1	2.5 / 8.2 / 0	4.0 / 8.9 / 0	1.0 / 0.5
4		3	150	2.0 / 9.8 / 3	3.0 / 11.1 / 0	3.5 / 14.8 / 1	2.0 / 1.0
5		3	450	3.5 / 13.9 / 2	3.5 / 14.4 / 1	-	1.5 / 1.0
6	C	2	300	2.5 / 8.8 / 0	3.5 / 10.0 / 0	3.5 / 10.8 / 2	1.0 / 1.0
7		2	300	2.5 / 5.5 / 0	3.0 / 9.4 / 0	3.5 / 1.04 / 2	2.0 / 1.0
8	A	2	150	2.5 / 5.2 / 0	6.5 / 12.2 / 2	-	2.5 / 1.5
9		2	450	1.5 / 6.9 / 1	2.0 / 7.3 / 0	2.5 / 11.5 / 0	1.0 / 0.5
10		3	150	3.0 / 7.6 / 0	3.5 / 9.7 / 2	4.0 / 4.5 / 0	2.5 / 1.5

1		3	450	3.0 / 10.9 / 0	3.0 / 11.3 / 0	3.5 / 9.1 / 0	3.0 / 2.0
1							

* this process applied via immersion; all others spray applied

** filiform results for three (or two) separate wheel sections; reported as maximum filament along scribe (in mm) / number of filaments along scribe per length (in cm) of scribe / number of filaments noted at design features of sharp, painted edges on wheel sections.

***CAASS results given for maximum and average blister diameter in mm

Example 2

Cast and polished aluminum wheel sections and panels were prepared in accordance with Protocol #1 above using solutions D, E, and chrome controls F. Non-chrome treatments were evaluated with and without the addition of □-APS or Dequest 2000. The wheel sections were painted with a clear coat acrylate powder from PPG.

			paint performance evaluation				
			filiform corrosion resistance (max / # along scribe / # design failures)			CAASS (max / avg)	
#	treatment	pH					
1	5%F (chrome controls)	-	1.0 / 2.9 / 0 2.5 / 5.4 / 0	-	-	-	2.0 / 1.5
2	5% D + 300 ppm □-APS	2.2	2.0 / 6.9 / 0	4.0 / 11.8 / 0	2.0 / 7.9 / 1		1.5 / 1.0

	□-APS		4.0/9.4/0	4.5/9.6/2	3.0/1.8/0	
3	5% D + 300 ppm ATMP	3.0	3.0/5.9/0 4.0/4.7/0	3.5/7.7/0 4.5/4.4/0	2.5/2.5/0 3.0/5.0/0	1.0/1.0
4	5%E	2.5	2.0/8.6/0 3.5/8.5/0	/6.5/1 4.5/7.4/0	2.5/4.9/0 3.0/4.9/0	1.5/1.0
5	5%E + 300 ppm □- APS	2.5	4.0/12.6/0 4.0/8.8/0	3.0/9.5/0 4.5/7.4/3	2.0/6.0/0 2.0/7.4/0	1.0/0.5
6	5% E + 300 ppm ATMP	3.0	1.5/2.7/0 4.5/3.0/0	1.5/3.5/0 4.0/6.6/0	/0.8/0 1.5/4.1/0	2.0/1.5

Example 3

[0038] Basic formulations were tested in order to assess the performance of and optimal concentrations of H_2ZrF_6 , HF_4 and H_3BO_3 components. Wheel sections were pretreated in accordance with Protocol #1 and painted with clear coat powder acrylic from PPG.

[0039] The basic formulation that was varied as shown was as follows:

	G	H	I	J	K	L	M	N
fluozirconic acid (45%)	1.3	1.3	1.3	1.3	5.3	5.3	5.3	5.3
nitric acid (42 Be)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ammonium hydroxide (26 Be)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

fluoboric acid (48%)	0.5	0.5	2.0	2.0	0.5	0.5	2.0	2.0
boric acid	0.0	1.0	0.0	1.0	0.0	1.0	0.0	1.0
gluconic acid (50%)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Water	95.3	94.3	93.8	92.8	91.3	90.3	89.8	88.8

#	Solution	filiform corrosion resistance (max / # / # design failures)		thermal shock adhesion loss (mm) / blush	CAASS max / avg
		wheel type 1	wheel type 2		
1	5% F	3.0 / 4.0 / 0	2.5 / 5.8 / 0	0.0 / none	3.0 / 1.5
		4.0 / 4.4 / 0	4.0 / 10.7 / 0		
2	2.5% G	4.5 / 5.1 / 0	3.0 / 9.0 / 0	0.0 / none	2.0 / 1.0
		5.0 / 6.6 / 0	3.5 / 10.7 / 0		
3	2.5% H	6.5 / 6.8 / 0	4.0 / 7.4 / 0	0.0 / none	2.0 / 1.5
		7.0 / 13.4 / 10	5.0 / 8.0 / 0		
4	2.5% I	0.5 / 3.5 / 0	3.0 / 7.8 / 0	2.8 / none	2.5 / 1.5
		3.5 / 6.1 / 0	5.5 / 5.6 / 0		
5	2.5% J	1.5 / 5.3 / 0	2.5 / 5.8 / 0	0.0 / none	1.5 / 1.0
		3.0 / 4.3 / 1	6.0 / 10.0 / 0		
6	2.5% K	1.0 / 3.8 / 1	2.0 / 11.1 / 0	0.0 / none	2.0 / 1.5

		2.5 / 4.5 / 0	4.5 / 8.4 / 0		
7	2.5% L	3.5 / 4.0 / 0 4.0 / 3.3 / 0	3.0 / 9.5 / 0 3.5 / 8.5 / 0	0.0 / none	1.5 / 1.0
8	2.5% M	2.5 / 7.0 / 1 3.0 / 7.9 / 0	3.0 / 7.5 / 0 4.5 / 7.7 / 0	0.0 / none	-
9	2.5% N	3.0 / 4.8 / 0 3.5 / 8.2 / 0	- -	0.0 / none	-

	O	P	Q
fluozirconic acid (45%)	2.6	0.0	1.3
fluotitanic acid (60%)	0.0	1.6	0.8
nitric acid (42 Be)	1.5	1.5	1.5
ammonium hydroxide (26 Be)	0.8	0.8	0.8
fluoboric acid (48%)	1.0	1.0	1.0
boric acid	0.5	0.5	0.5
gluconic acid (50%)	0.6	0.6	0.6
Water	93.0	94.0	93.5

Example 4

Tests were conducted using formulation O, modified by the addition of either 300 ppm \square -APS or 300 ppm of an acrylic acid / vinyl phosphonic acid co-polymer.

A variety of cleaners, deoxidizing acid and rinses were employed as pretreatment, but these showed little effect on filiform performance. The pretreated wheel samples were painted with acrylic clear coats from PPG and from Ferro.

#	treatment conditions	filiform (max / # / # design failures)	
		PPG acrylic	Ferro acrylic
	production samples	2.0 / 5.8 / 1	0.5 / 0.6 / 1
1	5% F	- / - / 0	2.5 / 7.1 / 0
2		3.0 / 5.9 / 0	3.0 / 12.7 / 0
3		2.0 / 4.6 / 0	2.0 / 8.7 / 0
4		2.0 / 4.6 / 1	3.0 / 10.4 / 0
7		2.5 / 5.7 / 1	2.0 / 6.8 / 1
8		2.5 / 3.2 / 1	2.5 / 9.7 / 1
5		-	2.5 / 4.4 / 0
6		2.5 / 6.1 / 0	2.0 / 5.2 / 3
9	2.5% O +	4.0 / 5.5 / 1	2.5 / 9.5 / 1
10		- / - / 2	3.0 / 9.5 / 2
11		300 ppm AA/VPA copolymer	2.0 / 6.9 / 0

12	copolymer	- / - / 3	3.0 / 8.3 / 0
13		3.0 / 6.9 / 0	4.0 / 12.5 / 1
14		4.0 / 7.3 / 4	6.0 / 15.4 / 5
15		- / - / 0	3.5 / 11.6 / 1
16		4.0 / 4.5 / 2	2.0 / 8.3 / 0
17		2.5% O + 300 ppm □-APS	2.0 / 8.5 / 0
18	2.0 / 7.2 / 1		2.5 / 8.1 / 2
19	- / - / 0		3.0 / 8.8 / 2
20	2.5 / 10 / 0		2.5 / 7.2 / 0
23	- / - / 1		2.0 / 7.7 / 2
24	2.0 / 6.6 / 1		2.0 / 9.0 / 1
21	3.5 / 7.5 / 2		2.0 / 8.7 / 0
22	- / - / 1		2.0 / 10.0 / 2

Example 5

Sections of cast aluminum wheels and cast and polished aluminum wheels were treated in accordance with pretreatment Protocol #1. Wheel sections were painted with clear coat acrylic powder paint and evaluated by CAASS and filiform corrosion resistance.

process conditions				performance evaluation		
#	treat	conc (%)	temp (F)	filiform corrosion resistance (max / # / # design failures)		CAASS (max / avg)
1	no treatment			4.5 / 14.1 / 1	4.0 / 11.7 / 2	7.0 / 5.0
2	F	5.0	100	1.5 / 5.8 / 0	3.0 / 5.1 / 1	-
3	P	1.0	100	3.5 / 10.7 / 0	4.0 / 9.1 / 7	7.0 / 4.0
4	P	1.0	140	3.0 / 6.2 / 0	3.0 / 9.6 / 2	3.5 / 2.0
5	P	5.0	140	2.5 / 8.3 / 3	3.5 / 11.9 / 1	5.0 / 3.5
6	P	5.0	100	1.5 / 2.4 / 1	2.5 / 7.2 / 1	6.0 / 4.0
7	Q	2.5	120	3.0 / 4.2 / 0	4.0 / 7.4 / 0	-
				2.5 / 9.6 / 1	3.5 / 6.4 / 0	7.0 / 4.0
				3.0 / 10.4 / 0	4.0 / 9.8 / 0	-
8	O	1.0	100	2.5 / 8.4 / 0	3.5 / 10.7 / 1	3.0 / 2.5
9	O	1.0	140	2.5 / 3.6 / 0	4.0 / 5.8 / 0	4.0 / 3.0
10	O	5.0	140	3.0 / 8.7 / 0	5.5 / 7.4 / 1	4.0 / 3.0
11	O	5.0	100	3.5 / 7.1 / 0	5.0 / 8.3 / 1	2.5 / 1.5

Example 6

Sections of cast aluminum wheels were treated in accordance with Protocol #1. The treated wheel sections were painted with clear coat acrylic powder. A variety of additives, as shown, were added to the basic formulation listed in Example 5.

process conditions			paint performance evaluation					
#	sol'n	300 ppm	filiform corrosion resistance (max / # / # design failures)				thermal shock adhesion loss / blush	CAASS (max / avg)
			wheel type 1 (Mazda)		wheel type 2 (Ford)			
1	5% F	none	-	-	2.5 / 9.4 / 0	3.0 / 8.2 / 0	0.0 / none	2.0 / 1.5
2	2.5% O	none	4.0 / 11.6 / 3	-	3.0 / 7.4 / 0	3.5 / 9.5 / 0	0.0 / none	3.0 / 2.0
3	2.5% O	□- APS	2.5 / 7.6 / 1	3.0 / 11.7 / 0	2.0 / 7.9 / 0	2.5 / 4.6 / 0	0.0 / none	2.0 / 1.5
4	2.5% O	AA/A M	4.0 / 11.4 / 0	4.5 / 10.3 / 0	3.0 / 6.0 / 0	4.0 / 12.2 / 2	0.0 / none	6.0 / 4.0
5	2.5% O	ATMP	4.0 / 4.8 / 0	5.0 / 3.1 / 0	2.0 / 6.0 / 0	4.0 / 4.0 / 0	0.5 / none	2.0 / 1.5

WHAT IS CLAIMED IS:

1. A method of coating an aluminum or aluminum alloy metal surface comprising contacting said surface with an effective amount of a chromate free, acidic aqueous treatment solution comprising a (a) water soluble fluoacid of a Group IVB (CAS) metal or mixtures thereof, (b) fluoboric acid, (c) boric acid, (d) gluconic acid, and, optionally a topping agent (e) wherein said topping agent is selected from the group of (ei) aminosilane adhesion promoter and /or (eii) organophosphonate corrosion inhibitors.
2. A method as recited in claim 1 including spraying said treatment solution onto said surface.
3. A method as recited in claim 1 including immersing said surface in said treatment solution.
4. A method as recited in claim 1 wherein said (ei) is present and comprises an alkoxyated amino silane.
5. A method as recited in claim 4 wherein said alkoxyated aminosilane is gamma aminopropyltriethoxysilane.
6. A method as recited in claim 1 wherein said (eii) comprises amino tri (methylene phosphoric acid).
7. A method as recited in claim 1 wherein said (a) comprises H_2ZrF_6 and H_2TiF_6 .
8. A method as recited in claim 7 wherein said treatment solution further includes nitric acid and ammonium hydroxide.
9. Chromate free aqueous conversion coating adapted for contact with an aluminum or aluminum alloy surface, said composition comprising:
 - (a) water soluble fluoacid of a Group IVB (CAS) metal or mixtures of said fluoacid

- (b) fluoboric acid
 - (c) boric acid
 - (d) gluconic acid and
 - (e) a topping agent, wherein said topping agent is selected from the group consisting of (ei) aminosilane adhesion promoters and/or (eii) organophosphonate corrosion inhibitors.
10. Compositions as recited in claim 9 wherein said (a) comprises H_2ZrF_6 and H_2TiF_6 .
11. Composition as recited in claim 10 wherein (ei) is present and comprises an alkoxyated aminosilane.
12. Composition as recited in claim 11 wherein said (ei) is gamma aminopropyltriethoxysilane.
13. Composition as recited in claim 9 wherein (eii) is present and comprises amino tri(methylene phosphonic acid).
14. Composition as recited in claim 13 further including nitric acid and ammonium hydroxide and wherein the pH of said aqueous conversion coating composition is about 0.5-5.

INTERNATIONAL SEARCH REPORT

Internati application No
PCT/US 03/35660

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C22/34 C23C22/73

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 370 177 A (FRELIN FRANK J ET AL) 25 January 1983 (1983-01-25)	1-3,7,8
Y	column 3, line 43 -column 8, line 31; claims; examples	4-6,9-14
Y	WO 99 14399 A (BRENT INT PLC ;AFFINITO JOHN C (US)) 25 March 1999 (1999-03-25) page 5, line 4 -page 6, line 2; claims page 9, line 1 - line 28	4,5, 9-12,14
Y	US 5 441 580 A (TOMLINSON CHARLES E) 15 August 1995 (1995-08-15) column 2, line 5 -column 4, line 48; claims	6,9,10, 13,14
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

10 March 2004

Date of mailing of the international search report

23/03/2004

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/35660

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 20657 A (HENKEL CORP ;KELLY TIMM L (US); ROCHFORD GARY L (US); BANASZAK RIC) 13 April 2000 (2000-04-13) claims; examples -----	1-14

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