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(54) Title: ZINC PHOSPHATE CONVERSION COATING COMPOSITION AND PROCESS (57) Abstract Zinc phosphate coatings for metal surfaces and phosphating process. Concentrates containing (a) hydroxylamine sulfate and (b) zinc, nickel, manganese and phosphate ions are formulated into aqueous coating solutions for treating metal surfaces, including ferrous, zinc and aluminum surfaces.		

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ZINC PHOSPHATE CONVERSION COATING COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTIONField of the Invention

This invention relates to zinc phosphate coatings for metal surfaces and a process for phosphatizing a metal surface with acidic aqueous phosphate solution. The invention is applicable to a variety of substrates including cold rolled steel (CRS), zinc alloys and aluminum.

Statement of Related Art

Present day phosphate coating solutions are dilute aqueous solution of phosphoric acid and other chemicals which, when applied to the surface of a metal react with the metal surface forming an integral layer on the surface of the metal of a substantially insoluble phosphate coating, amorphous or crystalline. Generally the crystalline coatings are preferred.

Typically the solutions include phosphate ions, zinc and other metal ions to provide specific characteristics desired in the final coating. Other ions typically present may be nitrate, nitrite, chlorate, fluoroborate or silicofluoride. A typical phosphating process is comprised of the following sequence:

- (1) Cleaning and conditioning
- (2) Phosphating and
- (3) Post treating.

5 Rinses are generally employed between each step to prevent any carry over of materials to the next step.

10 Despite advances in both the composition of the phosphate coating solution and the phosphating process, there is a continued demand for still further improvements in the compositions and processes, to provide more control over the process, to form adequate coating weights, to reduce formation of scale or white spots, reduce environmental impact and safety concerns.

15 U.S. Patent 4,838,957 describes a zinc phosphating process employing aqueous phosphate solution containing zinc ion, phosphate ion, manganese ion, fluoride ion and a phosphating accelerator. The accelerator may be one or more of (a) nitrate ion, (b) nitrite ion, (c) hydrogen peroxide, (d) m-nitrobenzene sulfonate ion, (e) m-nitrobenzoate ion or (f) p-nitrophenol. Nickel is
20 indicated as an optional ingredient. While morphology of the coating is not discussed, the coatings are primarily a crystalline platelet structure.

25 In U.S. Patent 4,865,653 phosphate coating solutions are described in which the accelerator employed is hydroxylamine sulfate (HAS) which is employed so as to alter the morphology of the resulting coating from platelet to a columnar and/or nodular structure over a broad range of zinc concentration. While Ni and Mn are generally mentioned as additional ions, there is no
30 description of specific amounts of either in the patent or any specific examples thereof. The patent further describes a relatively large number of other patents which include hydroxylamine sulfate in zinc phosphate solutions, as well as various oxidizing agents including

U.S. Patents 2,743,204 and 2,298,280.

U.S. Patent 4,793,867 describes a coating composition which includes zinc and another divalent cation, such as manganese or nickel in addition to a non-coating monovalent cation, such as sodium or potassium to provide improved alkaline solubility of conversion coatings applied to zinc-coated substrates. HAS is noted as eliminating any unwanted precipitation which may arise in adding any manganese alkali. Three U.S. Patents 4,389,260; 4,486,241 and 4,612,060 are cited in the list of references cited in U.S. 4,793,867. These patents relate to zinc phosphating solutions which contain nickel and/or manganese.

DESCRIPTION OF THE INVENTION

In this description, except in the operating examples or where explicitly otherwise indicated, all numbers describing amounts of ingredients or reaction conditions are to be understood as modified by the word "about".

It has now been discovered that certain zinc phosphate compositions containing both nickel and manganese with hydroxylamine sulfate (HAS) as the accelerator, provide polycrystalline coatings and retain the advantages of the use of manganese and nickel, and the accelerator properties of the HAS without changing the platelet or needle like crystalline morphology, as described in U.S. Patent 4,865,653 noted earlier above. The HAS accelerated zinc phosphating mixture of the present invention produces a desirable uniform, gray manganese and nickel modified zinc phosphate coating on a variety of substrates including ferrous alloys, zinc alloys and aluminum and its alloys at desirable temperatures in the range of about 100 to 150°F,

preferably about 115° to 130°F, and can be applied by either spray or immersion applications. The hydroxylamine sulfate accelerator can be incorporated into the makeup and replenishing mixtures, when needed, without the need of traditional or supplemental undesirable accelerators, such as nitrite.

In addition to providing overall desirable advantages, without many of the disadvantages encountered in the art, the present invention provides for improved process uniformity at the low temperature, and reduces environmental impact and safety concerns associated with nitrite. The polycrystalline coating contains Zn, Mn and Ni in the coating, and Fe in coatings on ferrous surfaces.

The present invention deals with a make-up or concentrate composition, which may then be diluted with water to form an aqueous, acidic coating solution for a spray or immersion coating process. In general, the coating solution will contain concentrations by weight of

20	PO ₄ ion	0.5 - 2.5%
	Zn ion	0.05 - .2%
	Ni ion	0.02 - 0.15%
	Mn ion	0.02 - 0.15%
	HAS	0.1 to 0.25%
25	NO ₃ ion	0 to 0.2%
	F ion	0 to 0.15%

The foregoing coating solution may be formed by diluting a concentrate containing the material providing the foregoing concentration when the concentrate is diluted with water in an amount of about 48 g/liter of concentrate. The concentrate is accordingly formulated to provide a coating solution containing from

- 5 (a) from about 0.5 to about 2 g/l, preferably from about 0.8 to about 1.2 g/l of zinc ion;
- (b) from about 5 to about 25 g/l, preferably from about 10 to about 15 g/l, or phosphate ion;
- 10 (c) from about 0.2 to about 1.5 g/l, preferably from about 0.5 to about 1 g/l of manganese ion;
- (d) from about 0.2 to about 1.5 g/l, preferably 0.5 to about 1 g/l nickel ion;
- (e) from about 1 to about 2.5 g/l, preferably 1.5 to about 1.75 g/l of hydroxylamine accelerator.
- 15 (f) 0 to about 1.5 g/l, of total fluoride ion with preferably a free fluoride content of about 400-600 parts per million;
- (g) 0 to about 2 g/l nitrate ion.

15 In the phosphating solutions, it is preferable that the weight ratio of zinc ion to phosphate ion be 1: about 10 to 25, and the weight ratio of zinc to the sum of manganese and nickel 1:0.5 to 1.5, with the ratio of manganese to nickel being preferably about 1:1 with a

20 ratio of 1:0.5 to 1.5 being satisfactory.

In the phosphating solution of the present invention, it is desirable for the solution to have a total acidity of about 15 to 25, preferably about 17-21, typically about 19-20 with a free acidity of about .5-

25 1.0, more desirably about 0.6-0.9, and preferably about 0.7-0.8. Acidity herein is expressed in points, in which "points" as used herein is meant the mls of 0.1 NaOH required to titrate a 10 ml aliquot sample to a pH of 8.2, with phenolphthalein indicator for total acid and to

30 a pH of 3.8 with bromophenol blue indicator for free acid.

Sources of the ingredients of the phosphating solutions of the invention include the following: as to the zinc ion: zinc oxide, zinc carbonate, zinc nitrate,

etc.; as to the phosphate ion: phosphoric acid, zinc phosphate, zinc monohydrogen phosphate, zinc dihydrogen phosphate, manganese phosphate, manganese monohydrogen phosphate, manganese dihydrogen phosphate, etc.; as to the manganese ion: manganese oxide, manganese carbonate, manganese nitrate, the above manganese phosphate compounds, etc.; as to nickel ion: nickel oxide, nickel nitrate, nickel carbonate, etc.; as to the fluoride ion, hydrofluoric acid, fluoroboric acid, fluorosilicic acid, fluorotitanic acid, and their metal salts (e.g., zinc salt, nickel salt, etc., as to nitrate ion: nitric acid, nickel nitrate etc.

Hydroxylamine is the accelerator and in the present invention can be added to the concentrate before dilution to the coating solution. The hydroxylamine can be added in any suitable form and from any conventional source. The term "hydroxylamine agent", as used herein, means any compound that provides hydroxylamine or a derivative thereof such as a hydroxylamine salt or complex. Suitable examples include hydroxylamine phosphate, nitrate, sulfate, or mixtures thereof. More preferably, the hydroxylamine agent or source is hydroxylamine sulfate ("HAS"), a stable form of hydroxylamine.

As stated above, the metal surfaces treated in accordance with the present invention include iron-based surfaces, zinc-based surfaces, aluminum-based surfaces, and their respective alloy-based surfaces. These metal surfaces can be treated either separately or in combination. The advantage of the present invention is most prominently exhibited when the treatment is carried out on metal surfaces which include both an iron-based surface and a zinc-based surface, as, for example, in a car body.

It is conventional to perform other steps before and

after the improved phosphating step of the present invention. Thus, it is advantageous to take steps to see that the part, workpiece or other article to be coated is substantially free of grease, dirt, or other extraneous matter. This is preferably done by employing conventional cleaning procedures and materials known to those skilled in the art. These would include, for example, mild or strong alkali cleaners, acidic cleaners, and the like. Such cleaners are generally followed and/or preceded by a water rinse.

It is highly preferred to employ a conditioning step following or as part of the cleaning step. These conditioning solutions which are known to the art typically employ condensed titanium compounds and preferably a condensed phosphate.

After the coating is formed by application of the compositions of the invention, the coated article is preferably rinsed with water and dried. The drying may be accomplished by simple ambient air drying but a forced air drying at elevated temperatures may be employed. In the coating step the temperature is preferably maintained at about 115 to about 130°F although temperatures up to 150°F are sometimes employed. At lower temperatures, longer time periods are typically required to achieve a uniform coating. The coating may be applied by immersion or spray techniques or a combination of each. Treatment times may vary from 30-180 seconds dependent on the temperature and technique of application.

Practical and preferred embodiments of the invention can be further illustrated by means of the following examples, which are not intended as limiting the invention, in which all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

In this example a concentrate is prepared from the following materials in the amounts indicated.

	<u>MATERIAL</u>	<u>PARTS BY WEIGHT</u>
5	Water	368.5
	H ₃ PO ₄ (75%)	390.0
	HNO ₃ (42°Be)	5.0
	Hydroxylamine Sulfate	35.0
	MnO	13.5
10	ZnO	26.0
	Ni(NO ₃) ₂ (30% Solution)	75.0
	H ₂ SiF ₆ (25%)	80.0
	HF (70%)	<u>7.0</u>
	Total	1000.0

- 15 * Initially 331 parts of water, 37.5 added at end to make up 1000 parts total.

20 The concentrate when diluted to a 6% w/v in water has a free acid (FA) value of about 15 points and a total acid (TA) value of about 42 points. The ratio of Mn to Ni ion is 1:1, the ratio of Zn ion to the sum of Mn to Ni ion is 1:1, and the ratio of Zn ion to phosphate ion is 1:13.7.

EXAMPLE 2

25 In this example another concentrate is prepared from the following materials in the amounts indicated.

	<u>MATERIAL</u>	<u>PARTS BY WEIGHT</u>
	Water	315.5
	H ₃ PO ₄ (75%)	390.0
	HNO ₃ (42°Be)	5.0
30	Hydroxylamine Sulfate	35.0
	MnO	21.5
	ZnO	26.0y
	Ni(NO ₃) ₂ Solution (30%)	120.0
	HF (70%)	7.0
35	H ₂ SiF ₆ (25%)	80.0

The concentrate when diluted with water to a 6% w/v in water has an FA of about 13.5 and a TA of about 40. The ratio of Mn to Ni ion is 1:1, the ratio of Zn ion to the sum of Mn to Ni ion is 1:1.6, and the ratio of Zn ion to phosphate ion is 1:13.7.

EXAMPLE 3

This example will serve to illustrate the phosphating coating process employing the spray technique using the concentrate of Example 1. The concentrate was diluted with water to a concentration of 48 grams of concentrate per liter of coating solution and NaOH added to reduce the free acid level of the coating solution to 0.7 points and a total acid to 20.

In the typical procedure, after degreasing and cleaning of 4 inch by 6 inch metal panels with a commercial alkaline cleaner (Parcolene 1500 C), followed by water rinse, the panels were conditioned with a commercial titanium salt (Fixodine Z8). The panels were then treated with the phosphate coating solution formed from the concentrate of Example 1 as noted above. After the phosphating treatment, the panels were water rinsed at ambient temperature using a 30 second water spray rinse followed by a 30 second deionized water spray rinse. The panels were then forced air dried at ambient temperature.

The results of the phosphating coating at a temperature of 115°F and a 120 second spray time are as shown in Table 1 below with several runs on both cold rolled steel (CRS) and hot dipped galvanized (HDG).

TABLE 1

		COATING WEIGHT mg/ft ²	
	<u>SAMPLE</u>	<u>CRS</u>	<u>HDG</u>
5	A	168	189
	B	150	180
	C	159	180
	D	120	153
	E	120	147
10	F	156	159
	G	120	138
	H	129	162
	I	120	168
	J	156	168
15	K	129	159
	L	156	141
	M	156	168
	N	126	159
	O	162	171
20	P	149	148
	Q	121	156
	R	117	153
	S	121	151
	T	136	156
25	U	120	145

The coatings were crystalline, platelet or needle-like, structure with a crystal size in the range of 3-15 microns for the CRS and 2-10 microns for the HDG. Other samples were run at different spray times and temperatures, and visual observation of the coatings indicated that satisfactory coatings may be obtained at temperatures as low as 105°F, but higher temperatures are preferred.

EXAMPLE 4

A series of aluminum 4 inch by 6 inch panels, 2036 Al and 5052 Al, were processed in the same manner as the CRS and HDG in Example 3, except that a potassium fluoride additive (8.6% free F ion, and 8.99% K ion) was

employed to achieve a free fluoride level of 500-600 parts per million. Temperatures between 115-130°F were acceptable although a 120 second time was required at the lower temperatures. The panels exhibited coating weights ranging from 122-173 mg/ft² for the aluminum 2036 alloy and 150-195 mg/ft² for the aluminum 5052 alloy. Crystal size varied from 5 to 30 microns for both alloys.

EXAMPLE 5

In this example, several different substrates were treated for a 60 second spray following the procedure of Example 3. In addition to the aluminum alloys and the cold rolled steel (CRS), two different electrogalvanized (EG) substrates, and zinc-nickel alloy and AOI (zinc-iron alloy) are shown in the results of Table 2 below.

15

TABLE 2

	SUBSTRATE	CT.WT. (mg/ft ²)	CRYSTAL SIZE (MICRONS)	VISUAL APPEARANCE	BATH TEMPERATURE (°F)
	CRS	127	3-12	GOOD	120
20	90E EG	180	2-8	GOOD	120
	NAT. 70/70 EG	280	2-8	GOOD	120
	Zn-Ni	164	3-10	GOOD	120
	AOI	183	3-10	GOOD	120
	2036 AL	179	5-20	GOOD	130
25	5052 AL	195	5-18	GOOD	130

EXAMPLE 6

In this example, the concentrate of Example 2 was employed and instead of the spray application in Example 3, the metal panels were immersed in a bath of the coating solution, which was again formed by diluting the

concentrate to 48 g/l, as was done in Example 3. The results on various substrate panels (4 in. X 6 in.) with a 2 minute immersion time at a temperature of 115°F. are shown in the following Table 3, which also illustrates the coating composition analysis.

TABLE 3

SUBSTRATE	COATING WEIGHT					
	mg/ft ²	Zn	Ni	Mn	PO ₄	Fe
CRS	177	27	1.3	2.9	38	9.5
EG	185.1	37.5	1.3	4.3	38	0.16
HDG	168.6	37	1.8	4.5	38.9	0.14
Al 2036	168.6	29.9	2.2	6.7	42.5	0.32

In general, the crystal size was 1-5 microns for all substrates. Also as in Example 3, bath temperatures above 105°F are preferred, such as about 115°-135°F, with time periods above 60 seconds, and preferably above 80 seconds, being most preferred.

In all cases, the presence of the hydroxylamine sulfate did not change the morphology from a needle-like or nodular structure, but retained the morphology associated with the application method and substrate, as well as the presence of the manganese, in addition to the nickel, in the amounts described and in the ratios with the other components such as the zinc and phosphate ions in the coating solution and the amount of the hydroxylamine employed. The coatings in the invention are accordingly of either the platelet or nodular (in the case of immersion coating of CRS) crystalline structure providing excellent coating weights in a low temperature application either by spray or immersion techniques. The hydroxylamine accelerator may be added to the concentrate itself, avoiding the necessity of adding it when the coating solution is being later formulated from the concentrate. The coating solution requires no nitrite

ion as an accelerator, thereby reducing environmental impact and safety concerns associated with nitrites.

5 The preferred compositions will provide a coating solution for either spray or immersion, of the following ingredients and ions in the amounts typically about those set forth below:

	<u>Ingredient</u>	<u>% by Weight</u>
	Hydroxylamine Sulfate	0.168
10	Zinc ion	0.10
	Nickel ion	0.05
	Manganese ion	0.05
	Phosphate ion	1.37
	Nitrate ion	0.12
15	Complex fluoride	0.074
	Free fluoride	0.022

20 In the foregoing, the zinc to phosphate ratio is 1:13.7; the ratio of zinc to the sum of manganese and nickel of 1:1. With such composition, phosphate coatings can be satisfactorily formed in desirable coating weights not only on ferrous substrate such as cold rolled steel, including galvanized substrates but also on aluminum substrates.

25 As a practical matter, in coating operations, the coating solution may need to be replenished to maintain the appropriate levels of the materials in the coating solution and to maintain the acidity levels. Replenishing compositions will contain the various materials and ions in amounts effective, upon addition to
30 the coating solution, to maintain the ions at the appropriate levels for coating and will contain ammonium carbonate or bicarbonate, and preferably ammonium hydroxide, in an amount effective, upon addition of the

replenisher to the coating solution, to maintain the acidity level of the coating solution.

An example of a replenishing composition for the coating solutions of the present invention is:

5	Water	270.2
	H ₃ PO ₄ (75%)	378.0
	Hydroxylamine Sulfate	100.0
	MnO	12.8
	ZnO	68.0
10	Ni(NO ₃) ₂ Solution (30%)	60.0
	HF (70%)	2.5
	H ₂ SiF ₆ (25%)	50.0
	Ammonium Hydroxide (26°Be)	58.5

What is claimed is:

1. A concentrate composition for use in formulating an aqueous coating solution for the treatment of metal substrates, said concentrate comprising on aqueous solution containing zinc ions, nickel ions, manganese ions and phosphate ions, wherein the ions are present in sufficient amounts to produce a coating solution upon dilution with water in which, after dilution to form the coating solution, the ions are present in the formed coating solution in the percent by weight as follows:

phosphate ion	0.5 to 2.5
zinc ion	0.05 to 0.2
nickel ion	0.02 to 0.15
manganese ion	0.02 to 0.15

and further provided that the ratio of zinc ion to phosphate ion is 1:about 10-25; the ratio of zinc to the sum of manganese and nickel ion is 1:about 0.5-1.5; the ratio of manganese to nickel is 1:about 0.5-1.5 and said hydroxylamine accelerator is present in said coating solution in an amount from about 0.1 to about 0.25 percent by weight.

2. A concentrate composition as defined in Claim 1, wherein said hydroxylamine accelerator is hydroxylamine sulfate and is present in said concentrate in an amount to provide about 0.1 to about 0.25 percent by weight in said coating solution.

3. A concentrate composition as defined in Claim 2, wherein the ratio of zinc to phosphate is 1:about 10-15; the ratio of zinc to the sum of manganese and nickel is about 1:1 and the ratio of manganese to

nickel about 1:1.

4. A concentrate as defined in Claim 3, wherein said hydroxylamine sulfate is present in an amount of about 0.17 percent by weight.
5. A concentrate as defined in Claim 3, wherein the ratio of zinc to phosphate is 1:about 13.7
6. A concentrate composition as defined in Claim 3, wherein said metal substrates is selected from the group consisting of a ferrous substrate, a zinc substrate and an aluminum substrate.
7. A concentrate composition for use in formulating an aqueous coating solution for the treatment of metal surfaces, said concentrate composition being selected from the group consisting of

		<u>Parts by Weight</u>
15	(A)	
	Water	368.5
	H ₃ PO ₄ (75%)	390.0
	HNO ₃ (42°Be)	5.0
	Hydroxylamine Sulfate	35.0
20	MnO	13.5
	ZnO	26.0
	Ni(NO ₃) ₂ (30% Solution)	75.0
	H ₂ SiF ₆ (25%)	80.0
	HF (70%)	7.0
25	(B)	
	Water	315.5
	H ₃ PO ₄ (75%)	390.0
	HNO ₃ (42°Be)	5.0
	Hydroxylamine Sulfate	35.0
	MnO	21.5
	ZnO	26.0
30	Ni(NO ₃) ₂ Solution (30%)	120.0

Parts by Weight

HF(70%)	7.0
H ₂ SiF ₆ (25%)	80.0

- 5 8. An aqueous phosphate coating solution for producing crystalline coatings on a metal surface containing zinc ions, nickel ions, manganese ions and phosphate ions in the percent by weight as follows:
- | | | |
|----|---------------|--------------|
| | phosphate ion | 0.5 to 2.5 |
| | zinc ion | 0.05 to 0.2 |
| 10 | nickel ion | 0.02 to 0.15 |
| | manganese ion | 0.02 to 0.15 |
- 15 and further provided that the ratio of zinc ion to phosphate ion is 1: about 10-25; the ratio of zinc to the sum of manganese and nickel ion is 1:about 0.5-1.5; the ratio of manganese to nickel is 1:about 0.5-1.5 and said coating solution contains from about 0.1 to about 0.25 percent by weight of an hydroxylamine accelerator.
- 20 9. An aqueous phosphate coating solution as defined in Claim 8, wherein the ratio of zinc to phosphate is 1:about 10-15; the ratio of zinc to the sum of manganese and nickel is about 1:1 and the ratio of manganese to nickel is about 1:1.
- 25 10. An aqueous phosphate coating solution as defined in Claim 9, wherein said hydroxylamine sulfate is present in an amount of about 0.17 percent by weight.
- 30 11. An aqueous phosphate coating solution as defined in Claim 9, wherein the ratio of zinc to phosphate is 1:about 13.7.

12. An aqueous phosphate coating solution for producing crystalline coatings on a metal substrate comprising the composition by weight of

		<u>%</u>
5	hydroxylamine sulfate	0.168
	zinc ion	0.10
	nickel ion	0.05
	manganese ion	0.05
	phosphate ion	1.37
10	nitrate ion	0.12
	free fluoride	0.022
	complex fluoride	0.074

13. An aqueous phosphate coating solution for producing crystalline coatings on a metal surface, said composition comprising

- 15
- (a) from about 0.5 to 2 g/l zinc ion
 - (b) from about 5 to 25 g/l phosphate ion
 - (c) from about 0.2 to 1.5 g/l manganese ion
 - (d) from about 0.2 to 1.5 g/l nickel ion
 - 20 (e) From about 1 to 2.5 g/l of an hydroxylamine accelerating agent.
 - (f) 0 to about 1.5 g/l fluoride ion
 - and (g) 0 to about 2 g/l nitrate ion

14. An aqueous phosphate coating composition as defined in Claim 13, wherein said zinc ion is present in an amount of about 0.8 - 1.2 g/l; said phosphate is present in an amount of about 10 - 15 g/l; said manganese ion is present in an amount of about 0.5 - 1 g/l; said nickel ion is present in an amount of about 0.5 to 1 g/l; and said hydroxylamine agent is hydroxylamine sulfate.
- 25
- 30

15. A process for phosphating a metal surface comprising

treating the metal surface with the aqueous coating solution as defined in Claim 8.

- 5
16. A process for phosphating a metal surface comprising treating the metal surface with the aqueous coating solution defined in Claim 12.
17. A process as defined in Claim 16 in which said metal surface is a ferrous, zinc or aluminum surface.
- 10
18. A process for phosphating a metal surface comprising treating said metal surface with the aqueous coating solution defined in Claim 13.
19. A process as defined in Claim 18 and fluoride is present in said coating solution to provide a total fluoride content of 1.5 g/l.
- 15
20. A process as in Claim 18, wherein said surface is aluminum and fluoride is added to said coating solution to provide a free fluoride content of 400 - 600 parts per million.
- 20
21. A process for phosphating a metal surface comprising treating said metal surface with the aqueous coating solution defined in Claim 14.
- 25
22. A replenisher composition for addition to the coating solution as defined in Claim 8 to maintain the appropriate levels of the materials in the coating solution said replenisher composition containing said hydroxylamine accelerator and said zinc, phosphate, manganese and nickel ions in amounts effective, upon addition to said coating solution, to maintain the hydroxylamine accelerator and said zinc, phosphate, manganese and nickel ions, at the appropriate levels for coating, and further
- 30

containing ammonium carbonate or bicarbonate, or ammonium hydroxide, in an amount effective, upon addition of the replenisher, to the coating solution, to maintain the acidity level of the coating solution.

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INTERNATIONAL SEARCH REPORT

PCT/US 92/05861

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C23C22/36; C23C22/18

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

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C23C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 261 597 (CHEMFIL CORPORATION) 30 March 1988 *table 18 page 24-examples 15,16 page 13 see claims 1,4,7,8,11 ---	1-6,8-21
X	EP,A,0 287 133 (METALLGESELLSCHAFT AG) 19 October 1988 see page 3, line 18 - line 27; claims 1,3,5-7 ---	8,9,11, 13,15, 18,19
A	FR,A,2 258 463 (SOCIETE CONTINENTALE PARKER) 18 August 1975 see claims 1,3 ---	22
A	EP,A,0 370 535 (GEHMECKER, HORST) 30 May 1990 --- -/--	

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

23 SEPTEMBER 1992

Date of Mailing of this International Search Report

01. 12. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

LANDAIS A.M.

Landais

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP, A, 0 315 059 (PARKER CHEMICAL COMPANY) 10 May 1989	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9205861
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