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(54) **Solution and process for black chromating**

Lösung und Verfahren zum Schwartzchromationen

Solution et procédé de chromatisation noire

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- **CHEMICAL ABSTRACTS**, vol. 114, no. 12, 25 March 1991 Columbus, Ohio, US; abstract no. 106811c, YANAGAWA: "Black chromating bath for conversion coating of steel strip galvanized with zinc-nickel alloy" page 277; XP000193449 & JP-A-02 097 682 (NIPPON HYOMEN) 10 April 1990

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EP 0 805 222 B1

Description

[0001] The present invention relates to a black chromate solution used for forming a highly anticorrosive black chromate film on a Zn plate, Zn-plating, Zn alloy plating such as Zn-Ni alloy plating, and a method of forming a chromate film thereon, especially on a Zn-Ni alloy.

[0002] The treatment of a zinc plating with a chromate is still widely employed for the purposes of decoration and anticorrosion in the fields of automobiles, domestic electric appliances, etc.

[0003] However, the plating thus formed has defects that the corrosion resistance thereof is yet insufficient under severe conditions when it is kept in an overheated engine room or on an icy road, when it is exposed to a chemical used for removing snow when it snows, or when it is damaged by salty sea breezes. Under these conditions, various Zn alloy platings capable of forming a plating film having a corrosion resistance far superior to that of a zinc plating were investigated and developed. Among them, a high corrosion resistance of a Zn-Ni alloy attracts attention mainly in the automobile field. As a monotony tint and a high grace are inclined to be liked by the users recently, a substance for blacking the Zn-Ni alloy plating is demanded. In addition, there is investigated a black chromate which does not impair the properties of the Zn-Ni alloy plating and further a chemically stable black chromate solution useful when the Ni deposition rate is in the practical range of 3 to 12% by weight. The best technique comprises adding an aliphatic carboxylic acid to an ordinary black chromate solution for treating Zn to form a black chromate film on the Zn-Ni alloy plating. Examples of solutions which comprise an organic acid added to an ordinary black chromate solution are disclosed in JP-A-0297682 and JP-A-04056782.

[0004] However, the process wherein formic acid, citric acid or tartaric acid is used as the aliphatic carboxylic acid has a problem that the treating solution is impractical, since the solution is chemically unstable and the ingredients in the solution tend to be decomposed. The process disclosed in JP-A-04056782 wherein succinic acid is used has a problem that the appearance thereof is yet insufficient in the blackness and gloss, though the treating solution is chemically stable.

[0005] The use of soluble silver compounds in a solution for treating Zn, Zn/Mg and Cd/Mg to form a black chromate film is disclosed in GB-A-618667.

[0006] A primary object of the present invention is to provide a chemically stable black chromate solution capable of forming a highly anticorrosive black chromate film on a Zn-plating, Zn alloy plating and the like, the components being easily soluble in the solution.

[0007] Another object of the present invention is to provide a method of forming a black chromate film on a Zn-Ni alloy.

[0008] These and other objects of the present invention will be apparent from the following description and examples.

[0009] The present invention has been completed on the basis of a finding that the above-described problems can be efficiently solved by using a sulfo-aromatic carboxylic acid, its salt, sulfonated aliphatic dicarboxylic acid or its salt as the organic acid to be contained in the black chromate solution.

[0010] Namely, the present invention provides a black chromate solution which comprises hexavalent chromium, sulfate ions, soluble silver, a carboxylic acid, and water; characterised in that the carboxylic acid is a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids, sulfonated aliphatic dicarboxylic acids and salts thereof.

[0011] The present invention further provides a method of forming a black chromate film on a Zn-Ni alloy plating which comprises immersing the Zn-Ni alloy plating into a black chromate solution comprising hexavalent chromium, sulfate ions, soluble silver, a carboxylic acid and water; characterised in that the carboxylic acid is a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids, sulfonated aliphatic dicarboxylic acids and salts thereof.

[0012] Examples of the sulfo-aromatic carboxylic acids usable in the present invention include those having 7 to 15 carbon atoms such as sulfobenzoic acid, sulfophthalic acid, sulfoterephthalic acid and sulfonated naphthalic acid. The sulfonated aliphatic dicarboxylic acids include, for example, those having 3 to 10 carbon atoms such as sulfonated succinic acid and adipic acid. The salt of them may be any of those soluble in the black chromate solution. Examples of the salts include sodium and ammonium salts.

[0013] The sulfonated carboxylic acids can be used either singly or in the form of a mixture of two or more of them in the present invention. Although the amount of the sulfonated carboxylic acid is not particularly limited, it is preferable that the concentration thereof in the black chromate solution be 0.5 to 100 g/l, more preferably 5 to 40 g/l.

[0014] The black chromate solution of the present invention contains hexavalent chromium, sulfate ion (SO_4^{2-}) and soluble silver. Compounds usable as the hexavalent chromium source are, for example, chromic acid, salts thereof, bichromic acid, salts thereof and mixtures of two or more of them. The compounds for forming the sulfate ion include sulfuric acid, salts thereof (such as sodium, potassium and ammonium salts thereof) and mixtures of two or more of them. The compounds for forming the soluble silver include, for example, silver sulfate.

[0015] The black chromate solution of the present invention can contain these components in optional amounts. Preferably, it contains 1 to 50 g/l of hexavalent chromium, 1 to 50 g/l of sulfate ion, 0.05 to 1.0 g/l of soluble silver and

0.5 to 100 g/l of the sulfonated carboxylic acid. The pH of the black chromate solution of the present invention is preferably controlled in the range of 0.5 to 2.5. The weight ratio of the sulfate ion to hexavalent chromium is preferably in the range of from 0.2 to 2.0.

[0016] The black chromate solution of the present invention contains water as the balance. Further, amines such as methylamine, ethylenediamine and diethylenetriamine can be incorporated into the solution.

[0017] The black chromate solution of the present invention is effective in forming a black chromate film on a Zn-Ni alloy plating having any composition. It exhibits an excellent effect particularly when a black chromate film is formed on a Zn-Ni alloy plating having a Ni deposition rate of not higher than 15% by weight, preferably in the range of 3 to 12 % by weight. Namely, when the black chromate film is to be conventionally formed on the Zn-Ni alloy plating of this composition, the formed film, even when it can be obtained, is not uniform and the corrosion resistance is seriously impaired, since the pH is rapidly increased at the boundary (interface) between them. On the contrary, in the present invention wherein the specified sulfonated carboxylic acid is used, the interface formed by the chromate film is exposed to a stable pH atmosphere to make the stable formation of the film possible. Thus, the high anticorrosive function of the Zn-Ni alloy plating is not impaired, and further, more excellent anticorrosive effect can be obtained.

[0018] The treatment with the black chromate is usually conducted by immersing the substrate to be treated in the black chromate solution of the present invention. For example, the substrate is immersed in the solution having a temperature of 15 to 50°C for 30 to 300 seconds, preferably 30 to 180 seconds to form a black chromate film having a thickness of 0.5 to 3 μm , preferably 1 to 2 μm .

[0019] Thus, in a preferred embodiment, the substrate is plated with a Zn-Ni alloy (Ni deposition rate: preferably 3 to 12 % by weight) (thickness of the plating: at least 2 μm , preferably 5 to 20 μm) and then the black chromate film is formed by the above-described process.

[0020] By the process of the present invention, the black chromate film can be uniformly formed on the Zn-Ni alloy plating. Since the specified sulfonated carboxylic acid exhibits a buffer action under chromic acid-acidic conditions in a pH range of 1 to 3.5, the uniform black chromate film can be formed and, as a result, the corrosion resistance can be improved and excellent stability can be obtained.

[0021] Therefore, the products obtained by forming the black chromate film by the process of the present invention can be widely used in the fields of automobiles, domestic electric appliances, building materials and parts, etc.

[0022] The following Examples will further illustrate the present invention.

Example 1

[0023] A steel plate plated with a Zn-Ni alloy (Ni content: 3, 5, 7, 9, 12 or 15 % by weight) in a thickness of 8 μm was immersed in a chromate solution having a composition given below at 25°C for 90 seconds. As a result, an excellent black chromate film was formed when the Ni content was 3, 5, 7, 9 or 12 % and, on the contrary, a black chromate film having an interference color was obtained when the Ni content was 15 %.

CrO ₃	10 g/l
Na ₂ SO ₄	15 g/l
AgNO ₃	0.8 g/l
sulfonaphthalic acid	7 g/l
water	balance
pH	1.3 (adjusted with NaOH).

Example 2

[0024] A Zn-Ni plating having a thickness of 6 μm and Ni content of 6 % was treated with a chromate solution having the following composition at 20°C for 3 minutes to obtain a uniform black chromate film:

CrO ₃	5 g/l
Na ₂ Cr ₂ O ₇ · 2H ₂ O	20 g/l
Na ₂ SO ₄	25 g/l
H ₂ SO ₄	2 g/l
Ag ₂ SO ₄	0.5 g/l
sulfoterephthalic acid	3 g/l
water	balance
pH	1.6 (adjusted with NaOH).

Example 3

[0025] A Zn-Ni plating having a thickness of 10 μm and Ni content of 8 % was treated with a chromate solution having the following composition at 25 °C for 2 minutes to obtain a uniform black chromate film:

Na ₂ Cr ₂ O ₇ · 2H ₂ O	15 g/l
H ₂ SO ₄	5 g/l
Ag ₂ SO ₄	0.5 g/l
sodium salt of sulfonated adipic acid	15 g/l
water	balance
pH	1.5 (adjusted with NaOH).

Comparative Example 1

[0026] A steel plate was plated with Zn to form a plating film having 8 μm thickness. The plate was then treated with a black chromate solution ZB-547 (a product provided by Dipsol Chemical Co., Ltd.) for Zn plating at 25 °C for 1 minute.

[0027] Table 1 shows the results of the corrosion resistance tests of the products having the black chromate film obtained in above Examples 1 to 3 and Comparative Example 1 (the salt water spray test was conducted according to JIS 2371).

Table 1

	Kind of plating	Ni content (%)	Plating thickness (μm)	Tint
Ex. 1	Zn-Ni	3	8	uniform black
	ditto	5	ditto	ditto
	ditto	7	ditto	ditto
	ditto	9	ditto	ditto
	ditto	12	ditto	ditto
	ditto	15	ditto	black having inter- ference color
Ex. 2	Zn-Ni	6	6	uniform black
Ex. 3	Zn-Ni	8	10	ditto
Comp. Ex. 1	Zn	0	8	ditto

Table 1 (continued)

<u>Salt water spray test</u>		
	Time taken for white	Time taken for red
	rust formation (h)	rust formation (h)
Ex. 1	at least 500	at least 2000
	ditto	ditto
	ditto	ditto
	ditto	ditto
	ditto	ditto
	ditto	ditto
Ex. 2	ditto	ditto
Ex. 3	ditto	ditto
Comp. Ex. 1	144	600

Claims

1. A black chromate solution which comprises hexavalent chromium, sulfate ions, soluble silver, a carboxylic acid, and water; characterised in that the carboxylic acid is a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids, sulfonated aliphatic dicarboxylic acids and salts thereof.
2. A chromate solution as claimed in claim 1 wherein the sulfo-aromatic carboxylic acids or salts thereof have from 7 to 15 carbon atoms.
3. A chromate solution as claimed in claim 1 wherein the sulfonated aliphatic dicarboxylic acids or salts thereof have from 3 to 10 carbon atoms.
4. A chromate solution as claimed in any one of the preceding claims which comprises in the range of from 1 to 50 g/l of hexavalent chromium, 1 to 50 g/l of sulfate ion, 0.05 to 1.0 g/l of soluble silver and 0.5 to 100 g/l of the sulfonated carboxylic acid.
5. A chromate solution as claimed in any one of the preceding claims wherein the pH of the solution is in the range of from 0.5 to 2.5.
6. A chromate solution as claimed in any one of the preceding claims wherein the weight ratio of the sulfate ion to hexavalent chromium is in the range of from 0.2 to 2.0.

7. A black chromate solution as claimed in claim 1 which comprises in the range of from 1 to 50 g/l of hexavalent chromium, 1 to 50 g/l of sulfate ion, 0.05 to 1.0 g/l of soluble silver, 0.5 to 100 g/l of a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids having from 7 to 15 carbon atoms, sulfonated aliphatic dicarboxylic acids having from 3 to 10 carbon atoms and salts thereof, and water, the solution having a pH in the range of from 0.5 to 2.5.
8. A method of forming a black chromate film on a Zn-Ni alloy plating which comprises immersing the Zn-Ni alloy plating into a black chromate solution comprising hexavalent chromium, sulfate ions, soluble silver, a carboxylic acid, and water; characterised in that the carboxylic acid is a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids, sulfonated aliphatic dicarboxylic acids and salts thereof.
9. A method as claimed in claim 8 wherein the Zn-Ni alloy plating contains not more than approximately 15 % by weight of Ni.
10. A method as claimed in claim 8 or claim 9 wherein the Zn-Ni alloy plating is immersed in the solution having a temperature in the range of from 15 to 50 °C for from 30 to 300 seconds.
11. A method as claimed in any one of claims 8 to 10 wherein the sulfo-aromatic carboxylic acids or salts thereof have from 7 to 15 carbon atoms.
12. A method as claimed in any one of claims 8 to 10 wherein the sulfonated aliphatic dicarboxylic acids or salts thereof have from 3 to 10 carbon atoms.
13. A method as claimed in any one of claims 8 to 12 wherein the black chromate solution comprises in the range of from 1 to 50 g/l of hexavalent chromium, 1 to 50 g/l of sulfate ion, 0.05 to 1.0 g/l of soluble silver and 0.5 to 100 g/l of the sulfonated carboxylic acid, the solution having a pH in the range of from 0.5 to 2.5.
14. A method as claimed in any one of claims 8 to 13 wherein a weight ratio of the sulfate ion to hexavalent chromium is in the range of from 0.2 to 2.0.
15. A method of forming a black chromate film on a Zn-Ni alloy plating as claimed in claim 8 which comprises immersing the Zn-Ni alloy plating into a black chromate solution comprising in the range of from 1 to 50 g/l of hexavalent chromium, 1 to 50 g/l of sulfate ion, 0.05 to 1.0 g/l of soluble silver, 0.5 to 100 g/l of a sulfonated carboxylic acid selected from the group consisting of sulfo-aromatic carboxylic acids having from 7 to 15 carbon atoms, sulfonated aliphatic dicarboxylic acids having from 3 to 10 carbon atoms and salts thereof, and water, the solution having a pH in the range of from 0.5 to 2.5, at a temperature in the range of from 15 to 50 °C for from 30 to 300 seconds.
16. A method as claimed in claim 15 wherein the Zn-Ni alloy plating contains not more than approximately 15 % by weight of Ni.
17. A method as claimed in claim 15 or claim 16 wherein the Zn-Ni alloy plating contains in the range of from 3 to 12 % by weight of Ni.

Patentansprüche

1. Schwarzchromatlösung, welche sechswertiges Chrom, Sulfationen, lösliches Silber, eine Carbonsäure und Wasser umfaßt; **dadurch gekennzeichnet**, daß die Carbonsäure eine sulfonierte Carbonsäure ist, ausgewählt aus der Gruppe bestehend aus sulfo-aromatischen Carbonsäuren, sulfonierten aliphatischen Dicarbonsäuren und Salzen davon.
2. Chromatlösung nach Anspruch 1, worin die sulfo-aromatischen Carbonsäuren oder Salze davon 7 bis 15 Kohlenstoffatome aufweisen.
3. Chromatlösung nach Anspruch 1, worin die sulfonierten aliphatischen Dicarbonsäuren oder Salze davon 3 bis 10 Kohlenstoffatome aufweisen.
4. Chromatlösung nach einem der vorangehenden Ansprüche, welche im Bereich von 1 bis 50 g/l sechswertiges

Chrom, 1 bis 50 g/l Sulfationen, 0,05 bis 1,0 g/l lösliches Silber und 0,5 bis 100 g/l der sulfonierten Carbonsäure umfaßt.

5 5. Chromatlösung nach einem der vorangehenden Ansprüche, worin der pH der Lösung im Bereich von 0,5 bis 2,5 liegt.

6. Chromatlösung nach einem der vorangehenden Ansprüche, worin das Gewichtsverhältnis des Sulfations zu sechswertigem Chrom im Bereich von 0,2 bis 2,0 liegt.

10 7. Schwarzchromatlösung nach Anspruch 1, welche im Bereich von 1 bis 50 g/l sechswertiges Chrom, 1 bis 50 g/l Sulfationen, 0,05 bis 1,0 g/l lösliches Silber, 0,5 bis 100 g/l einer sulfonierten Carbonsäure, ausgewählt aus der Gruppe bestehend aus sulfo-aromatischen Carbonsäuren mit 7 bis 15 Kohlenstoffatomen, sulfonierten aliphatischen Dicarbonsäuren mit 3 bis 10 Kohlenstoffatomen und Salzen davon, und Wasser umfaßt, wobei die Lösung einen pH im Bereich von 0,5 bis 2,5 aufweist.

15 8. Verfahren zum Bilden eines Schwarzchromatfilms auf einer Zn-Ni-Legierungs-Überzugsschicht, welches das Eintauchen der Zn-Ni-Legierungs-Überzugsschicht in eine Schwarzchromatlösung umfaßt, die sechswertiges Chrom, Sulfationen, lösliches Silber, eine Carbonsäure und Wasser umfaßt; **dadurch gekennzeichnet**, daß die Carbonsäure eine sulfonierte Carbonsäure ist, ausgewählt aus der Gruppe bestehend aus sulfo-aromatischen Carbonsäuren, sulfonierten aliphatischen Dicarbonsäuren und Salzen davon.

20 9. Verfahren nach Anspruch 8, worin die Zn-Ni-Legierungs-Überzugsschicht nicht mehr als ungefähr 15 Gew.-% Ni enthält.

25 10. Verfahren nach Anspruch 8 oder Anspruch 9, worin die Zn-Ni-Legierungs-Überzugsschicht in die Lösung mit einer Temperatur im Bereich von 15 bis 50°C 30 bis 300 Sekunden lang eingetaucht wird.

30 11. Verfahren nach einem der Ansprüche 8 bis 10, worin die sulfo-aromatischen Carbonsäuren oder Salze davon 7 bis 15 Kohlenstoffatome aufweisen.

35 12. Verfahren nach einem der Ansprüche 8 bis 10, worin die sulfonierten aliphatischen Dicarbonsäuren oder Salze davon 3 bis 10 Kohlenstoffatome aufweisen.

40 13. Verfahren nach einem der Ansprüche 8 bis 12, worin die Schwarzchromatlösung im Bereich von 1 bis 50 g/l sechswertiges Chrom, 1 bis 50 g/l Sulfationen, 0,05 bis 1,0 g/l lösliches Silber und 0,5 bis 100 g/l der sulfonierten Carbonsäure umfaßt, wobei die Lösung einen pH im Bereich von 0,5 bis 2,5 aufweist.

45 14. Verfahren nach einem der Ansprüche 8 bis 13, worin das Gewichtsverhältnis der Sulfationen zu sechswertigem Chrom im Bereich von 0,2 bis 2,0 liegt.

50 15. Verfahren zum Bilden eines Schwarzchromatfilms auf einer Zn-Ni-Legierungs-Überzugsschicht nach Anspruch 8, welches das 30 bis 300 Sekunden lange Eintauchen der Zn-Ni-Legierungs-Überzugsschicht in eine Schwarzchromatlösung, die im Bereich von 1 bis 50 g/l sechswertiges Chrom, 1 bis 50 g/l Sulfationen, 0,05 bis 1,0 g/l lösliches Silber, 0,5 bis 100 g/l einer sulfonierten Carbonsäure, ausgewählt aus der Gruppe bestehend aus sulfo-aromatischen Carbonsäuren mit 7 bis 15 Kohlenstoffatomen, sulfonierten aliphatischen Dicarbonsäuren mit 3 bis 10 Kohlenstoffatomen und Salzen davon, und Wasser umfaßt, wobei die Lösung einen pH im Bereich von 0,5 bis 2,5 aufweist, bei einer Temperatur im Bereich von 15 bis 50°C umfaßt.

55 16. Verfahren nach Anspruch 15, worin die Zn-Ni-Legierungs-Überzugsschicht nicht mehr als ungefähr 15 Gew.-% Ni enthält.

17. Verfahren nach Anspruch 15 oder Anspruch 16, worin die Zn-Ni-Legierungs-Überzugsschicht im Bereich von 3 bis 12 Gew.-% Ni enthält.

Revendications

1. Solution de chromate noir, qui comprend du chrome hexavalent, des ions sulfate, de l'argent soluble, un acide

carboxylique et de l'eau; caractérisée en ce que l'acide carboxylique est un acide carboxylique sulfoné, choisi dans le groupe constitué par les acides carboxyliques sulfo-aromatiques, les acides dicarboxyliques sulfonés aliphatiques et leurs sels.

- 5 **2.** Solution de chromate telle que revendiquée dans la revendication 1, dans laquelle les acides carboxyliques sulfo-aromatiques ou leurs sels comportent de 7 à 15 atomes de carbone.
- 3.** Solution de chromate telle que revendiquée dans la revendication 1, dans laquelle les acides dicarboxyliques sulfonés aliphatiques ou leurs sels comportent de 3 à 10 atomes de carbone.
- 10 **4.** Solution de chromate telle que revendiquée dans l'une quelconque des revendications précédentes, qui comprend dans la gamme de 1 à 50 g/l de chrome hexavalent, de 1 à 50 g/l d'ions sulfate, de 0,05 à 1,0 g/l d'argent soluble et de 0,5 à 100 g/l d'acide carboxylique sulfoné.
- 15 **5.** Solution de chromate telle que revendiquée dans l'une quelconque des revendications précédentes, dans laquelle le pH de la solution est dans la gamme comprise entre 0,5 et 2,5.
- 6.** Solution de chromate telle que revendiquée dans l'une quelconque des revendications précédentes, dans laquelle le rapport en poids entre les ions sulfate et le chrome hexavalent est dans la gamme comprise entre 0,2 et 2,0.
- 20 **7.** Solution de chromate telle que revendiquée dans la revendication 1, qui comprend dans la gamme de 1 à 50 g/l de chrome hexavalent, de 1 à 50 g/l d'ions sulfate, de 0,05 à 1,0 g/l d'argent soluble, de 0,5 à 100 g/l d'un acide carboxylique sulfoné, choisi dans le groupe constitué par les acides carboxyliques sulfo-aromatiques ayant de 7 à 15 atomes de carbone, les acides dicarboxyliques sulfonés aliphatiques ayant de 3 à 10 atomes de carbone et leurs sels, et de l'eau, la solution ayant un pH dans la gamme comprise entre 0,5 et 2,5.
- 25 **8.** Procédé de formation d'un film de chromate noir sur un revêtement en alliage Zn-Ni, qui comprend l'immersion du revêtement en alliage Zn-Ni dans une solution de chromate noir, qui comprend du chrome hexavalent, des ions sulfate, de l'argent soluble, un acide carboxylique et de l'eau; caractérisé en ce que l'acide carboxylique est un acide carboxylique sulfoné, choisi dans le groupe constitué par les acides carboxyliques sulfo-aromatiques, les acides dicarboxyliques sulfonés aliphatiques et leurs sels.
- 30 **9.** Procédé tel que revendiqué dans la revendication 8, dans lequel le revêtement en alliage Zn-Ni ne contient pas plus d'environ 15 % en poids de Ni.
- 35 **10.** Procédé tel que revendiqué dans la revendication 8 ou la revendication 9, dans lequel le revêtement en alliage Zn-Ni est immergé dans la solution ayant une température dans la gamme comprise entre 15 et 50°C, pendant 30 à 300 secondes.
- 40 **11.** Procédé tel que revendiqué dans l'une quelconque des revendications 8 à 10, dans lequel les acides carboxyliques sulfo-aromatiques ou leurs sels comportent de 7 à 15 atomes de carbone.
- 12.** Procédé tel que revendiqué dans l'une quelconque des revendications 8 à 10, dans lequel les acides dicarboxyliques sulfonés aliphatiques ou leurs sels comportent de 3 à 10 atomes de carbone.
- 45 **13.** Procédé tel que revendiqué dans l'une quelconque des revendications 8 à 12, dans lequel la solution de chromate noir comprend dans la gamme de 1 à 50 g/l de chrome hexavalent, de 1 à 50 g/l d'ions sulfate, de 0,05 à 1,0 g/l d'argent soluble et de 0,5 à 100 g/l d'acide carboxylique sulfoné, la solution ayant un pH dans la gamme comprise entre 0,5 et 2,5.
- 50 **14.** Procédé tel que revendiqué dans l'une quelconque des revendications 8 à 13, dans lequel le rapport en poids entre les ions sulfate et le chrome hexavalent est dans la gamme comprise entre 0,2 et 2,0.
- 55 **15.** Procédé de formation d'un film de chromate noir sur un revêtement en alliage Zn-Ni tel que revendiqué dans la revendication 8, qui comprend l'immersion du revêtement en alliage Zn-Ni dans une solution de chromate noir comprenant dans la gamme de 1 à 50 g/l de chrome hexavalent, de 1 à 50 g/l d'ions sulfate, de 0,05 à 1,0 g/l d'argent soluble, de 0,5 à 100 g/l d'acide carboxylique sulfoné, choisi dans le groupe constitué par les acides carboxyliques sulfo-aromatiques ayant de 7 à 15 atomes de carbone, les acides dicarboxyliques sulfonés alipha-

EP 0 805 222 B1

tiques ayant de 3 à 10 atomes de carbone et leurs sels, et de l'eau, la solution ayant un pH dans la gamme comprise entre 0,5 et 2,5, à une température dans la gamme comprise entre 15 et 50°C pendant 30 à 300 secondes.

5 **16.** Procédé tel que revendiqué dans la revendication 15, dans lequel le revêtement en alliage Zn-Ni ne contient pas plus d'environ 15 % en poids de Ni.

17. Procédé tel que revendiqué dans la revendication 15 ou la revendication 16, dans lequel le revêtement en alliage Zn-Ni contient dans la gamme de 3 à 12 % en poids de Ni.

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