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(54) **Titre : SUBSTRAT DOTE D'UN REVETEMENT RESISTANT A LA CORROSION ET SON PROCEDE DE PRODUCTION**
(54) **Title: SUBSTRATE WITH A CORROSION RESISTANT COATING AND METHOD OF PRODUCTION THEREOF**

(57) **Abrégé/Abstract:**
The invention relates to a substrate with a corrosion resistant coating comprising at least one nickel layer and at least one chromium layer as finish. Between these layers, at least one tin-nickel alloy layer is deposited for suppression of corrosion reactions determined by CASS and Russian mud tests. The invention relates also to a method for producing such substrates with corrosion resistant coating.

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(54) **Title**: SUBSTRATE WITH A CORROSION RESISTANT COATING AND METHOD OF PRODUCTION THEREOF

(57) **Abstract**: The invention relates to a substrate with a corrosion resistant coating comprising at least one nickel layer and at least one chromium layer as finish. Between these layers, at least one tin-nickel alloy layer is deposited for suppression of corrosion reactions determined by CASS and Russian mud tests. The invention relates also to a method for producing such substrates with corrosion resistant coating.

Substrate with a corrosion resistant coating and method of production thereof

The invention relates to a substrate with a corrosion resistant coating which comprises at least one nickel layer and, as finish, at least one chromium layer. Between these layers, a tin-nickel alloy layer is deposited for suppression of corrosion reactions. The invention also relates to a method of production of such substrates with corrosion resistant coating.

By means of the present invention, the corrosion resistance of articles having a metal finish on a chromium basis is considerably increased.

In the state of the art, different methods are known which lead to an increase in corrosion resistance of articles having a chromium coating as decorative finish. Such items can be plastic parts, brass articles, aluminium alloys and zinc die cast parts or also

steel bodies. These parts having a chromium coating are applied in many areas, in particular in sanitary facilities, automotive and aerospace.

Electrolytic chromium and nickel depositions are generally chosen for realizing of a high corrosion resistance. In this regard, the nickel layer is divided in three different types. The first type is known as semi-bright nickel layer or sulfur-free layer, because it is a semi-bright layer having a sulfur content < 0.005 weight-%. These layers have a higher electrochemical potential than bright nickel layers.

On top of the semi-bright nickel layer, a bright nickel layer is regularly electroplated. This leads to a bright appearance of the coated articles. These layers have a sulfur content of more than 0.03 weight-%.

The last nickel layer is a layer which has small disruptions on a micro-scale. This layer can comprise micro-particles or organic additives and can be coated with a chromium layer which has a micro-porous layer or a layer with micro cracks. These layers are usually nobler than bright nickel layers i.e. their potential is higher than that of bright nickel layers. Such coatings are known from US 3,268,424 and US 3,563,864. In these applications, the main aim is to decrease galvanic corrosion between chromium and nickel. The chromium layer is thereby electroplated as finish with an electrolyte comprising hexavalent chromium.

A further process is known which increases corrosion protection of the above-mentioned parts described before which are electroplated. In this regard,

EP 1 343 924 B1 discloses a layer of silver or silver alloy which is located between the chromium and nickel layer. It is a problem that very toxic cyanide salts are used in the process which represent a serious threat for health and safety and are therefore no longer acceptable with regard to environmental aspects. Furthermore, silver as noble metal demonstrates two important disadvantages which are the high cost as well as the significant difference of the electrochemical potential in comparison to a bright nickel layer.

Different electrolytes based on trivalent chromium have been developed for the deposition of chromium layers over the years to prevent the use of environmentally precarious hexavalent chromium. Such processes are disclosed in EP 0 058 044 and GB 1 455 580. Trivalent chromium electrolytes have been used for years as decorative coatings, but show the disadvantage that they do not demonstrate sufficient corrosion resistance because it is not a pure chromium layer, but a special alloy comprising constituents of chromium, carbon, iron, sulfur, oxygen and nitrogen and thus have structural features different to pure chromium. Commonly, the UNI EN ISO 9227 CASS standard procedure (so-called CASS test) is applied for the investigation of the corrosion resistance of coated parts. In this test, the corrosion resistance (in hours) is measured in a room filled with salt spray at 50 °C, wherein the salt consists of a sodium chloride solution which comprises copper ions with acetic acid (pH 3).

In recent years, a new test procedure has been introduced in the automotive industry to solve the problem that calcium chloride is used as antifreeze on frozen

streets in northern countries. It turned out that calcium chloride reacts very aggressively with chromium covered parts. This is the reason why identical tests were introduced by e.g. Volkswagen (VW PV1067) and Nissan (NES M4063) (so-called „Russian Mud test"), in which the resistance of chrome deposited parts can be determined by using calcium chloride in the corrosion test.

Starting herefrom, it was the object of the present invention to provide a method in which the corrosion protection of articles with a chromium finish can be improved compared to systems known from the prior art. At the same time, the method should be easily applicable.

The problem is solved by the substrate with corrosion resistant coating with the features of claim 1 and the method for production of said substrates with the features of claim 10. The further dependent claims reveal advantageous embodiments thereof.

According to the invention, a substrate with a corrosion resistant coating is provided which comprises at least one nickel layer and at least one chromium layer as finish. Between a nickel layer and a proximate chromium layer, at least one tin-nickel alloy layer is deposited for the suppression of corrosion reactions.

In the context of the present invention a suppression of corrosion reactions also means an essential or significant reduction of corrosion reactions.

The inventive idea for increasing corrosion resistance is based on replacing the prior art nickel

layer having micro-scale disruptions with a tin-nickel alloy layer. This tin-nickel alloy layer enables the use of a variety of chromium-containing electrolytes for galvanic deposition of a chromium finish. Tin-nickel alloys with an increased amount of tin have good corrosion resistance and are often used as coating for prevention of surface clouding.

According to the invention it is provided that the corrosion rate between nickel and chromium layers during the corrosion test UNI EN ISO 9227 NSS or UNI EN ISO 9227 CASS (so-called CASS test) can be reduced. The present invention allows that corrosion, which arises due to the use of antifreeze and particularly affects automotive components which are exposed to the weather during winter, can be drastically reduced. Hence, significantly improved results could be achieved in the mentioned standard tests of VW (VW PV1067) and Nissan (NES M4063) compared to methods for corrosion protection known in the prior art.

According to the invention the tin-nickel alloy layer comprises preferably 55 to 75 weight-%, more preferably 60 to 70 weight-% and most preferably 64 to 68 weight-% tin and preferably 45 to 25 weight-%, more preferably 40 to 30 weight-% and most preferably 36 to 32 weight-% nickel. A layer of this alloy has a grey-pink color, as it is known from the ISO 2179:1986 standard.

The tin-nickel alloy layer preferably has a thickness in the range of 0.1 µm to 10 µm, more preferably 0.2 µm to 6 µm and most preferably 0.5 µm to 5 µm.

The at least one nickel layer preferably has a thick-

ness of 1 to 50 µm. The at least one chromium layer preferably has a thickness of 0.05 to 2 µm.

It is further preferred that the coating consists of a bright nickel layer which is deposited on the substrate or a further metallic layer as well as the tin-nickel alloy layer and the chromium layer. The further metallic layer herewith preferably consists of copper or essentially comprises copper. Furthermore, it is preferred that a further semi-bright nickel layer is arranged between the bright nickel layer and the substrate or the further metallic layer.

The inventive coating can be combined with almost any number of substrate materials. Among these are in particular substrates of a metal or a metal alloy, particularly steel, brass or an aluminium alloy. Similarly, zinc die cast elements can be provided with the inventive coating. Further materials are selected from the group consisting of plastics, in particular acrylnitril-butadien-styrol (ABS), acrylnitril-butadien-styrol/polycarbonate (ABS-PC), polypropylene (PP) or polyamide (PA).

According to the invention, also a method is provided for the production of a corrosion resistant coating for a substrate, wherein the following layers are electroplated on the substrate subsequently:

a) at least one nickel layer;
b) at least one layer of a tin-nickel alloy;
c) at least one chromium layer.

It is preferred that c) is one chromium layer which is a electroplated finish, i.e. the last electroplat-

ed layer of the corrosion resistant coating. This does not exclude that at least one further non-metallic layer is deposited on the chromium finish, e.g. an organic or inorganic passivation or a sealing.

There are arbitrary variants for carrying out the method which lead to the desired result.

A first preferred variant provides that the at least one tin-nickel alloy layer is electroplated from an acidic aqueous electrolyte with a pH in the range of 2 to 6. The electrolyte comprises at least one tin salt and at least one nickel salt. Furthermore, the electrolyte can comprise fluorides or chlorides which act as activators of the nickel layer for an improved adhesion of the tin-nickel alloy layer on the nickel layer. Moreover, fluoroborates, methanesulfonate and sulfates can be comprised.

Another preferred variant provides that the at least one tin-nickel alloy layer is electroplated from an alkaline aqueous electrolyte, wherein the electrolyte comprises at least one tin salt and at least one nickel salt and the salts are particularly selected from the group consisting of sulfates, sulfamates, phosphates, pyrophosphate, glycine, and mixtures thereof.

Another preferred embodiment provides that the at least one tin-nickel alloy layer is electroplated from a neutral aqueous electrolyte, wherein the electrolyte comprises at least one tin salt and at least one nickel salt and the salts are particularly selected from the group consisting of sulfates, sulfamates, phosphates, pyrophosphate, glycine, and

mixtures thereof.

A further preferred embodiment provides that the at least one tin-nickel alloy layer is electroplated from a cyanide-containing aqueous electrolyte, wherein the electrolyte comprises at least one tin salt and at least one nickel salt are particularly selected from the group consisting of sulfates, sulfamates, phosphates, pyrophosphate, glycine, and mixtures thereof.

The cyanide containing electrolyte can comprise the following further additives:

- sodium stannate, potassium stannate, sodium cyanide, potassium cyanide, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate;
- sodium tartrate, potassium tartrate, sodium gluconate, and
- amphoteric, anionic or non-ionic surfactants.

The above-mentioned aqueous electrolytes for tin-nickel can comprise the following further additives:

- tin methane sulfonate, tin pyrophosphate, tin sulfate, sodium stannate;
- conducting salts, as sodium methane sulfonate, sodium pyrophosphate, potassium pyrophosphate, sodium sulfate, potassium sulfate, sodium carbonate, potassium carbonate, sodium phosphate, potassium phosphate;
- complexing agents, preferably amines, polyamines, preferably selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine,

- aminoethylethanolamine, triethanolamine, diethanolamine, monoethanolamine, as well as their combinations with organic acids, preferably selected from the group consisting of citric acid, tartaric acid and lactic acid;
- wetting agents, as amphoteric, anionic, cationic or non-ionic surfactants;
- antioxidants, as hydrochinone or benz-catechin;
- methane sulphonic acid, boric acid, malic acid, tartaric acid, gluconic acid, phosphonic acids, aminophosphonic acids and sodium or potassium salts thereof.

The tin salts used according to the invention are preferably selected from the group consisting of chlorides, fluorides, fluoroborates, sulfates, methane sulfonates and mixtures thereof and the nickel salt is preferably selected from the group consisting of chlorides, fluorides, fluoroborates, sulfates, sulfamates, pyrophosphates, methane sulfonates, and mixtures thereof.

Regarding the deposition of the chromium finish, preferably an electroplating from an acidic aqueous electrolyte is carried out, wherein the electrolyte comprises chromium(VI)-salts, in particular chromic acid.

A further variant provides that the electroplating of the chromium finish is carried out from an acidic aqueous electrolyte with a pH in the range of 2 to 6, wherein the electrolyte comprises chromium(III)-salts, in particular chromium(III)-sulfate or chromium(III)-chloride, which are preferred because of environmental aspects. In this variant, the electrolyte may comprise further additives selected from the group consisting of: (a) organic acids, in particular formic acid, acetic acid, aminoacetic acid, oxalic acid, malic acid, aspartic acid, and salts thereof; (b) inorganic acids, in particular boric acid, hydrochloric acid, sulfuric acid, and salts thereof; (c) conducting salts, in particular sodium chloride, potassium chloride, ammonium chloride, sodium sulfate, potassium sulfate, ammonium sulfate, sodium bromide, potassium bromide, ammonium bromide, iron sulfate, iron chloride or sodium hypophosphite; (d) additives including blackening agents, in particular thiourea and other organo-sulphur compounds, urea, sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, saccharin sodium salt, sodium vinylsulfonate, cationic polymers; (e) wetting agents, in particular amphoteric, anionic, cationic or non-ionic surfactants.

Regarding the elementary components, the chromium deposit can comprise 1 to 25 weight-% carbon, 1 to 30

weight-% oxygen, 0 to 10 weight-% sulfur, 0 to 10 weight-% nitrogen and 0 to 30 weight-% iron.

With reference to the following figures and subsequent examples, the subject matter according to the invention is intended to be explained in more detail without restricting said subject to the special embodiments shown therein.

Fig. 1 shows different combinations of the inventive substrate coating.

Fig. 2 shows a 100-fold magnification of a microscopic image of the surface produced according to example C (as it is known from the prior art) before carrying out the CASS test. Micropores are recognizable herein which are attributed to the nickel layer having micro-scale disruptions.

Fig. 3 shows a 100-fold magnification of a microscopic image of an inventive surface produced according to example D before performing the CASS test.

Fig. 4 shows a 100-fold magnification of a microscopic image of an inventive surface produced according to example C after 96 hours in the CASS test. The surface according to example C has strongly changed its appearance compared to the surface shown in Fig. 2, which indicates increased corrosion.

Fig. 5 shows a 100-fold magnification of a microscopic image of an inventive surface produced according to example D after 96 hours in the CASS test. The surface according to example D has changed its appearance only marginal in contrast to the surface produced according to example C which illustrates the

drastically improved corrosion resistance of the inventive coatings compared to the coatings known in the prior art.

Examples

Formed parts of acrylonitrile-butadienestyrene (ABS) with a size of 5 to 7 cm were initially subjected to a preliminary processing to render the surface conductive for galvanic deposition.

Subsequently, a nickel layer having micro-scale disruptions was deposited according to the prior art (as it is known from US 3,268,424) with the following composition and following parameters:

$NiSO_4*6H_2O$	200-300 g/l
$NiCl_2*6H_2O$	20-80 g/l
H_3BO_3	30-80 g/l
kaolin (fine powder)	0.1-1.5 g/l
pH	3-5
temperature	40-60°C

These nickel-coated parts were used as comparison for the coatings according to the invention.

The coatings according to the invention were deposited from an electrolyte with the following composition and parameters:

$NiCl_2*6H_2O$	200-300 g/l
NH_4HF_2	30-80 g/l
$SnCl_2*2H_20$	20-60 g/l
pH	2-5
temperature	40-60°C

In a further inventive embodiment, the coating was deposited from an electrolyte with the following composition and parameters:

$NiCl_2*6H_2O$	200-300 g/l
NH_4HF_2	30-80 g/l
$SnCl_2*2H_20$	20-60 g/l
Diethylenetriamine	20-100g/l
pH	3.8-5.5
Temperature	40-60°C

Subsequently, the chromium finish was deposited.

An electrolyte with the following composition and parameters was used for the deposition of a chromium(VI)-layer:

CrO_3	200-300 g/l
H_2SO_4	0.5-2 g/l
F^-	1-2 g/l
temperature	30-40°C

Four different electrolytes were used for the deposition of a chromium(III)-layer. These electrolytes are distributed under the names TRISTAR 300, TRISTAR 300 AF, TRISTAR 700 and TRISTAR 720 by the company Coventya.

The TRISTAR 300 process is a chloride-based process and provides a white chromium layer wherein the electrolyte has the following composition and parameters:

Cr^{3+}	15-25 g/l
organic acid	25-250 g/l
Conducting salts	150-300 g/l
pH	2-6

temperature	25-35°C

The TRISTAR 700 process is comparable with the process described before wherein a chromium layer with a darker coloration results. The electrolyte used herein has the following composition and parameters:

Cr^{3+}	15-25 g/l
organic acid	25-50 g/l
conducting salts	150-300 g/l
blackening agent	1-10 g/l
pH	2-3
temperature	25-35°C

The TRISTAR 300 AF process is a sulfate-based process and results in a chromium layer with white color. The electrolyte comprises the following composition and parameters:

Cr^{3+}	5-15 g/l
organic acid	5-20 g/l
conducting salts	150-300 g/l
pH	3-4
temperature	45-65°C

The TRISTAR 720 process is comparable to the TRISTAR 300 AF process, but results in a chromium layer with darker coloration. The electrolyte comprises the following composition and parameters:

Cr^{3+}	5-15 g/l
organic acid	5-20 g/l
conducting salts	150-300 g/l
blackening agent	2-10 g/l
pH	3-4

temperature 45-65°C

A first corrosion test according to UNI EN ISO 9227 CASS was carried out with such produced samples. The duration of the test was 24, 48, 72, 96 and 120 hours.

As a second corrosion test, the standard procedure VW PV1067 of Volkswagen AG and NES M4063 of Nissan, respectively, was applied. A muddy corrosion accelerator was produced including a mixture of a solution of 3 g Kaolin and 5 ml of an aqueous solution saturated with calcium chloride. Subsequently, a certain amount of mud was evenly distributed on the surface of the individiual samples. The test samples were stored in a chamber at constant temperature and humidity (60 °C and 23 % rel. air humidity). The duration of the test was 48 hours.

The evaluation of the above-described corrosion tests was carried out with an evaluation method which is similar to the evaluation method of ISO 10289 and performs an evaluation based on the size of the defective areas. This is illustrated in Table 1.

Table 1

Defective areas A(%)	**Quotation**
no defects	10
0 < A ≤ 0,1	9
0,1 < A ≤ 0,25	8
0,25 < A ≤ 0,5	7
0,5 < A ≤ 1,0	6
1,0 < A ≤ 2,5	5
2,5 < A ≤ 5	4
5 < A ≤ 10	3
10 < A ≤ 25	2
25 < A ≤ 50	1
50 < A	0

In the first corrosion tests (CASS test), the respective samples were investigated after 24 hours of testing phase. They were cleaned and dried during each inspection without damaging the surface to ensure a correct evaluation. In this way, any changes to the appearance of the surface during the test, like e.g. spots, mattness, flaking, rust, or pitting, could be monitored.

The samples were evaluated during the second corrosion test with calcium chloride at the end of the test (after 48 hours). The samples were cleaned and dried without damaging the surface. Any change of the surface could be also monitored exactly.

In table 2, the individual samples are illustrated together with the test results. The samples A, C, E, G and I are those which represent the prior art. These samples comprise a nickel layer with micro-scale disruptions as intermediate layer between the bright nickel layer and the chromium finish.

Examples B, D and D', F, F', H, L and L' are coatings according to the invention and comprise a tin-nickel alloy layer between the bright nickel layer and the chromium finish.

As can be seen from table 2, sample B demonstrates a better corrosion resistance compared to sample A both in CASS test and CaCl2 test. Sample D and D' demonstrates a better corrosion resistance compared to sample C both in CASS test and CaCl2 test. Sample F and F' demonstrates a better corrosion resistance compared to sample E both in CASS test and CaCl2 test. Sample H demonstrates a better corrosion resistance compared to sample G both in CASS test and CaCl2 test. Sample L and L' demonstrates a better corrosion resistance compared to sample I both in CASS test and CaCl2 test.

Particularly the samples D, D', F and F' demonstrate excellent results and pass both the 96-hours CASS-test and the 48-hours VW PV1067 standard test. More particularly the sample D', F' showed the best corrosion resistance to CASS test passing both the 120h.

Table 2

Samples	micro-discontinuous noble Nickel	Tin-Nickel	Chromium	24h	48h	72h	96h	120h	$CaCl_2$ TEST
A	2-5µm	-	Hexavalent Chromium	10	10	8	7	4	5
B	-	0.1-1.0µm Sn65-Ni35	Hexavalent Chromium	10	10	9	8	7	6
C	2-5µm	-	TRISTAR 300	4	3	3	2	2	9
D		0.1-1.0µm Sn65-Ni35	TRISTAR 300	10	10	10	10	8	10
D'		2.0-5.0µm Sn65-Ni35	TRISTAR 300	10	10	10	10	10	10
E	2-5µm	-	TRISTAR 700	9	9	8	7	6	9
F	-	0.1-1.0µm Sn65-Ni35	TRISTAR 700	10	10	9	8	8	10
F'		2.0-5.0µm Sn65-Ni35	TRISTAR 700	10	10	10	10	9	10
G	2-5µm	-	TRISTAR 300 AF	10	9	8	8	6	5
H	-	0.1-1.0µm Sn65-Ni35	TRISTAR 300 AF	10	10	10	9	8	6
I	2-5µm	-	TRISTAR 720	9	9	8	7	5	5
L	-	0.1-1.0µm Sn65-Ni35	TRISTAR 720	10	10	9	8	8	6
L'	-	2.0-5.0µm Sn65-Ni35	TRISTAR 720	10	10	10	10	8	6

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CLAIMS

1. Substrate with corrosion resistant coating,
wherein the coating comprises at least one bright nickel layer, which is deposited on the substrate, and at least one chromium layer as finish,

wherein between the at least one bright nickel layer and the at least one chromium layer, at least one tin-nickel alloy layer is deposited for suppression of corrosion reactions, and

wherein the at least one bright nickel layer, the at least one chromium layer and the at least one tin-nickel alloy layer are electroplated.

2. Substrate according to claim 1, wherein the tin-nickel alloy consists of 55 to 75 weight-% tin and 45 to 25 weight-% nickel.

3. Substrate according to claim 2, wherein the tin-nickel alloy consists of 60 to 70 weight-% tin and 40 to 30 weight-% nickel.

4. Substrate according to claim 3, wherein the tin-nickel alloy consists of 64 to 68 weight-% tin and 36 to 32 weight-% nickel.

5. Substrate according to any one of claims 1 to 4, wherein the at least one tin-nickel alloy layer has a thickness of 0.1 to 10 µm.

6. Substrate according to any one of claims 1 to 5, wherein the nickel layer has a thickness of 1 to 50 µm.

7. Substrate according to any one of claims 1 to 6, wherein the chromium layer has a thickness of 0.05 to 2 µm.

8. Substrate according to any one of claims 1 to 7, wherein the coating consists of the bright nickel layer which is deposited on the substrate as well as the tin-nickel alloy layer and the chromium layer.

9. Substrate according to claim 8, wherein the coating comprises a further metallic layer which consists of copper or essentially comprises it.

10. Substrate according to any one of claims 1 to 9, wherein a semi-bright nickel layer is arranged between the bright nickel layer and the substrate.

11. Substrate according to any one of claims 1 to 10, wherein the substrate consists of a metal or a metal alloy, or plastics.

12. Substrate according to claim 11, wherein the metal alloy is selected from the group consisting of: steel, brass, aluminium alloy, and zinc diecast.

13. Substrate according to claim 11 or 12, wherein the plastics are selected from the group consisting of: acrylnitril-butadien-styrol (ABS), acrylnitril-butadien-styrol/polycarbonate (ABS-PC), polypropylene (PP) and polyamide (PA).

14. Method for production of a corrosion resistant coating for a substrate, wherein the following layers are electroplated subsequently:
a) at least one bright nickel layer,
b) at least one tin-nickel alloy layer, and
c) at least one chromium layer as finish,
wherein corrosion reactions are suppressed by the tin-nickel alloy layer.

15. Method according to claim 12, wherein the at least one tin-nickel alloy layer is electroplated from an acidic aqueous electrolyte with a pH in the range of 2 to 6, wherein the electrolyte comprises additives apart from at least one tin salt and at least one nickel salt.

16. Method according to claim 15, wherein the additives are selected from the group consisting of: chlorides, fluorides, and fluoroborates.

17. Method according to claim 14, wherein the at least one tin-nickel alloy layer is electroplated from an alkaline aqueous electrolyte, wherein the electrolyte comprises at least one tin salt and at least one nickel salt.

18. Method according to claim 17, wherein the salts are selected from the group consisting of: sulfates, sulfamates, phosphates, pyrophosphates, glycine, and mixtures thereof.

19. Method according to claim 14, wherein the at least one tin-nickel alloy layer is electroplated from a cyanide-containing aqueous electrolyte, wherein the electrolyte comprises at least one tin salt and at least one nickel salt.

20. Method according to claim 19, wherein the salts are selected from the group consisting of: sulfates, sulfamates, phosphates, pyrophosphates, glycine, and mixtures thereof.

21. Method according to claim 14, wherein the at least one tin-nickel alloy layer is electroplated from a neutral or weakly alkaline aqueous electrolyte with a pH in the range of 6 to 10, wherein the electrolyte comprises at least one tin salt and at least one nickel salt.

22. Method according to claim 21, wherein the salts are selected from the group consisting of: sulfates, sulfamates, phosphates, pyrophosphates, glycine, and mixtures thereof.

23. Method according to any one of claims 15 to 22, wherein the electrolyte comprises further additives selected from the group consisting of

- complexing agents;
- wetting agents; and
- mixtures thereof.

24. Method according to claim 23, wherein the complexing agents are selected from the group consisting of: amines, polyamines, and their combinations with organic acids.

25. Method according to claim 24, wherein the polyamines are selected from the group consisting of: ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, aminoethylethanolamine, triethanolamine, diethanolamine, and monoethanolamine.

26. Method according to claim 24 or 25, wherein the organic acids are selected from the group consisting of: citric acid, tartaric acid and lactic acid.

27. Method according to any one of claims 23 to 26, wherein the wetting agents are selected from the group consisting of: amphoteric, anionic, cationic and non-ionic surfactants.

28. Method according to any one of claims 15 to 27, wherein the tin salt is selected from the group consisting of: chlorides, fluorides, fluoroborates, sulfates, methane sulfonates and mixtures thereof, and the nickel salt is selected from the group consisting of: chlorides, fluorides, fluoroborates, sulfates, sulfamates, pyrophosphates, methane sulfonates, and mixtures thereof.

29. Method according to any one of claims 14 to 28, wherein the at least one chromium layer is electroplated from an acidic aqueous electrolyte, wherein the electrolyte for the electroplating of the at least one chromium layer comprises at least one chromium(VI)-salt.

30. Method according to claim 29, wherein the at least one chromium(VI)-salt comprises chromic acid (CrO_3).

31. Method according to any one of claims 14 to 28, wherein the at least one chromium layer is electroplated from an acidic aqueous electrolyte with a pH in the range of 2 to 6, wherein the electrolyte for the electroplating of the at least one chromium layer comprises at least one chromium(III)-salt.

32. Method according to claim 31, wherein the at least one chromium(III)-salt is selected from the group consisting of: chromium sulfate and chromium chloride.

33. Method according to claim 31 or 32, wherein the electrolyte for the electroplating of the at least one chromium layer comprises further additives selected from the group consisting of:

- organic acids;

- inorganic acids;

- conducting salts;

- additives selected from the group consisting of: blackening agents, urea, sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, saccharin sodium salt, sodium vinylsulfonate, and cationic polymers; and

- wetting agents.

34. Method according to claim 33, wherein the organic acids are selected from the group consisting of: formic acid, acetic acid, aminoacetic acid, oxalic acid, malic acid, aspartic acid, and salts thereof.

35. Method according to claim 33 or 34, wherein the inorganic acids are selected from the group consisting of: boric acid, hydrochloric acid, sulfuric acid, and salts thereof.

36. Method according to any one of claims 33 to 35, wherein the conducting salts are selected from the group consisting of: sodium chloride, potassium chloride, ammonium chloride, sodium sulfate, potassium sulfate, ammonium sulfate, sodium bromide, potassium bromide, ammonium bromide, iron sulfate, iron chloride and sodium hypophosphite.

37. Method according to any one of claims 33 to 36, wherein the blackening agents are selected from the group consisting of: thiourea and other organo-sulphur compounds.

38. Method according to any one of claims 33 to 37, wherein the wetting agents are selected from the group consisting of: amphoteric, anionic, cationic, and non-ionic surfactants.

Fig. 1

chromium layer (chromium(III)- or chromium(VI)-layer)
tin-nickel
bright nickel
semi-bright nickel
copper
metallisation
plastics (ABS, ABS-PC, PP, PA)

chromium layer (chromium(III)- or chromium(VI)-layer)
tin-nickel
bright nickel
Copper
Metallisation
plastics (ABS, ABS-PC, PP, PA)

chromium layer (chromium(III)- or chromium(VI)-layer)
Tin-nickel
bright nickel
semi-bright nickel (possible)
copper (possible)
Brass

chromium layer (chromium(III)- or chromium(VI)-layer)
tin-nickel
bright nickel
semi-bright nickel (possible)
copper (possible)
aluminium alloy

chromium layer (chromium(III)- or chromium(VI)-layer)
tin-nickel
bright nickel
semi-bright nickel
Copper
Steel

chromium layer (chromium(III)- or chromium(VI)-layer)
tin-nickel
bright nickel
semi-bright nickel (possible)
Copper
zinc-diecast

Fig. 2

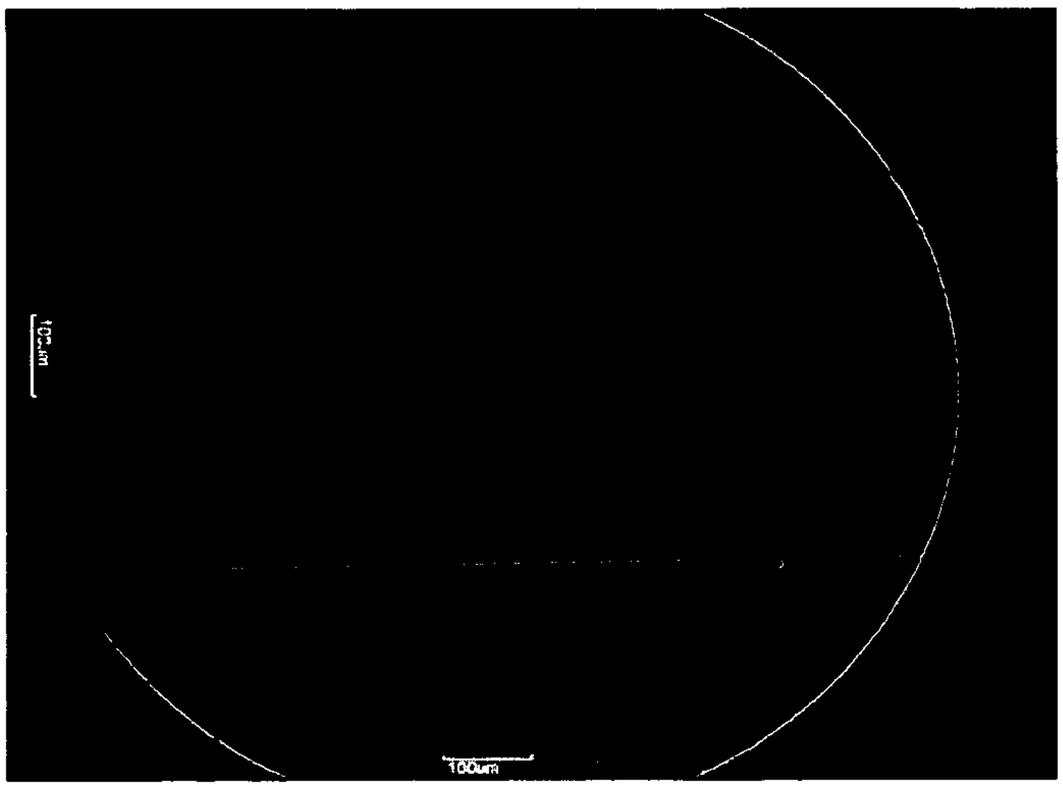

Fig. 3

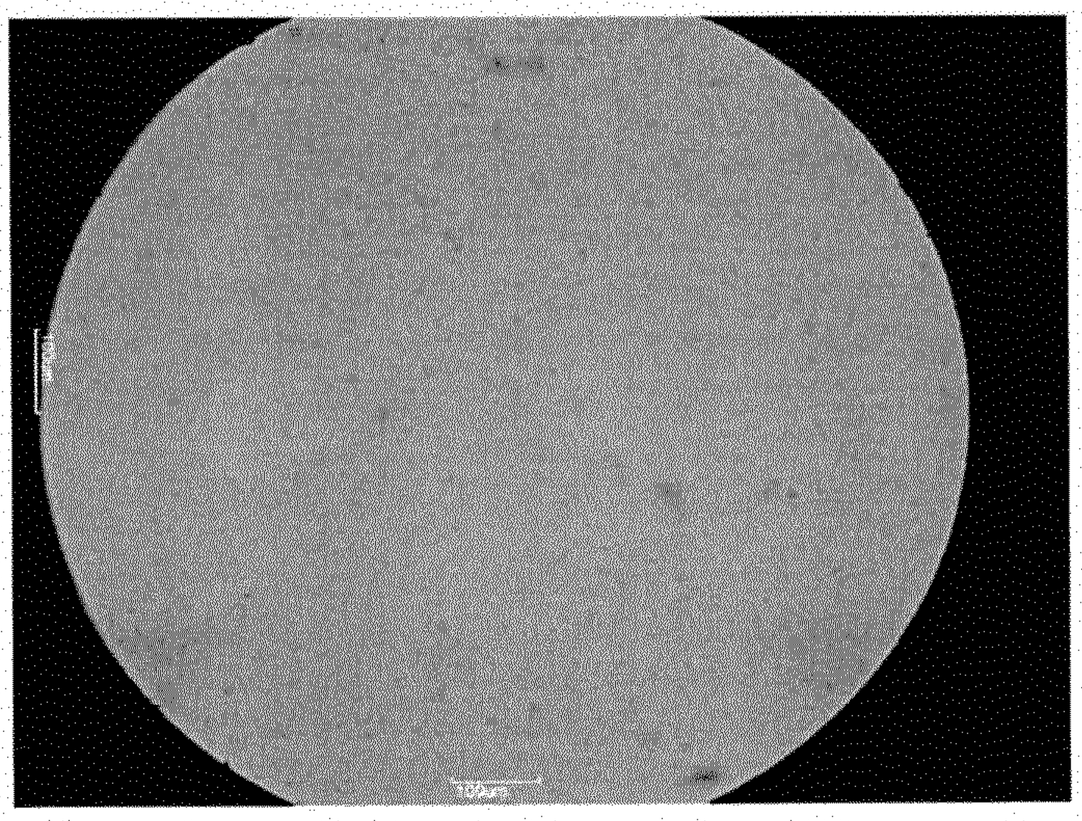

Fig. 4

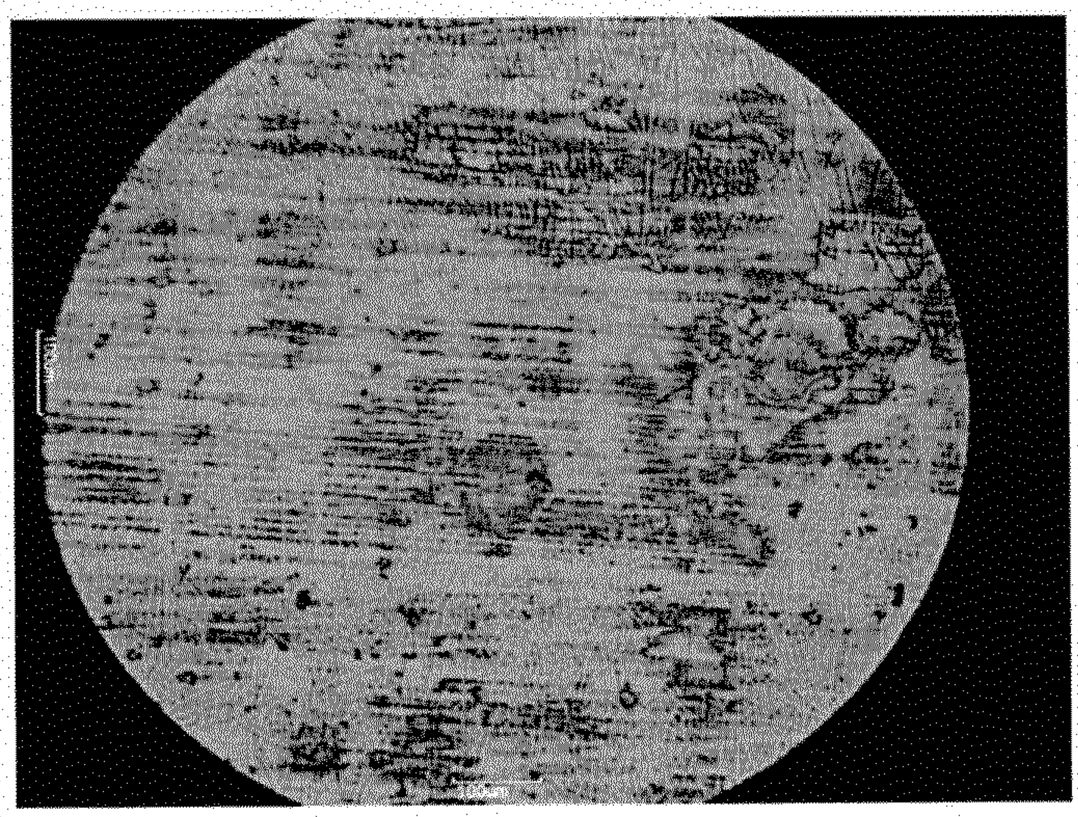

Fig. 5