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⑰ **Organic coated steel strip having improved bake hardenability and method for making.**

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EP 0 230 320 B1

EP 0 230 320 B1

Description

This invention relates to corrosion resistant, organic coated steel strips having improved bake hardenability and drawability and finding application in automobiles.

5 As often encountered in the manufacture of automobiles, strip steel is pressed formed to a desired shape and then coated with a protective coating typically by electrophoretic painting followed by baking at elevated temperatures. The term bake hardenability designates that the strip steel hardens during the baking of such a coating. Usually, the bake hardenability of strip steel is evaluated in terms of an increase of yield strength by baking a 2% pre-stressed, steel strip at 170°C for 20 minutes and measuring the yield strength.

10 In these years, there exists a greater demand for further improving the corrosion resistance of automotive strip steel. A number of rust-preventive steel strips have been proposed to meet such a demand and many of them are successfully used. These rust or corrosion-preventive steel strips are surface treated steel strips including zinc and zinc alloy hot dipped steel, zinc and zinc alloy electroplated, and zinc rich painted, typically organic zinc rich painted steel strips. In addition, composite coated steel strip have also been developed wherein a plated steel strip is covered with an organic coating. These composite coated steel strips are known to be the currently most improved corrosion-preventive steel strips.

15 For energy saving and drivability improvement, an increasing amount of high tensile strip steel has been used in the manufacture of automobiles. To compensate for the loss of dent resistance resulting from thickness reduction, desired is a steel strip which exhibits a low yield strength prior to press forming and increases its yield strength during paint baking. Also in common drawing steel strips, bake hardening after press forming is a phenomenon favourable for increasing dent resistance particularly when the strips are used as automobile outer plates. Steel strips are thus desired to have both deep drawability and bake hardenability.

20 Thus, there is a need for corrosion-preventive steel strips capable of satisfying not only corrosion resistance, but also a variety of requirements such as light weight, safety and rigidity.

25 One conventional commercially available steel meeting such considerations is a class of zinc and zinc alloy plated steel strips having bake hardenability. An organic coating is applied to a zinc or zinc alloy plated steel strip. The organic coating on the steel must be baked at a temperature of higher than 150°C in order to convert it into a hardened one. Thus the organic coated steel strip has been hardened prior to press forming and is thus not amenable to drawing.

30 More particularly, some of conventional automotive organic coated or painted steel strips are known under the trademark of Zincro metal (Diamond Shamrock) as disclosed in Japanese Patent Publication Nos. 47-6882, 52-904, and 53-44887 and some are disclosed in Japanese Patent Application Kokai Nos. 57-189842, 60-174879, 60-86281, and 60-105535. All these coated strips suffer from the above-mentioned problem because they must be baked at a temperature in excess of 150°C in order to convert the organic coating into a hardened one. The bake hardenability of steel substrates themselves could not be beneficially utilized.

35 EP-A-0 149 461 discloses a steel strip coated with a zinc alloy, a chromate layer, and an organic layer which contains silica, wherein a relatively large amount of 10 to 30 parts by weight of melamine resin is used as a curing agent of carboxylated polyethylene resin. The curing agent may behave as a plasticizer when it is left after baking to make adverse effects of the properties of the coating.

40 From DE-A-3 151 115 also a basic organic coated steel strip comprising a steel substrate, a zinc alloy coating, a chromate coating, and an organic coating containing silica is known. In connection with this product, however, the bake hardenability, the use of extra low carbon steel as a substrate and the baking of the organic coating at a temperature beyond 150°C are not mentioned.

45 JP-A-58-224 175 relates to the manufacture of a surface-treated steel plate having a superior adhesive strength to paint after degreasing comprising the steps of treating a steel plate plated with Zn, a Zn alloy or Al with a chromating solution containing chromic acid, a water-soluble acrylic resin and a mineral acid, washing the treated plate in water, and subjecting the plate to a sealing treatment with an organic resin solution. A surface-treatment of a steel plate having a bake hardenability of 3.5 to 6.1 kgf/mm² starting with an extra low carbon steel substrate, however, and subjecting the substrate to a chromate treatment after depositing a zinc or a zinc base alloy layer and baking an organic coating at a temperature of up to 150°C are not mentioned.

50 Finally, FR-A-1 576 677 discloses a process for the chromate treatment on Zn, Al and Fe metal surfaces and a treatment solution therefor. A combination of an extra low carbon steel substrate, a layer of zinc base alloy, a chromate layer and an organic coating are not cited.

55 An object of the present invention is to provide a novel and improved organic coated steel strip which exhibits bake hardenability and good workability even after baking of the organic coating..

Another object of the present invention is to provide a method for making such an organic coated steel strip.

A further object of the present invention is to provide a method for making an organic coated steel strip having improved bake hardenability and capable of maintaining a high proportion of chromium fixed while

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EP 0 230 320 B1

preventing chromium from being dissolved out during alkaline degreasing and/or chemical conversion as used in an automotive coating process.

According to one aspect of the present invention, there is provided an organic coated steel strip having improved bake hardenability, of 3.5 to 6.1 kgf/mm² comprising

5 an extra low carbon steel substrate containing 0.001 to 0.008 percent by weight of carbon and having bake hardenability,

a layer of a zinc base alloy deposited on one surface of said substrate in a weight of 10 to 40 g/m²,
a chromate layer formed on said zinc base alloy layer in a weight of at least 10 mg/m² calculated as metallic chromium, and

10 an organic coating of a thickness of 0.5 to 3µm attached to said chromate layer by baking at a temperature of up to 150°C.

In one preferred embodiment, the organic coating contains silica.

According to another aspect of the present invention, there is provided a method for making an organic coated steel strip having improved bake hardenability, of 3.5 to 6.1 kgf/mm² comprising the steps of:

15 depositing a layer of a zinc base alloy on one surface of an extra low carbon steel substrate containing 0.001 to 0.008 percent by weight of carbon and having hardenability in a weight of 10 to 40 g/m²,

subjecting said substrate to a chromate treatment to form a chromate layer on the zinc base alloy layer in a weight of at least 10 mg/m² calculated as metallic chromium, and

20 applying an organic coating of a thickness of 0.5 to 3µm on the chromate layer and baking the coating at a temperature of up to 150°C.

The chromate treatment is conducted using an aqueous chromate solution containing a chromate compound, a reducing agent, and at least one member selected from acid residues, resins and silica.

Brief Description of the Drawings

25 In order that those skilled in the art will readily understand the practice of the present invention, the following description is made with reference to the accompanying drawings, in which:

FIG. 1 is a diagram showing a stable chromium fixing region in relation to baking temperature and Cr⁶⁺/Cr³⁺;

30 FIG. 2 is a diagram showing a chromium fixing proportion as a function of the amount of methanol added to a chromate solution;

FIG. 3 is a diagram showing a chromium fixing proportion as a function of the amount of phosphoric acid added to a chromate solution;

FIG. 4 is a diagram showing a chromium fixing proportion as a function of the amount of a resin added to a chromate solution;

35 FIG. 5 is a diagram showing a chromium fixing proportion as a function of the amount of silica added to a chromate solution; and

FIG. 6 is a diagram showing the bake hardenability expressed in BH value of steel strip as a function of the baking temperature of organic coating.

40 The present invention provides a highly corrosion resistant, organic coated steel strip capable of maintaining improved bake hardenability after press forming, which is prepared by preparing a drawing extra low carbon steel substrate having bake hardenability, depositing a layer of a zinc base alloy on one surface of the substrate, subjecting said substrate to a chromate treatment to form a chromate layer on the zinc base alloy layer, and applying an organic coating on the chromate layer and baking the coating at a temperature of up to 150°C.

45 As previously described, automotive organic coated or painted steel strips must be baked at a temperature in excess of 150°C in order to convert the organic coating into hardened one. The reason is that in case of Zincrometal[®] with which cold rolled steel is coated, for example, baking must be effected at a sufficiently high temperature to cause the powder zinc-containing chromate to react with the steel substrate. The use of a high-boiling solvent to dissolve a high molecular weight resin also requires a baking treatment at a temperature of higher than 150°C.

50 A similar requirement is imposed on plated steel strips, for example, composite zinc rich/organic coated steel strips as disclosed in Japanese Patent Application Kokai No. 57-189842. That is, baking of the organic coating must be at a high temperature as encountered for the cold rolled steel mentioned above.

55 Also, steel strips having a thin film organic coating other than the zinc rich paint are baked at a high temperature because a binding agent capable of crosslinking at a high temperature, for example, melamine resin must be added in the state of the art.

For all these conventional organic coatings, it is not contemplated to take advantage of the bake hardenability of strip steel as done in the present invention. Therefore, the conventional coated strips have poor workability.

60 In order to take advantage of the bake hardenability of strip steel while maintaining the corrosion resistance as available with conventional coatings, we have investigated the organic coating which can exhibit sufficient corrosion resistance even when baked at a temperature of 150°C or lower. We have discovered that when a cold rolled substrate of extra low carbon steel having bake hardenability by nature is provided with an organic corrosion-preventive coating by a baking treatment at a temperature of up to 65 150°C so as not to lose the inherent bake hardenability, there is available an optimum range of overall

EP 0 230 320 B1

coating consisting of plating plus pre-treatment plus organic coating in which the organic corrosion-preventive coating can provide corrosion resistance, workability and weldability equal or superior to those of conventional highly corrosion resistant organic coated or painted steel strips.

Therefore, the present invention provides an organic coated steel strip having improved bake hardenability, comprising an extra low carbon steel substrate having bake hardenability, a layer of a zinc base alloy deposited on one surface of said substrate in a weight of 10 to 40 g/m², a chromate layer formed on said zinc base alloy layer in a weight of at least 10 mg/m² calculated as metallic chromium, and an organic coating, optionally containing silica, attached to said chromate layer by baking at a temperature of up to 150°C.

According to the present invention, the temperature at which the organic coating is baked is limited to 150°C or lower in order to maintain the bake hardenability. The reason will become clear from the description of a series of experiments.

The starting steel was an extra low carbon steel consisting of, in percentage by weight, 0.003% C, 0.01% Si, 0.16% Mn, 0.04% Al, 0.070% P, 0.026% Nb and balance essentially Fe. The strip steel was cold rolled at a draft of 80% to a thickness of 0.7 mm, heat treated by soaking at 850°C for 30 seconds and cooled to 650°C at a rate of 45°C/sec. in a continuous annealing furnace, and then skin pass rolled at a draft of 1.0%. The resulting extra low carbon steel strip having bake hardenability was determined for mechanical properties, exhibiting a yield strength (YS) of 20 kgf/mm², a tensile strength (TS) of 35 kgf/mm², an elongation (EI) of 45%, and a bake hardenability (BH) of 5 kgf/mm². As previously defined, BH is equal to YS of baked strip minus YS of initial strip.

An organic coating was applied to the steel strip and baked at various temperatures for one minute. The bake hardenability of the baked steel strip is shown in FIG. 6 as a function of the baking temperature. As seen from the curve in FIG. 6, the steel strip experiences a sudden drop in BH value when the baking temperature exceeds 150°C, losing the inherent bake hardenability.

The preferred cold rolled steel strips having bake hardenability with which the present invention starts are bake hardenable, cold rolled steel strips comprising, in percentage by weight, 0.001 to 0.008% of C, up to 0.5% of Si, 0.05 to 1.2% of Mn, up to 0.1% of P, 0.01 to 0.08% of Al, the aluminum being at least 8 times the percent N, from 3 times the percent C to 8 times the percent C plus 0.02% of Nb, up to 0.05% of Ti, and balance essentially Fe, the strips being continuously annealed to have a BH value of 3 to 6 kgf/mm². The extra low carbon steel materials undergo little hardening during mild baking at temperatures of 150°C or lower so that they maintain their own bake hardenability.

Although the reason is not exactly understood, it is expected that bake hardenable steel strips of extra low carbon steel and those of low carbon steel have a different distribution of C in solid solution form within grains even though both have the same apparent BH value.

In the extra low carbon steels previously defined as providing the preferred bake hardenable cold rolled steel strips, the contents of the respective elements are limited to certain ranges.

Carbon, C ranges from 0.001 to 0.008 wt%. Contents of less than 0.001 wt% lead to the loss of the solid solution carbon contributing to bake hardening. Steels having more than 0.008 wt% of carbon exhibit too high yield strength and low ductility and r value (Lankford value).

Silicon, Si preferably ranges up to 0.5 wt%. In excess of 0.5 wt%, an oxide film will form to detract from chemical conversion amenability.

Manganese, Mn preferably ranges from 0.05 to 1.2 wt%. Red shortness diminishes at less than 0.05 wt% whereas r value is reduced in excess of 1.2 wt%.

Phosphorus, P preferably ranges up to 0.1 wt%. Steel becomes brittle with P contents in excess of 0.1 wt%.

Aluminum, Al preferably ranges from 0.01 to 0.08 wt% and at least 8 times the percent N. At least 0.01 wt% of Al is necessary to fix nitrogen. Al contents of more than 0.08 wt% undesirably generate many inclusions. The function of Al to fix nitrogen provides the additional requirement that its content be at least 8 times the percent N.

Niobium, Nb preferably ranges from 3 times the percent C to 8 times the percent C plus 0.02%. Below the lower limit of 3 times the percent C, a too larger amount of solid solution carbon is left, inhibiting the formation of an aggregate structure contributing to drawability during cold rolling recrystallization. Ductility is impaired in excess of 8 times the percent C plus 0.02%.

Titanium, Ti preferably ranges up to 0.05 wt% because the bake hardenability of steel is lost in excess of this limit.

The steel strips are preferably controlled to a BH value of 3 to 6 kgf/mm². A value of less than 3 kgf/mm² is a substantial loss of bake hardenability. Steels having BH values in excess of 6 kgf/mm² undergo severe deterioration upon aging and stretcher strain during working.

The extra low carbon steel strips are plated with zinc based alloys by any known deposition techniques, typical electrodeposition. Some non-limiting examples of the zinc base alloy platings include Zn-Ni alloy platings preferably having a nickel content of 5 to 13 wt%; Zn-Fe alloy plating preferably having an iron content of 8 to 25 wt%; Zn-Co-Al₂O₃-Cr₂O₃ alloy platings preferably having a cobalt content of 1 to 5 wt%; Zn-Al alloy platings preferably having an aluminum content of 1 to 15 wt%; Zn-Ni/Fe-P double-layered alloy platings preferably having a phosphorus content of 0.0003 to 5% by weight based on the weight of FeP; Zn-Fe/Fe-P double-layered alloy platings preferably having a phosphorus content of 0.0003 to 5% by weight

EP 0 230 320 B1

based on the weight of Fe-P. These zinc base alloy platings which have corrosion resistance several times higher than the conventional pure zinc plating are effective in achieving the objects of the present invention. The amount of zinc alloy plated, that is, plating weight should range from 10 to 40 gram per square meter (g/m^2). Corrosion resistance is insufficient with less than 10 g/m^2 whereas plating weights in excess of 40 g/m^2 provide no additional benefit in corrosion resistance improvement and are thus uneconomical.

In the above-listed zinc base alloys, the contents of the respective elements are preferably limited to certain ranges.

The Zn-Ni alloys preferably have a nickel content of 5 to 13 wt%. Less than 5 wt% of Ni provides insufficient corrosion resistance whereas a plating containing more than 13 wt% of Ni is too hard..

The Zn-Fe alloys preferably have an iron content of 8 to 25 wt%. Less than 8 wt% of Fe provides insufficient corrosion resistance whereas red rust will often generate in excess of 25 wt% of Fe.

The Zn-Co- Al_2O_3 - Cr_2O_3 alloys preferably have a cobalt content of 1 to 5 wt%. Less than 1 wt% of Co provides insufficient corrosion resistance whereas more than 5 wt% of Co is uneconomical.

The Zn-Al alloys preferably have an aluminum content of 1 to 15 wt%. Less than 1 wt% of Al provides insufficient corrosion resistance whereas sacrificial corrosion prevention is lost in excess of 15 wt% of Al.

The Fe-P alloys for the double-layered Zn-Ni/Fe-P and Zn-Fe/Fe-P platings preferably have a phosphorus content of 0.0003 to 5% by weight based on the weight of Fe-P. Platings having less than 0.0003 wt% of P are less susceptible to chemical conversion. More than 5 wt% of P is uneconomical because of reduced current efficiency during plating process.

The zinc base alloy platings are subjected to a chromate treatment in order to improve their adherence to subsequently applied organic coatings and hence, the corrosion resistance of the overall structure. The chromate treatment is carried out to produce a chromate film of at least 10 mg/m^2 of metallic chromium. Either coating or electrolytic chromate treatment is advantageous in controlling the amount of chromate film to such a level. Chromate films of less than 10 mg/m^2 of metallic chromium have insufficient corrosion resistance and poor adherence to the subsequently applied organic coatings.

On the chromate layer thus formed is applied an organic coating which is baked at a temperature of up to 150°C and assists in improving corrosion prevention. The organic coating compositions used in the practice of the present invention contain as a main ingredient, a resin, selected from the following three groups:

(1) water dispersible resins including acrylic, polyethylene, epoxy, and alkyd resins and modified ones thereof;

(2) solvent type resins including epoxy and polyester resins and modified ones thereof; and

(3) UV- or electron radiation-curable resins such as acrylic, epoxy, and polyurethane resins, alone or a mixture thereof.

When resin (1) or (2) listed above is used, there are contemplated some methods for assisting in fully hardening the resin by a heat treatment at a low temperature of up to 150°C , for example, the use of low temperature curing agents, for example, metal salt catalysts such as cobalt naphthenate, optionally in combination with amine curing agents such as diethylene triamine. With these curing agents added, the curing process can proceed at room temperature. An organic coating may be more readily formed by using a method adequate for the particular type of organic resin used. Examples of the curing agents which exert their function upon heating include urea resins, melamine resins, benzoguanamine resins, block isocyanate resins, and phenol resins.

Known examples of UV- or electron radiation-curable resins (3) are acrylic resin coatings utilizing a benzoin ether as a photopolymerization initiator and epoxy resin coatings utilizing an aromatic diazonium salt as a photopolymerization initiator. Exemplary of the resins having an electron radiation-curable functional group there may be given acrylic and epoxy resins utilizing epoxy-acid addition reaction and polyurethane resins utilizing isocyanate-hydrogen group addition reaction. These resins (3) can advantageously maintain the bake hardenability of the steel substrate substantially unchanged because they can be baked at temperatures of several ten degree in Centigrade.

The resinous coating composition of any of resins (1) to (3) is applied to the chromate layer to a thickness of 0.5 to $3 \mu\text{m}$. Organic coatings of less than $0.5 \mu\text{m}$ thick provide insufficient corrosion resistance whereas more than $3 \mu\text{m}$ thickness adversely affects weldability.

The resinous coating composition may further contain up to 60% by weight of silica sol for the purpose of improving corrosion resistance. Coating compositions containing more than 60% by weight of silica sol are too viscous and tend to gel.

The composite coated steel strips mentioned above are improved rust-preventive steel strips. As previously mentioned, a chromate treatment is often employed as a preliminary treatment for the organic coating in order to enhance corrosion resistance. A usual automotive part coating process proceeds according to the scheme of blank (organic coated steel) assembly alkaline degreasing chemical conversion electrophoretic deposition intermediate coating top coating. Since the temperature at which the chromate and resin films are baked is controlled relatively low to maintain bake hardenability according to the present invention, there is the likelihood that when a conventional chromate solution is used in the preliminary treatment, chromium be dissolved out during the alkaline degreasing and chemical conversion, imposing a problem to spent liquid disposal.

EP 0 230 320 B1

We have found that in alkaline degreasing of an automotive steel strip comprising a zinc alloy-plated steel substrate which has been subjected to a chromate treatment and an organic coating treatment, the chromium can be dissolved out so that the degreased steel strip has only a markedly reduced amount of chromate attached thereto.

5 To overcome this drawback, we have studied the addition of reducing agents, acids, resins, and silica to the chromate solution, and arrived at the method of the present invention.

Therefore, the present invention according to the other aspect provides a method for making an organic coated steel strip having improved bake hardenability, comprising the steps of:

10 preparing an extra low carbon steel substrate having bake hardenability,
depositing a layer of a zinc base alloy on one surface of the substrate, preferably in a weight of 10 to 40 g/m²,

15 subjecting said substrate to a chromate treatment to form a chromate layer on the zinc base alloy layer, preferably in a weight of at least 10 mg/m² calculated as metallic chromium, the chromate treatment using an aqueous chromate solution containing a chromate compound, a reducing agent, and at least one member selected from acid residues, resins and silica, and

applying an organic coating on the chromate layer and baking the coating at a temperature of up to 150°C.

The organic coated steel strips produced by the method of the present invention experience controlled dissolving out of chromium during alkaline degreasing and/or chemical conversion in the automotive coating process without a loss of corrosion resistance.

20 The chromate treatment will be described in more detail. We have made an experiment to examine the proportion of chromium fixed during alkaline degreasing and/or chemical conversion in the automotive coating process. The starting steel strip is an extra low carbon steel consisting of, in percentage by weight, 0.003% C, 0.01% Si, 0.16% Mn, 0.04% Al, 0.070% P, 0.026% Nb, and balance essentially Fe. A zinc base alloy, typically Zn-Ni alloy was plated on the strip in a plating weight of 10 to 40 g/m², a chromate solution having a ratio of hexavalent to trivalent chromium (Cr⁶⁺/Cr³⁺) of from 80/20 to 20/80 was applied and baked to the zinc base plating, and then a resin in water or solvent, typically epoxy resin was applied and baked to the chromate film. It is to be noted that the ratio of Cr⁶⁺/Cr³⁺ was measured by the redox titration technique. The maximum temperature to which the strip was heated was from room temperature to 150°C for both the chromate and resin film baking steps.

30 When a conventional chromate solution, that is, free of any additives as defined in the present invention, is used, higher temperatures at which the applied chromate and resin films are baked cause more hexavalent chromium to be reduced to trivalent chromium, resulting in an increased chromium fixing proportion. For example, when the films were baked at temperatures of higher than 150°C, the percent of chromium remaining fixed after alkaline degreasing was at least 80%, which level is acceptable in the automotive coating process. With attention paid to the steel substrate, however, yield strains are induced therein during the process. There arise some problems including removal of such yield strain as well as increased yield stress and deteriorated press formability.

40 Therefore, it is intended in the present invention to improve the percent chromium fixed, provided that the maximum baking temperature is limited to the range between room temperature and 150°C.

45 According to one embodiment of the present invention, chromate solutions having added thereto methanol as a reducing agent and phosphoric acid as an acid residue was applied and baked to plated steel strips at temperatures of from room temperature to 150°C and then a resin was applied and baked to the chromate film at a temperature of from room temperature to 150°C. The chromium fixing proportion, that is, percent chromium fixed of the strips was plotted in FIG. 1 as a function of the Cr⁶⁺/Cr³⁺ ratio of the chromate solution and the maximum baking temperature. The range of Cr⁶⁺/Cr³⁺ ratio within which the percent chromium fixed is 80% or higher is depicted hatched as a favourable region in FIG. 1. Although the reducing agent used is methanol and the additive used is phosphoric acid, similar results are obtained when other reducing agents are used and/or other additives such as acids other than phosphoric acid, resins and silica are used.

50 To achieve a favourable percent chromium fixed of 80% or higher with the maximum baking temperature ranging from room temperature to 150°C as shown in FIG. 1, we have found that favourable results are obtained by adding a reducing agent and at least one additive selected from acid residues, resins, and silica to the chromate solution.

55 Examples of the reducing agents added to the chromate solution include methanol, aqueous hydrogen peroxide, ethylene glycol, succinic acid, succinimide, but are not limited thereto. The reducing agent is added in an amount sufficient to provide a RAH of 0.2 to 1.9 per gram molecule of CrO₃. The term RAH is the gram atoms of hydrogen contained in the reducing agent. With RAH of less than 0.2, the percent chromium fixed is reduced to an unacceptable level even when the additive as defined below is additionally used. The chromate solution becomes gel if RAH is above 1.9.

60 The additive which is used in the chromate solution in combination with the reducing agent are selected from acid residues, resins, and silica. They are described in more detail.

(1) Acid residues

65 Preferred acid residues are provided by such acids as phosphoric acid and boric acid. They are added

EP 0 230 320 B1

in an amount to give a A^{-x}/CrO_3 ratio of from 0.05 to 0.3 by weight wherein A^{-x} represents an acid residue. Ratios of less than 0.05 will result in a percent chromium fixed of less than 80% whereas ratios of more than 0.3 will result in poor corrosion resistance.

5 (2) Resins

Preferred examples of the resins added to the chromate solution include acrylic resins having an acid value of at least 250 and acrylic resins having acrylic acid monomer and/or methacrylic acid monomer added to stabilize them.

They are added in an amount to give a resin/ CrO_3 ratio of from 0.1 to 20 by weight. Ratios of less than 10 0.1 will result in a percent chromium fixed of less than 80% whereas ratios of more than 20 will deteriorate the adherence of the chromate film to the underlying substrate.

(3) Silica

15 Silica added to the chromate solution is preferably colloidal silica. Silica is added in an amount to give a SiO_2/CrO_3 ratio of from 0.3 to 3.0 by weight. Ratios of less than 0.3 will result in a percent chromium fixed of less than 80% whereas ratios of more than 3.0 will deteriorate the adherence of the chromate film to the underlying substrate.

When a steel strip carries a chromate film resulting from the chromate solution having added the reducing agent and the additive as defined above, the steel can maintain a significantly high percent 20 chromium fixed at the end of alkaline degreasing and chemical conversion in the automotive coating process. To demonstrate the maintenance of high percent chromium fixed, an experiment was made using an immersion type alkaline degreasing solution commonly used in the automotive coating process.

FIG. 2 graphically shows the percent chromium fixed as a function of the amount of methanol added as the reducing agent. It is seen that only the addition of methanol, that is, reducing agent mostly results in a 25 percent chromium fixed of less than 80%. However, the RAH/ CrO_3 ratio range from 0.2 to 1.9 gives a ratio of Cr^{6+}/Cr^{3+} in the range of from 80/20 to 20/80. Then, the percent chromium fixed can be 80% or higher as seen from FIG. 1 by adding at least one additive selected from (1) acid residues, (2) resins, and (3) silica to the chromate solution while keeping the maximum baking temperature within the range of from room temperature to 150°C.

30 FIG. 3 graphically shows the percent chromium fixed as a function of the amount of phosphoric acid added as producing an acid residue to the chromate solution having methanol added as the reducing agent (RAH/ $CrO_3=1.0$). It is seen that when the amount of phosphoric acid added is at least 0.1 calculated as PO_4^{3-}/CrO_3 , a percent chromium fixed of 100% is advantageously achieved even at a ratio of Cr^{6+}/Cr^{3+} of 80/20. It is also seen that when the ratio of Cr^{6+}/Cr^{3+} is 20/80, a percent chromium fixed of 100% is 35 advantageously achieved even at a ratio of PO_4^{3-}/CrO_3 of 0.01. When phosphoric acid is added in an amount to give a PO_4^{3-}/CrO_3 ratio of 0.3 or higher, the phosphoric acid due to its non-volatile nature adversely affects the subsequently applied and baked resin and hence, the corrosion resistance of the product.

40 FIG. 4 graphically shows the percent chromium fixed as a function of the amount of a resin added to the chromate solution having methanol added as the reducing agent (RAH/ $CrO_3=1.0$). The resin used is an acidic acrylic resin.

The amount of resin added is expressed as a weight ratio of resin solids/ CrO_3 . It is seen that a resin solids/ CrO_3 ratio in the range between 0.1 and 20.0 is effective in improving the percent chromium fixed. Such a ratio of more than 20.0 adversely affects the adherence of chromate film to the underlying substrate, 45 and hence, the workability and weldability of the product.

FIG. 5 graphically shows the percent chromium fixed as a function of the amount of silica added to the chromate solution having methanol added as the reducing agent (RAH/ $CrO_3=1.0$). The silica used is ultrafine particulate silica anhydride.

50 The amount of silica added is expressed as a weight ratio of SiO_2/CrO_3 . It is seen that a SiO_2/CrO_3 ratio of at least 0.3 is effective in achieving a percent chromium fixed of 80% or higher. Such a ratio of more than 3.0 adversely affects the adherence of chromate film to the underlying substrate, and hence, the weldability of the product.

The foregoing experimental results indicate that the addition of a reducing agent in combination with (1) an acid residue, (2) a resin or (3) silica to the chromate solution is effective in increasing the percent 55 chromium fixed at the end of alkaline degreasing in the automotive coating process. The additive effects of these agents are estimated as follows.

The reducing agent such as methanol, aqueous hydrogen peroxide and ethylene glycol is added to the chromate solution. The reducing agent reduces chromic acid to lower the Cr^{6+}/Cr^{3+} ratio. The percent chromium fixed is then increased because the proportion of hexavalent chromium which is more liable to 60 dissolve away is decreased.

The additives, (1) acid residue, (2) resin, and (3) silica added to the chromate solution have the following functions.

(1) Addition of acid residue to chromate solution

65 Two sets of samples were prepared by applying a chromate solution having phosphoric acid residue

EP 0 230 320 B1

added and an acid residue-free chromate solution followed by baking. Analysis of the samples from the acid residue-containing chromate solution indicates peaks probably attributable to the hydrate or hydroxide of trivalent chromium in addition to the peaks of trivalent and hexavalent chromium. No substantial difference is observed in the proportion of hexavalent chromium between the acid residue-introduced and free solutions. When the chromate films are evaluated as applied, the percent chromium fixed does not depend on the introduction of acid residue. However, when a resin is subsequently applied and baked to the chromate films, the hydrate or hydroxide of trivalent chromium is firmly attached to the resin, eventually preventing hexavalent chromium from dissolving out. It has also been observed that hexavalent chromium itself reacts with the resin to reduce its quantity. These two mechanisms decrease the dissolving out of hexavalent chromium.

(2) Addition of resin to chromate solution

When the chromate solution contains an acrylic resin or a similar resin which is of acidic type and stable in the chromate solution, the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio of the solution remains unchanged, but a bond is created between hexavalent chromium and the resin at the end of baking to prevent the hexavalent chromium from dissolving out.

(3) Addition of silica to chromate solution

When a chromate film is used alone without subsequent resin coating, the percent chromium fixed decreases with the increasing amount of silica added to the chromate solution.

Analysis of silica-containing chromate films indicates more OH groups than in silica-free chromate films. The distribution of silicon in the chromate film is also determined to find that Si is concentrated in a surface layer.

These indicate that silica forms a rigid film at the surface layer of the chromate film in which the chromate itself is present as the hydrate and hydroxide of trivalent chromium. When a resin is subsequently applied and baked to such a chromate film, the resin is firmly attached to the OH group of the chromate film so that the resulting resin coated steel strip is characterized by the controlled dissolving-out of chromium.

Examples

Examples of the present invention are given below by way of illustration and not by way of limitation.

Example 1

The composition of cold rolled steel strips having bake hardenability used in a series of runs is shown in Table 1 together with their mechanical properties.

Using bake hardenable steel strips, blank Nos. 1-6 as shown in Table 1, test specimens were prepared by depositing a zinc base alloy plating on the blank, subjecting the plating to a chromate treatment, and then applying an organic coating followed by baking. The treating procedure is shown in Table 2.

The test specimens were determined for corrosion resistance, weldability, workability, and bake hardenability, with the results shown in Table 3.

The tests are conducted by the following procedures.

1. Corrosion Resistance

1-a) Salt spray test (SST)

A salt spray test was carried out by crosshatching the organic coating on each specimen, and spraying a 5% NaCl solution at 35°C to the coating. The time was observed until red rust generated.

1-b) Cycle corrosion test (CCT).

A cycle corrosion test was carried out by subjecting each specimen to corrosion cycles each consisting of spraying of 5% NaCl at 35°C for 4 hours, drying at 60°C for 2 hours, and allowing to stand in wet conditions at 50°C, RH 95% for 2 hours. The number of cycles was counted until red rust generated.

2. Weldability

Two pieces of each specimen were partially overlapped and subjected to continuous spot welding using an R type electrode (40R) each under a compression force of 170 kg for a welding period of 10 cycles (50Hz, 1/5 sec). The number of permissible continuous welding spots was determined.

3. Workability

Each specimen in a disk form having a diameter of 90 mm was subjected to a cupping test by drawing to a cup shape having a diameter of 50 mm and a depth of 25 mm (Blank Hold Force 1 Ton). An adhesive tape was applied to and removed from the worked area to determine the removal of coating as expressed in mg/circumference.

4. Bake Hardenability

Each specimen was pre-stressed 2% and then subjected to a baking treatment at 170°C for 20 minutes. The yield strength (YS) of the specimen was measured to determine an increase of YS in kgf/mm^2 .

The data in Table 3 demonstrate that the organic coated steel strips obtained according to the present invention have high corrosion resistance, good weldability and workability while maintaining satisfactory bake hardenability.

T a b l e 1

Blank No.	Composition (wt%)							Thick-ness (mm)	Mechanical properties					
	C	Si	Mn	Al	P	Nb	Ti		N	YS (kgf/mm ²)	TS (kgf/mm ²)	El (%)	BH ₁ (kgf/mm ²)	
1	0.002	0.01	0.15	0.03	0.015	0.012	-	0.0020	0.75	16	30	50	2.0	4.5
2	0.003	0.01	0.15	0.02	0.013	0.030	-	0.0025	0.80	17	32	48	2.1	3.5
3	0.004	0.01	0.16	0.04	0.060	0.026	-	0.0018	0.80	22	37	43	1.9	4.6
4	0.004	0.01	0.40	0.03	0.040	0.025	-	0.0022	0.65	24	39	41	1.6	5.2
5	0.003	0.3	0.15	0.03	0.060	0.025	-	0.0016	0.70	25	41	39	1.7	6.1
6	0.003	0.01	0.14	0.04	0.012	0.012	0.02	0.0021	0.70	16	30	52	2.2	5.0

1) BH (bake hardenability): stress increase due to strain age hardening by equivalent coat baking treatment (170°C, 20 min.) after 2% stressing

Table 2

Blank No.	Plating		Chromate weight ₂ (mg/m ²)	Organic coating			Thickness (μm)	Baking temp. (°C)
	Type	weight (g/m ²)		Resin	Hardener	Silica sol		
A-1	Zn-Ni	10	20	Urethane-modified epoxy emulsion 68 parts	Diethylene triamine 2 parts	Colloidal silica 30 parts	0.5	120
A-2		20					0.5	120
A-3		30					0.5	120
A-4		40					0.5	120
A-5		20					1	120
A-6		20					2	120
A-7		20					3	120
A-8	Zn-Ni	10	20	Urethane-modified epoxy emulsion 68 parts	Diethylene triamine 2 parts	-	0.5	120
A-9		20					0.5	120
A-10		30					0.5	120
A-11		40					0.5	120
A-12		20					1	120
A-13		20					2	120
A-14		20					3	120
B-1	Zn-Ni	20	30	Carboxylated polyethylene emulsion 70 parts	Diethylene triamine 10 parts	Colloidal silica 20 parts	0.8	100
B-2		30					0.8	100
B-3		40					0.8	100
C-1	Zn-Fe	20	30	Fatty acid-modified styrene-acryl hydrosol 78 parts	Cobalt naphthenate 2 parts	Colloidal silica 20 parts	1.2	90
C-2		30					1.2	90
C-3		40					1.2	90
D-1	Zn-Ni/Fe-P	10	50	Carboxylated polyethylene emulsion 65 parts	Cobalt naphthenate 5 parts	Colloidal silica 30 parts	1.0	130
D-2		20					1.0	130
D-3		30					1.0	130
D-4		40					1.0	130

Table 2 (cont'd)

Invention	Blank No.	Plating		Chromate weight ^{1/2} (mg/m ²)	Organic coating			Thickness (μm)	Baking temp. (°C)
		Type	weight (g/m ²)		Resin	Hardener	Silica sol		
E-1 E-2 E-3	5	Zn-Co	20	40	Epoxy resin 82 parts	Diethylene triamine 3 parts	Cellosolve organosol 15 parts	0.8	120
		Al ₂ O ₃ , Cr ₂ O ₃ dispersed	30						
		Al ₂ O ₃ , Cr ₂ O ₃ dispersed	40						
F-1 F-2 F-3	6	Zn-Fe/Fe-P	20	50	Acrylic resin 89 parts	Benzoin ether initiator 1 part	Silica flour 10 parts	3.0	(UV)
		Zn-Fe/Fe-P	30						
		Zn-Fe/Fe-P	40						
Comparative runs	1	Zn-Ni	5	20	Urethane-modified epoxy emulsion 68 parts	Diethylene triamine 2 parts	Colloidal silica 30 parts	1	120
		Zn-Ni	20						
		Zn-Ni	20						
		Zn-Ni	20						
		Zn-Ni	20						
H Zincro-metal R	1	-	-	300 (contg. Zn powder)	Epoxy resin 15 parts	-	Zn powder 85 parts	15	270
		-	-						
I Composite zinc rich coating	1	Zn-Ni	20	300 (contg. Zn powder)	Epoxy resin 15 parts	-	Zn powder 85 parts	7	270
		-	-						
J Composite zinc rich coating	1	Zn-Ni	20	50	Epoxy resin 15 parts	-	Zn powder Al powder 85 parts	5	270
		-	-						

EP 0 230 320 B1

Table 3

	Blank No.	Corrosion resistance		Weld- ability (spots)	Workability (mg/circum- ference)	BH (kgf /mm ²)	
		SST (hour)	CCT (cycle)				
<u>Invention</u>	A-1	} 1	>2500	>200	>1000	<1	4.5
	A-2		>2500	>200	>1000	<1	4.5
	A-3		>2500	>200	>1000	<1	4.5
	A-4		>2500	>200	>1000	<1	4.5
	A-5		>2500	>200	>1000	<1	4.5
	A-6		>2500	>200	>1000	<1	4.5
	A-7		>2500	>200	>1000	<1	4.5
	A-8	} 1	>2000	>150	>1000	<1	4.5
	A-9		>2000	>150	>1000	<1	4.5
	A-10		>2000	>150	>1000	<1	4.5
	A-11		>2000	>150	>1000	<1	4.5
	A-12		>2000	>150	>1000	<1	4.5
	A-13		>2000	>150	>1000	<1	4.5
	A-14		>2000	>150	>1000	<1	4.5
B-1	} 2	>2500	>200	>1000	<1	3.5	
B-2		>2500	>200	>1000	<1	3.5	
B-3		>2500	>200	>1000	<1	3.5	
C-1	} 3	>2500	>200	>1000	<1	4.6	
C-2		>2500	>200	>1000	<1	4.6	
C-3		>2500	>200	>1000	<1	4.6	
D-1	} 4	>2500	>200	>1000	<1	5.2	
D-2		>2500	>200	>1000	<1	5.2	
D-3		>2500	>200	>1000	<1	5.2	
D-4		>2500	>200	>1000	<1	5.2	
E-1	} 5	>2500	>200	>1000	<1	6.1	
E-2		>2500	>200	>1000	<1	6.1	
E-3		>2500	>200	>1000	<1	6.1	
F-1	} 6	>2500	>200	>1000	<1	5.0	
F-2		>2500	>200	>1000	<1	5.0	
F-3		>2500	>200	>1000	<1	5.0	
<u>Comparative runs</u>	G-1	} 1	1000	100	>1000	<1	4.5
	G-2		1500	100	>1000	<1	4.5
	G-3		>2000	>150	700	1-2	4.5
	G-4		>2000	>150	500	1-2	4.5
	G-5		>2000	>150	300	1-2	4.5
	H	1	>2000	>150	500	60	0
	I	1	>2000	>150	>1000	10	0
	J	1	>2000	>150	>1000	5	0

EP 0 230 320 B1

Example 2

The cold rolled steel strips having bake hardenability used were the same as used in Example 1. Their compositions are shown in Table 1 together with their mechanical properties.

5 Using bake hardenable steel strips, blank Nos. 1-6 as shown in Table 1, test specimens were prepared by depositing a zinc base alloy plating on the blank, subjecting the plating to a chromate treatment, and then applying an organic coating followed by baking. The treating procedure is shown in Table 4.

The test specimens were determined for corrosion resistance, weldability, workability, bake hardenability, and percent chromium fixed, with the results shown in Table 5.

The procedures for measuring the former four properties are the same as in Example 1.

10 Percent chromium fixed was determined by degreasing a specimen with a commonly used immersing alkaline degreasing solution. Using fluorescent X-ray analysis, the number of chromium counts was determined before and after the alkaline degreasing.

15 The data in Table 5 demonstrate that the organic coated steel strips produced according to the method of the present invention have high corrosion resistance, good weldability and workability while maintaining satisfactory bake hardenability and high percent chromium fixed.

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Table 4

No.	Plating		Chromate				Organic Coating			Thick-ness (μm)	Baking temp. ($^{\circ}\text{C}$)					
	Blank No.	Type	Weight (g/m ²)	Reducing agent (H ₂ N/GrO ₃)	+1 Acid	+2 Resin	+3 Silica	Cr ⁶⁺ /Cr ³⁺ (adjusted)	Weight (mg/m ²)			Baking temp. ($^{\circ}\text{C}$)	Resin	Hardener	Silica sol	
Invention	A-1	Zn-12% Ni	30	Ethylene glycol (0.6)	0.05	—	—	00/20	70	70	Epoxy resin 60 parts	Diethylene triamine 2 parts	Colloidal Silica 30 parts	1.2	90	
	A-2	Zn-12% Ni	25		—	—	—	00/20	50	80	Urethane-modified epoxy emulsion 70 parts	Cobalt naphthenate 10 parts	Colloidal Silica 20 parts	1.2	90	
	A-3	Zn-12% Ni	25		—	—	—	0.3	00/20	20	120	Acrylic resin 80 parts	Diethylene triamine 1 part	Alcoholic silica sol 10 parts	1.2	90
	A-4	Zn-12% Ni	20	Methanol (1.0)	0.1	—	—	50/50	30	100	High molecular weight epoxy resin 65 parts	Melamine 5 parts	Cellosolve Silica sol 30 parts	1.0	150	
	A-5	Zn-12% Ni	20		—	—	—	50/50	30	100	Urethane-modified epoxy resin 65 parts	Urea 5 parts		Cellosolve Silica sol 30 parts	1.0	150
	A-6	Zn-12% Ni	20		—	—	0.3	50/50	30	100					Urethane-modified epoxy resin 65 parts	Benzoguanamine 5 parts
	A-7	Zn-12% Ni	20		0.1	—	—	—	50/50	30	100	Urethane-modified epoxy resin 65 parts		Urea 5 parts		
A-8	Zn-12% Ni	20	—	—	—	—	50/50	30	100	Carboxylated polyethylene emulsion 65 parts	Cobalt naphthenate 5 parts		Colloidal Silica 30 parts		0.8	80
A-9	Zn-12% Ni	20	H ₂ O ₂ in water (1.2)	0.1	—	—	50/50	30	100			Carboxylated polyethylene emulsion 65 parts		Cobalt naphthenate 5 parts	Colloidal Silica 30 parts	1.0
B	B-1	Zn-20% Fe	20	Methanol (1.5)	0.1	—	—	30/70	150	80	Carboxylated polyethylene emulsion 65 parts		Cobalt naphthenate 5 parts			Colloidal Silica 30 parts
	B-2	Zn-20% Fe	40		0.05	—	—	30/70	200	100		Carboxylated polyethylene emulsion 65 parts		Cobalt naphthenate 5 parts	Colloidal Silica 30 parts	
	B-3	Zn-12% Ni	30		—	0.2	—	1.0	30/70	80	60		Carboxylated polyethylene emulsion 65 parts			Cobalt naphthenate 5 parts
	B-4	Zn-12% Ni	40		0.1	—	—	0.3	30/70	50	70	Carboxylated polyethylene emulsion 65 parts		Cobalt naphthenate 5 parts	Colloidal Silica 30 parts	

+1: Phosphoric acid (A⁺⁺/CrO₃) +2: Acrylic resin (H/GrO₃) +3: Silica (SiO₂/CrO₃)

Table 4 (cont'd 1)

Invention	Plating		Chromate				Organic Coating				Baking Temp. (°C)			
	No. No.	Blank Type	Weight (g/m ²)	Reducing agent (H ₂ /CrO ₃)	Acid	+1 Resin	+2 Silica	+3 Cr ⁶⁺ /Cr ³⁺ (adjusted)	Weight (mg/m ²)	Baking Temp. (°C)		Resin	Hardener	Silica sol
C-1	3	Zn-12% Ni / Fe-0.03% P	10	Ethanol (1.5)	0.05	0.1	—	30/70	100	70	Urethane-modified epoxy emulsion 50 parts	Diethylene triamine 2 parts	Colloidal Silica 40 parts	0.0
			20											
			30											
			40											
C-5	3	Zn-12% Ni / Fe-0.03% P	40	Methanol (1.2)	0.1	—	—	100	80	Fatty acid-modified styrene acryl hydrosol 70 parts	Cobalt naphthenate 2 parts	Colloidal Silica 20 parts	0.0	
			20											
			30											
			40											
D-1	4	Zn-20% Fe	40	Methanol (0.6)	0.07	0.2	—	80	60	Epoxy resin 82 parts	Diethylene triamine 3 parts	Cellosolve silica sol 15 parts	0.0	
			20											
			30											
			40											
D-2	4	Zn-12% Ni	30	H ₂ O ₂ in water (1.2)	0.05	0.3	1.0	90	40	Acrylic resin 89 parts	Benzoin ether initiator 1 part	Silica flour 10 parts	1.1	
			20											
			30											
			40											
D-3	4	Zn-12% Ni	40	Methanol (0.3)	0.07	2.0	0.5	40	80	Unsaturated polyester resin 90 parts	Silica flour 10 parts	Electro radiation	1.2	
			20											
			30											
			40											
E-1	5	Zn-1% Co / Cr ₂ O ₃ (0.3%) / Fe-0.03% P / Cr ₂ O ₃ (0.6%) dispersed	40	Ethylene glycol (0.8)	0.1	—	—	80	70	Acrylic resin 89 parts	Benzoin ether initiator 1 part	Silica flour 10 parts	1.2	
			20											
			30											
			40											
F-1	6	Zn-20% Fe / Fe-0.03% P	30	Methanol (1.2)	0.2	—	0.5	60	60	Acrylic resin 89 parts	Benzoin ether initiator 1 part	Silica flour 10 parts	1.0	
			40											
			40											
			40											

+1: Phosphoric acid (H⁺/CrO₃). +2: Acrylic resin (H/CrO₃). +3: Silica (SiO₂/CrO₃)

Table 4 (cont'd 2)

Plating				Chromate				Organic Coating								
No.	Blank No.	Type	Weight (g/m ²)	Reducing agent (HAl/GrO ₃)	Acid	+1 Resin	+2 Silica	+3 Cr ³⁺ /Cr ⁶⁺ (adjusted)	Weight (mg/m ²)	Baking Temp. (°C)	Resin	Hardener	Silica sol	Thick-ness (μm)	Baking Temp. (°C)	
EP 0 230 320 B1																
Comparative runs																
G-1	G-2	Zn-12% Ni	20	—	—	—	—	—	50	30	Urethane-modified epoxy emulsion	Diethylene triamine	Colloidal silica	1.1	80	
G-3	1	Zn-12% Ni	40	—	—	—	—	—	100	30	60 parts	2 parts	30 parts	1.2	80	
G-4		Zn-12% Ni	30	—	—	—	—	—	100	60						
G-4		Zn-12% Ni	30	Methanol (0.3)	—	—	—	70/30	100	30				0.7	70	
H-1	H-2	Zn-20% Fe	20	Methanol (0.3)	0.4	—	—	—	100	100	65 parts	Melamine resin	Cellosolve silica sol	0.7	80	
H-2		Zn-20% Fe	30		0.5	—	—	—	100	100						
H-3	2	Fe-0.03% P	40		—	—	—	—	50	100						
H-4		Zn-20% Ni	20		—	5.0	—	—	50	100						
I-1		Zn-12% Ni	20	Ethanol (2.1)	—	—	—	10/90	50	100	5 parts	30 parts	1.1	80		
I-2	3	Zn-12% Ni	20	H ₂ O ₂ in water (2.1)	—	—	—	0/100	80	80				0.9	100	
I-3		Zn-12% Ni	20		—	—	—	—	—	70	120				1.1	100
I-4		Zn-12% Ni	20		—	—	—	—	—	80	50				1.2	50

+1: Phosphoric acid (H⁺/CrO₃), +2: Acrylic resin (H/CrO₃), +3: Silica (SiO₂/CrO₃)

EP 0 230 320 B1

Table 5

	Blank No.	Corrosion resistance		Weldability (spots)	Workability (mg/circumference)	BH (kgf ₂ /mm ²)	% Cr fixed	
		SST (hour)	CCT (cycle)					
<u>Invention</u>	A-1	1	>2500	>200	>1000	<1	4.6	>90
	A-2		>2500	>200	>1000	<1	4.7	>90
	A-3		>2500	>200	>1000	<1	4.3	>90
	A-4		>2500	>200	>1000	<1	4.4	>90
	A-5		>2500	>200	>1000	<1	4.4	>90
	A-6		>2500	>200	>1000	<1	4.4	>90
	A-7		>2500	>200	>1000	<1	4.4	>90
	A-8		>2500	>200	>1000	<1	4.4	>90
	A-9		>2500	>200	>1000	<1	4.4	>90
	B-1	2	>2500	>200	>1000	<1	4.7	>90
	B-2		>2500	>200	>1000	<1	4.5	>90
	B-3		>2500	>200	>1000	<1	4.7	>90
	B-4		>2500	>200	>1000	<1	4.5	>90
	C-1	3	>2500	>200	>1000	<1	4.5	>90
	C-2		>2500	>200	>1000	<1	4.5	>90
	C-3		>2500	>200	>1000	<1	4.5	>90
	C-4		>2500	>200	>1000	<1	4.3	>90
	C-5		>2500	>200	>1000	<1	4.5	>90
	C-6		>2500	>200	>1000	<1	4.5	>90
	D-1	4	>2500	>200	>1000	<1	4.5	>90
	D-2		>2500	>200	>1000	<1	4.5	>90
	D-3		>2500	>200	>1000	<1	4.5	>90
	E-1	5	>2500	>200	>1000	<1	4.7	>90
	E-2		>2500	>200	>1000	<1	4.7	>90
	E-3		>2500	>200	>1000	<1	4.7	>90
	E-4		>2500	>200	>1000	<1	4.5	>90
	F-1	6	>2500	>200	>1000	<1	4.5	>90
	F-2		>2500	>200	>1000	<1	4.5	>90
	F-3		>2500	>200	>1000	<1	4.7	>90
	F-4		>2500	>200	>1000	<1	4.7	>90
<u>Comparative runs</u>	G-1	1	>2500	>200	>1000	<1	4.7	50
	G-2		>2500	>200	>1000	<1	4.7	60
	G-3		>2500	>200	>1000	<1	4.8	50
	G-4		>2500	>200	>1000	<1	4.7	50
	H-1	2	1500	150	>1000	<1	4.5	>90
	H-2		1500	100	>1000	<1	4.3	>90
	H-3		>2500	>200	400	2.0	4.5	>90
	H-4		>2500	>200	400	1.5	4.0	>90
	I-1	3	-	-	coating	-	-	-
	I-2		-	-	gelled	-	-	-
	I-3		-	-		-	-	-
	I-4		-	-		-	-	-

EP 0 230 320 B1

Claims

1. An organic coated steel strip having improved bake hardenability of 3.5 to 6.1 kgf/mm², comprising an extra low carbon steel substrate containing 0,001 to 0.008 percent by weight of carbon and having
5 bake hardenability,
a layer of a zinc base alloy deposited on one surface of said substrate in a weight of 10 to 40 g/m²,
a chromate layer formed on said zinc base alloy layer in a weight of at least 10 mg/m², calculated as metallic chromium, and
an organic coating of a thickness of 0.5 to 3µm attached to said chromate layer by baking at a
10 temperature of up to 150°C.
2. The organic coated steel strip of claim 1 wherein said organic coating contains silica.
3. A method for making an organic coated steel strip having improved bake hardenability of 3.5 to 6.1 kgf/mm², comprising the steps of:
depositing a layer of a zinc base alloy on one surface of an extra low carbon steel substrate containing
15 0.001 to 0.008 percent by weight of carbon and having bake hardenability in a weight of 10 to 40 g/m²,
subjecting said substrate to a chromate treatment to form a chromate layer on the zinc base alloy layer
in a weight of at least 10 mg/m², calculated as metallic chromium, and
applying an organic coating of a thickness of 0.5 to 3µm on the chromate layer and baking the coating
at a temperature of up to 150°C.
4. The method of claim 3 wherein said chromate treatment uses an aqueous chromate solution
containing a chromate compound, a reducing agent, and at least one member selected from acid residues,
resins and silica.
5. The method of claim 4 wherein said reducing agent is selected from the group consisting of
methanol, hydrogen peroxide, ethylene glycol, succinic acid, and succinimid.
- 25 6. The method of claim 5 wherein said reducing agent added is added in a sufficient amount to provide
0.2 to 1.9 gram atoms of hydrogen per gram molecule of CrO₃.
7. The method of claim 4 wherein said acid residue is comprised of the residue of phosphoric or boric
acid.
8. The method of claim 7 wherein said acid residue is added in amount to give an acid residue to CrO₃
30 ratio of from 0.05 to 0.3 by weight.
9. The method of claim 4 wherein said resin is comprised of an acrylic resin.
10. The method of claim 9 wherein said resin is added in an amount to give a resin to CrO₃ ratio of from
0.1 to 20 by weight.
11. The method of claim 4 wherein said silica is comprised of colloidal silica.
- 35 12. The method of claim 11 wherein said silica is added in an amount to give a SiO₂/CrO₃ ratio of from
0.3 to 3.0 by weight.

Patentansprüche

- 40 1. Organisch beschichtetes Stahlband verbesserter Brennhärtbarkeit von 3,5 - 6,1 kgf/mm², umfassend
ein extra kohlenstoffarmes Stahlsubstrat mit 0,001 - 0,008 Gew.-% Kohlenstoff und Brennhärtbarkeit,
eine auf einer Oberfläche des Substrats in einer Gewichtsmenge von 10 - 40 g/m² abgelagerte Schicht
aus einer Legierung auf Zinkbasis,
45 eine auf der Schicht aus einer Legierung auf Zinkbasis in einer Gewichtsmenge von mindestens 10 mg/
m² (berechnet als metallisches Chrom) gebildete Chromatschicht und
einen an der Chromatschicht durch Brennen bei einer Temperatur von bis zu 150°C befestigten
organischen Überzug einer Dicke von 0,5 - 3 µm.
2. Organisch beschichtetes Stahlband nach Anspruch 1, dadurch gekennzeichnet, daß der organische
50 Überzug Siliziumdioxid enthält.
3. Verfahren zur Herstellung eines organisch beschichteten Stahlbandes verbesserter Brennhärtbarkeit
von 3,5 - 6,1 kgf/mm² in folgenden Stufen:
Ablagern einer Schicht aus einer Legierung auf Zinkbasis auf einer Oberfläche eines extra
kohlenstoffarmen Stahlsubstrats mit 0,001 - 0,008 Gew.-% Kohlenstoff und Brennhärtbarkeit in einer
55 Gewichtsmenge von 10 - 40 g/m²,
Unterwerfen des Substrats einer Chromatierbehandlung zur Bildung einer Chromatschicht in einer
Gewichtsmenge von mindestens 10 mg/m² (berechnet als metallisches Chrom) auf der Schicht aus der
Legierung auf Zinkbasis und
Applizieren eines organischen Überzugs einer Dicke von 0,5 - 3 µm auf die Chromatschicht und
60 Brennen des Überzugs bei einer Temperatur von bis zu 150°C.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß man bei der Chromatierbehandlung eine
wäßrige Chromatlösung mit einer Chromatverbindung, einem Reduktionsmittel und mindestens einem
aus Säureresten, Harzen und Siliziumdioxid ausgewählten Bestandteil verwendet.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man als Reduktionsmittel Methanol,
65 Wasserstoffperoxid, Ethylenglykol, Bernsteinsäure und Succinimid verwendet.

EP 0 230 320 B1

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß man so viel Reduktionsmittel zusetzt, daß pro Gramm Molekül CrO_3 0,2 - 1,9 g Atom(e) Wasserstoff bereitgestellt wird (werden).

7. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man als Säurerest einen Phosphor- oder Borsäurerest verwendet.

5 8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß man so viel Säurerest verwendet, daß sich ein Säurerest/ CrO_3 -Gewichtsverhältnis von 0,05 - 0,3 einstellt.

9. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man als Harz ein Acrylharz verwendet.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß man so viel Harz verwendet, daß sich ein Harz/ CrO_3 -Gewichtsverhältnis von 0,1 - 20 einstellt.

11. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man als Siliziumdioxid kolloidales Siliziumdioxid verwendet.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß man so viel Siliziumdioxid zusetzt, daß sich ein $\text{SiO}_2/\text{CrO}_3$ -Gewichtsverhältnis von 0,3 - 3,0 einstellt.

15 Revendications

1. Feuillard d'acier à revêtement organique ayant une capacité de durcissement à la cuisson améliorée, de 3,5 à 6,1 kgf/mm², comprenant:

20 un substrat en acier à très faible teneur en carbone contenant de 0,001 à 0,008 pour cent en poids de carbone, et durcissable par cuisson,

une couche d'un alliage à base de zinc, déposée sur une surface du substrat, selon un poids de 10 à 40 g/m²,

une couche de chromate formée sur ladite couche d'alliage à base de zinc, selon un poids d'au moins 10 mg/m², d'après calcul sur la base du chrome métallique, et

25 un revêtement organique d'une épaisseur de 0,5 à 3 µm, lié à ladite couche de chromate, par cuisson à une température allant jusqu'à 150°C.

2. Feuillard d'acier à revêtement organique selon la revendication 1, dans lequel le revêtement organique contient de la silice.

3. Procédé de fabrication d'un feuillard d'acier à revêtement organique, ayant une capacité de durcissement par cuisson améliorée, de 3,5 à 6,1 kgf/mm², comprenant les étapes consistant:

30 à déposer une couche d'un alliage à base de zinc sur une surface d'un substrat en acier à très faible teneur en carbone, contenant de 0,001 à 0,008 pour cent en poids de carbone, et ayant une capacité de durcissement par cuisson, selon un poids de 10 à 40 g/m²,

35 à soumettre ce substrat à un traitement au chromate pour former une couche de chromate sur la couche d'alliage à base de zinc, selon un poids d'au moins 10 mg/m², d'après calcul sur la base du chrome métallique, et

à appliquer un revêtement organique selon une épaisseur de 0,5 à 3 µm, sur la couche de chromate, et à cuire le revêtement à une température allant jusqu'à 150°C.

4. Procédé selon la revendication 3, dans lequel ledit traitement au chromate, met en oeuvre une solution aqueuse de chromate contenant un chromate, un agent réducteur, et au moins un composé choisi parmi des composés dérivés d'acide, des résines et la silice.

5. Procédé selon la revendication 4, dans lequel l'agent réducteur est choisi parmi le méthanol, le peroxyde d'hydrogène, l'éthylène glycol, l'acide succinique et le succinimide.

45 6. Procédé selon la revendication 5, dans lequel l'agent réducteur incorporé, est ajouté selon une quantité suffisante pour obtenir de 0,2 à 1,9 moles d'hydrogène par mole de CrO_3 .

7. Procédé selon la revendication 4, dans lequel le composé dérivé d'acide comprend un composé dérivé de l'acide phosphorique ou borique.

8. Procédé selon la revendication 7, dans lequel le composé dérivé d'acide est ajouté selon une quantité appropriée pour obtenir un rapport du composé dérivé d'acide à CrO_3 , de 0,05 à 0,3 en poids.

50 9. Procédé selon la revendication 4, dans lequel la résine comprend une résine acrylique.

10. Procédé selon la revendication 9, dans lequel la résine est ajoutée selon une quantité appropriée pour obtenir un rapport de la résine à CrO_3 de 0,1 à 20 en poids.

11. Procédé selon la revendication 4, dans lequel la silice comprend de la silice colloïdale.

55 12. Procédé selon la revendication 11, dans lequel la silice est ajoutée selon une quantité appropriée pour obtenir un rapport $\text{SiO}_2/\text{CrO}_3$, de 0,3 à 3,0 en poids.

60

65

FIG. 1

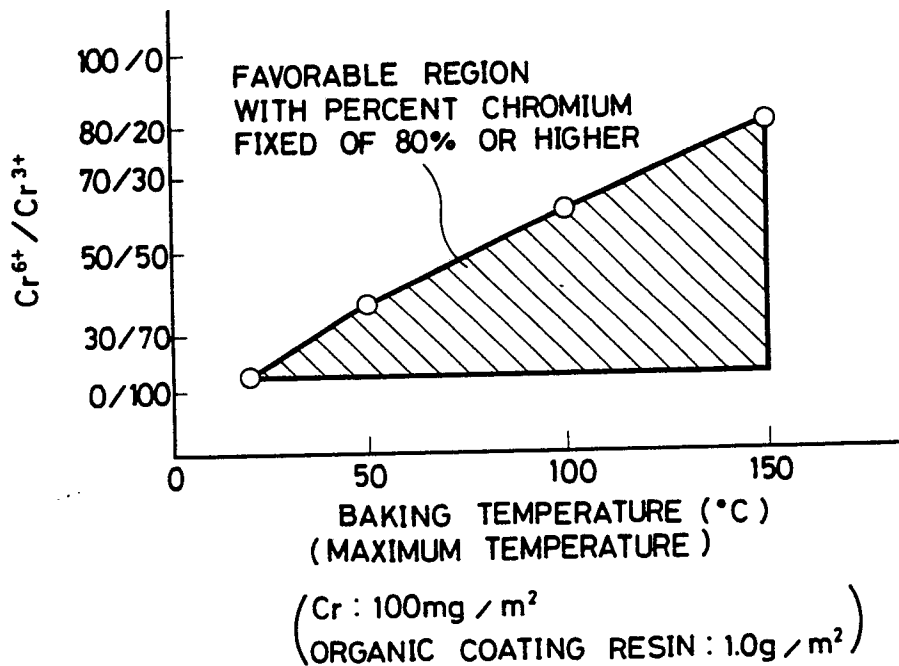


FIG. 2

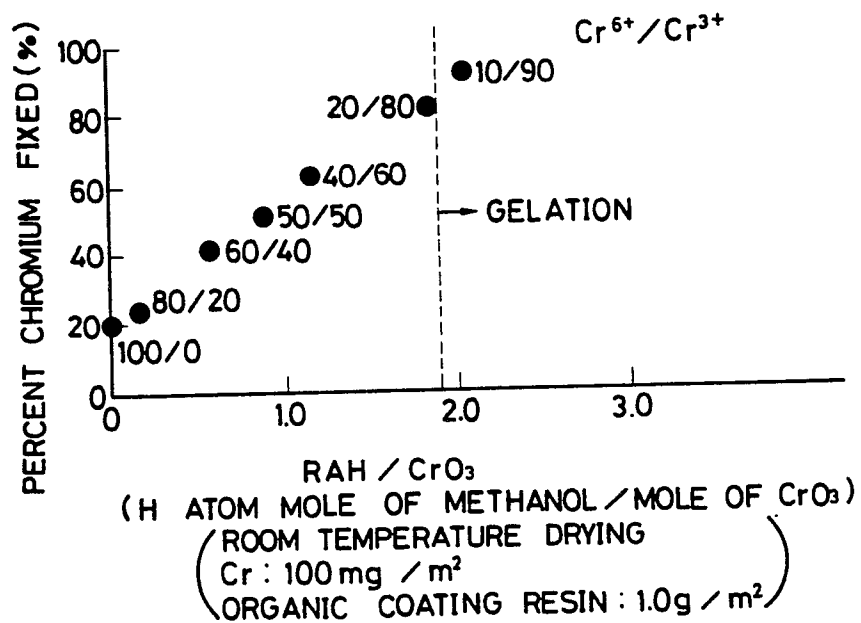


FIG. 3

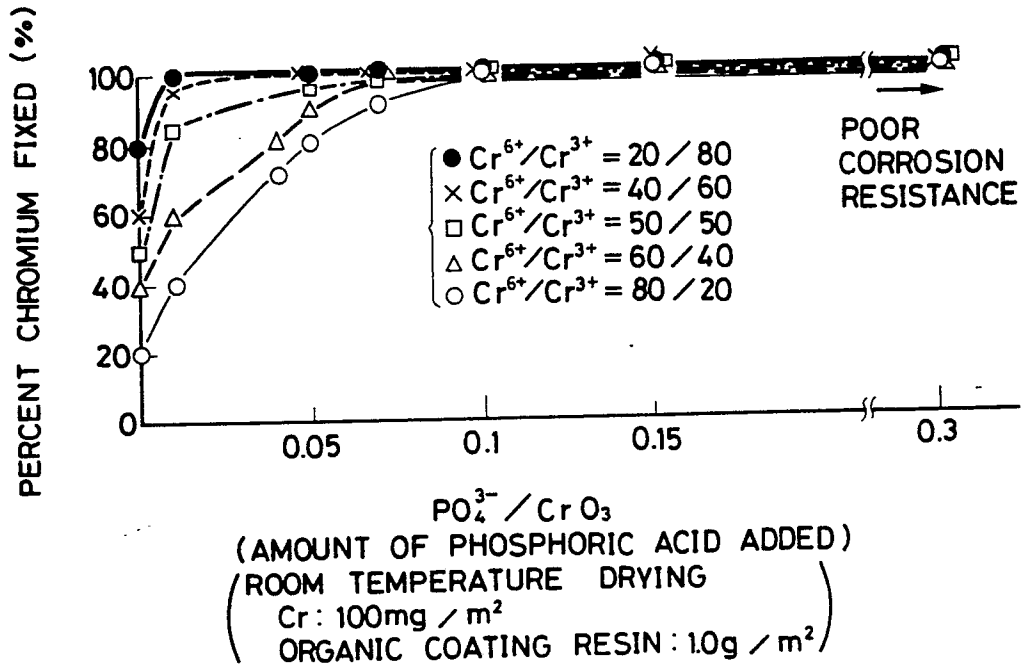


FIG. 4

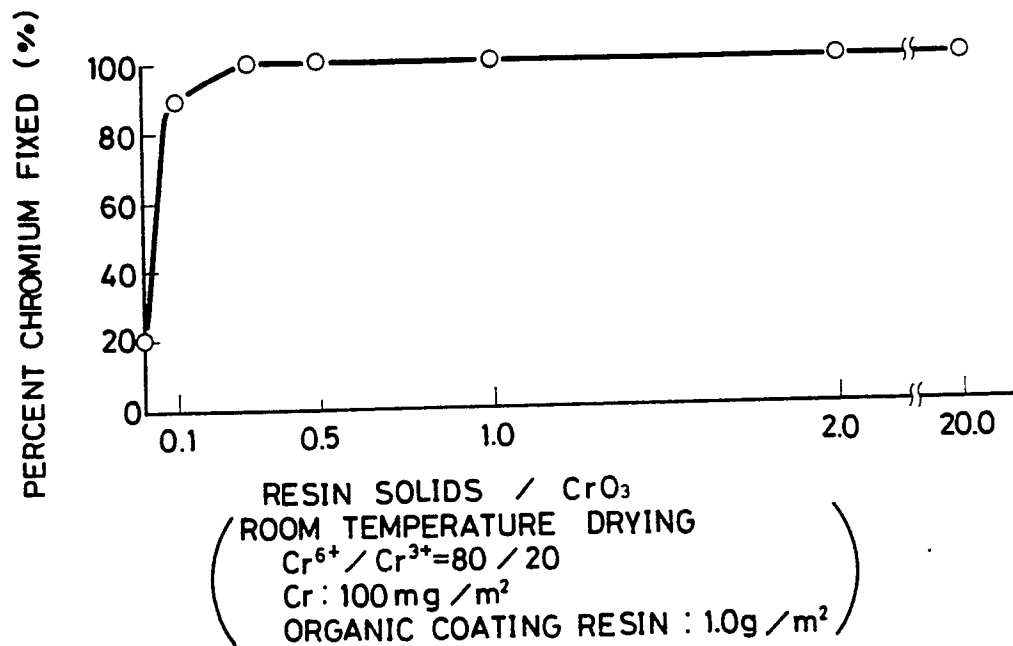
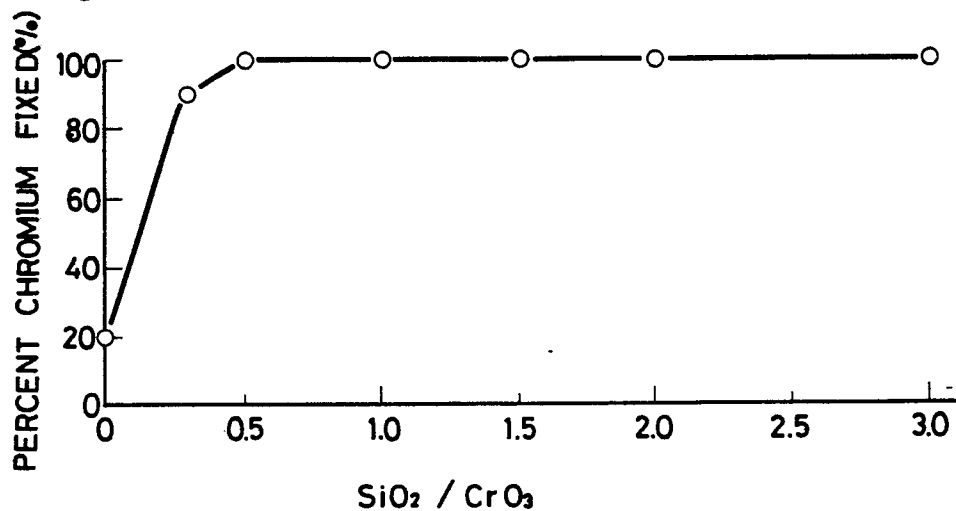


FIG. 5



(ROOM TEMPERATURE DRYING
Cr⁶⁺ / Cr³⁺ = 80 / 20
Cr : 100mg / m²
ORGANIC COATING RESIN : 1.0g / m²)

FIG. 6

