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㊺ Coated steel sheets and process for producing the same.

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CHEMICAL ABSTRACTS, vol. 101, no. 14, October 1, 1984, Columbus, Ohio, USA KAWASAKI STEEL CORP. "Steel sheets plated on one side with zinc or zinc alloys", page 524, abstract no. 119 424k & Jpn. Kokai Tokkyo Koho JP 59 96,291

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Description

The present invention relates to coated steel sheets or strips (herein called steel sheets) having a coating which can provide excellent corrosion resistance, particularly corrosion resistance in their worked portions, and useful for applications in automobiles home electric appliances, and constructions

Galvanized steel sheets have long been used widely as a surface treated steel sheet because they can be commercially produced on a mass-production scale without sacrificing their corrosion resistance before or after paint coating and workability as well as strength inherent to cold rolled steel sheets.

In more recent years, trials have been made using on galvanized steel sheets as rust preventive steel sheets in automobiles, particularly in cold regions for preventing the rust caused by salt dispersed on highway roads to prevent the freezing of the roads. The trend is, however, that more and more demands are being made for satisfactory corrosion resistance of the galvanized steel sheets under severe corrosive environments.

As the means for meeting with the demand for improved corrosion resistance of the galvanized steel sheets, it has been known and commonly practiced to increase the amount of the zinc coating itself and in addition to the increased zinc coating amount, various proposals have been made for alloy coatings as a means of inhibiting the dissolution of the zinc coating itself. Most of these proposed alloy coatings contain iron-group metals such as Fe, Ni and Co as the alloying element.

The steel sheets electro-plated with a zinc-iron-group-metal coating as disclosed in JP-B- 50-29821 and 57-61831, for example, are characterized by their excellent corrosion resistance before and after paint coating and have been successful in commercial production and application. However, a strong demand still exists for further improvement of their corrosion resistance.

Further, steel sheets coated with a zinc or zinc alloy coating containing chromium have been proposed as disclosed in JP-B-59-38313 and 59-40234, and in JP-A- 61-130498, 61-270398 and 62-54099.

All of these proposed chromium-containing coatings contain a very small amount of chromium, which produces only an auxiliary effect on corrosion resistance. Therefore, for the purpose of definitely improving the corrosion resistance, it has long been desired to precipitate a larger amount of chromium in the coating.

For applications in automobiles and home electric appliances, severer demands are being made for improved surface appearance in addition to corrosion resistance, and to meet with the demands, an appropriate treatment for the surface brightening of coatings is strongly desired.

Up to now, no successful art is known for increasing the chromium content in the zinc coating and no successful art is known for producing Zn-Cr coatings with a high-chromium content and yet excellent in the surface appearance.

Thus it is impossible to obtain a satisfactory coating having good surface brightness and workability merely by increasing the Cr^{3+} ion concentration in the plating bath. The increased chromium ion concentration causes various hindrances in the operation, such as a sharp lowering in the current efficiency, which prohibit a commercial production of steel sheets having a high-chromium alloy coating.

Meanwhile, to meet with the demands for improved corrosion resistance for applications in automobiles, in particular, a complex coated steel sheet has been developed by subjecting the metallic primer coating to a chromating treatment and then applying an organic coating thereon.

In the art of these steel sheets having the complex coating, main considerations have been given to improvements of the paint composition which forms the upper-most organic coating, and inevitably, no full satisfaction has been achieved concerning improvements of corrosion resistance, press formability and spot weldability. For example, a zinc-rich paint coated steel sheet shows inferior press formability and is not satisfactory with respect to corrosion resistance and weldability, and a steel sheet coated with a paint containing electric conductive pigments is not wholly satisfactory despite its improved press formability and weldability. Further, in all types of the organic coated steel sheets mentioned above, the organic coating is applied in a relatively large quantity exceeding 5 μm in thickness which are rather detrimental to press formability and weldability.

More recently, steel sheets having a metallic-organic complex coating also has been developed in which the organic coating is applied in a relatively small quantity of less than 5 μm in thickness. For these thin-type organic coatings, trials have been made to improve the corrosion resistance by introducing rust preventive pigments in the organic coatings. For example, JP-A-59-162278 discloses an organic coating in which chromium compounds as the rust preventive pigments are added to a water-dispersion type emulsion resin, and JP-A-60-50181 discloses an organic coating in which silica is added as the rust preventive pigment. However, these trials have been found unsuccessful in improving the corrosion resistance.

The corrosion resistance of the steel sheets having a metallic-organic complex coating mentioned above is imparted mainly by the organic coating. However, as the thickness of the organic coatings is required to be thinner from the points of press formability and weldability, improvement of the metallic primer coating itself is required from the point of corrosion resistance.

More specifically, as the metallic primer coating, Zn coating, Zn-Ni coating, Zn-Fe coating and the like are applied, and in the thin-type organic coatings, the organic coating is further thinned when subjected to the press forming and slight damage or scratches can easily penetrate the thinned organic coating to reach the metallic primer coating or even to the substrate steel sheet, thus causing local exposure of the metallic coating of the substrate sheet. Therefore, the corrosion resistance of these coated sheets must more and more rely on the corrosion resistance of the metallic primer coating alone. However, the conventional metallic coatings cannot impart satisfactory corrosion resistance, and is not reliable for maintaining good corrosion resistance after press forming.

Therefore it is an object of the present invention to provide a coated steel sheet which is free from the problems of the prior art is excellent in corrosion resistance, particularly corrosion resistance after press forming, and further excellent in workability, weldability and surface brightness.

The present invention is based on the discovery that it is possible to achieve a markedly enhanced chromium content in the alloy coating, which has never been conventionally achieved, if a water soluble cationic polymer is added to a plating bath containing Zn^{2+} and Cr^{3+} which promotes the precipitation of Cr, and that the resultant coating has satisfactory workability due to the co-precipitation of a very small amount of the cation polymer in the coating.

Further, the present invention is based on the discovery that addition of iron-group metal or metals, Fe, Ni and Co, to the coating will improve the spot weldability as required for the applications in automobiles and home electric appliances.

Still further, the present invention is based on the discovery made by further studies by the present inventors that chromium when present with zinc will not be passivated, but tends to take part in a sacrificial rust prevention together with zinc, and the corrosion product of chromium accumulates and forms a hard-to-dissolve protective film, thereby preventing a further progress of corrosion. This phenomenon is considered to provide a high degree of corrosion resistance.

However, under an exposing condition similar to the actual condition of service, the hard-to-dissolve protective film formed by the corrosion product of chromium is very likely to be cracked due to a long time of drying. Therefore, after the lapse of a certain period of time, corrosion can sharply progress. It is found by the present inventors that it is effective to co-precipitate fine particles of oxides in the coating for preventing such sharp development of corrosion. The fine particles of oxides intrude into the corrosion products of zinc and chromium to be strongly combined therewith. The corrosion products thus combined with the oxides can still provide good humidity absorbing ability so that the protective film formed with the corrosion products is hardly strained even under the dry condition, resulting in effective prevention of cracking occurring in the protective film.

Thus on the basis of the above discovery, it is possible to further stabilize the protective film formed by the corrosion products of the Zn-Cr alloy coatings by the addition of fine particles of oxides in the coating.

Therefore, a further object of the present invention is to provide a coated steel sheet having a primer Zn-Cr coating, an intermediate chromate film, and an upper-most organic coating, which shows excellent corrosion resistance particularly at worked portions, and excellent workability and weldability as well. For this object the Zn-Cr coating contains fine particles of oxide co-precipitated therewith so as to produce corrosion products which are very effective to protect the substrate sheet in event corrosion should occur locally at paint-coating-defective portions or worked portions.

A still further object of the present invention is to provide a process for consistently producing the coated steel sheets having a high-chromium alloy coating excellent in corrosion resistance and surface brightness. For this object, a water soluble cation polymer is introduced into the Zn-Cr electro-plating bath to promote the precipitation of chromium, and the ratio of Cr^{6+} ions to Cr^{3+} ions in the bath is maintained below a certain constant value by the anodic oxidation of Cr^{3+}.

Hereinbelow the coated steel sheets and the process for producing the same according to the present invention will be summarized.

(1) Electro-plated steel sheets having a primer coating composed of 5 to 30 % by weight of Cr, 0.005 to 5 % by weight of a cationic polymer, with the balance being Zn, with or without a further Zn or Zn-alloy coating formed on the primer coating.

(2) Electro-plated steel sheets having a primer coating composed of no less than 5 % by weight of Cr, no less than 1 % by weight of iron-group metal, with the total amount of Cr and the iron-group metal being not more than 30 % by weight, 0.005 to 5 % by weight of a cationic polymer with the balance being Zn, with or without a further Zn of Zn-alloy coating formed on the primer coating.

(3) Electro-plated steel sheets having a primer coating composed of 5 to 30 % by weight of Cr, 0.1 to 10 % by weight of fine particles of oxide, and 0.005 to 5 % by weight of a cationic polymer with the balance being Zn.

(4) Electro-plated steel sheets having a primer coating composed of 5 to 30 % by weight of Cr, 0.1 to 10 % by weight of fine particles of oxide, 0.005 to 5 % by weight of a cationic polymer, and 1 to 10 % by weight of iron-group metal with the balance being Zn.

(5) Electro-plated steel sheets according to (3) or (4) which further comprise a Zn or Zn-alloy coating formed on the primer coating.

(6) Coated steel sheets having a primer coating composed of 5 to 30 % by weight of Cr, 0.1 to 10 % by weight of fine particles of oxide, 0.005 to 5 % by weight of a cationic polymer, with the balance being Zn, a chromate film formed on the primer coating in an amount of 10 to 150 mg/m^2 in total chromium, and an organic coating formed on the chromate film in 0.3 to 3 μm thickness.

(7) Electro-plated steel sheets according to (6), in which the primer coating further contains 1 to 10 % by weight of an iron-group metal.

(8) Electro-plated steel sheets having a primer coating composed of 5 to 30 % by weight of Cr, 0.005 to 5 % by weight of a cationic polymer, with the balance being Zn, a chromate film formed on the primer coating in an amount of 10 to 150 mg/m^2 in total chromium, and an organic coating formed on the chromate film in 0.3 to 3 μm thickness.

(9) Electro-plated steel sheets having a primer coating composed of Cr and an iron-group metal in a total amount not more than 30 % by weight, with Cr being in an amount not less than 5 % by weight, and the iron-group metal being in a range from 1/10 to 1/2 of the Cr content, 0.005 to 5 % by weight of a cationic polymer, with the balance being Zn, a chromate film formed on the primer coating in an amount of 10 to 150 mg/m^2 in total chromium, and an organic coating formed on the chromate film in an amount of 0.3 to 3 μm.

(10) Electro-plated steel sheets according to any of (1) to (9) in which the cationic polymer is a quaternary amine polymer.

The process for producing the coated steel sheets according to the present invention will be summarized below.

(1) Process for producing an electro-plated steel sheet having excellent corrosion resistance and surface brightness, comprising performing electro-plating in an acidic Zn plating bath containing Cr ions and a cationic polymer, with the ratio of Cr^{6+} ions/Cr^{3+} ions being not more than 0.1.

(2) Process according to (1), in which the acidic bath contains Ni^{2+}, Fe^{2+} and/or Co^{2+}.

(3) Process according to (1), in which the acidic bath further contains fine particles of an oxide.

(4) Process according to any of (1) to (3), in which the cationic polymer is a quaternary amine polymer.

The excellent corrosion resistance of the electro-plated steel sheets according to the present invention is imparted mainly by the chromium content in the primer coating. For this purpose, 5 to 30 % by weight of Cr in the coating is desirable. With the Cr content less than 5 % by weight in the coating, the tendency of red rust formation is still present and the resultant corrosion resistance is not sufficient, although some improvement is obtained. While with the Cr content not less than 5 %, the red rust formation during a salt spray test, for example, can be inhibited and marked improvement can be obtained.

The high degree of corrosion resistance imparted by the coated steel sheets according to the present invention have never been achieved by the conventional Zn coating, or Zn-alloy coatings, such as Zn-Fe and Zn-Ni coatings.

As mentioned hereinbefore, Cr when co-present with Zn, is not passivated, but takes part in the sacrificial rust prevention together with Zn, and moreover the corrosion product of Cr precipitates and accumulates as hard-to-dissolve protective film at corroded portions, thus prohibiting the progress of corrosion and high corrosion resistance is assured.

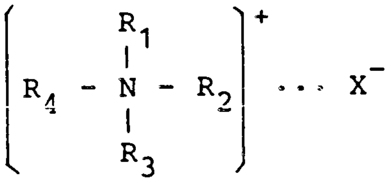
With the Cr content more than 30 % by weight, on the other hand, although the resultant corrosion resistance is satisfactory, the problem of so-called powdering that the coating strips off during the working such as press forming cannot be prevented despite the advantageous effect by the co-precipitation of the cation polymer as hereinafter described, and therefore such a high chromium content is not practically applied.

For satisfying both the corrosion resistance and the workability, 5 to 20 % by weight of Cr content is more desirable.

The cation polymer used in the present invention is discovered to be effective to promote the precipitation of Cr during the electro plating and also co-precipitates with Cr in the coating in a very small amount, thus improving the anti-powdering property. This advantageous effect by the co-precipitation of the cation polymer is assumed to derive from the fact that the co-precipitation prevents the Cr ions from hindering a uniform electro-deposition and growth of Zn and iron-group metals so that a uniform and smoothly coated structure is assured. Thus with the co-precipitation of the cation polymer in the coating, it is possible to obtain a dense coating in which Zn and Cr or Zn, Cr and the iron-group metals are uniformly mixed or alloyed. For this purpose, 0.005 to 5 % by weight of cation polymer contained in the coating is desirable. Less than 0.005 %, no tangible effect is obtained for improving the anti-powdering property. On the other hand, the cation polymer content more 5 % in the coating is difficult to obtain even if the cation polymer concentration in the plating bath is increased, and an excessive cation polymer content in the coating tends to lower the coating adhesion. From the point of working alone, it is enough if the cation polymer is co-precipitated in the coating in an amount not less than 1/1000 of the Cr content in the coating.

Among the water soluble cationic polymer used in the present invention, polymers of quaternary amine having a molecular weight from 10^3 to 10^6 are preferred. Among the amine polymers shown hereinbelow, polyaminesulfon (hereinafter called PAS) and polyamine (hereinafter called PA) are most effective to promote the precipitation of Cr. This is attributable to the adsorption effect by the amine group and the combination of the sulfo group with the metal ions or with the metal.

Basically, the cationic polymer used in the present invention is a homopolymer or copolymer having in its main chain a salt of quaternary amine (ammonium salt) shown below.

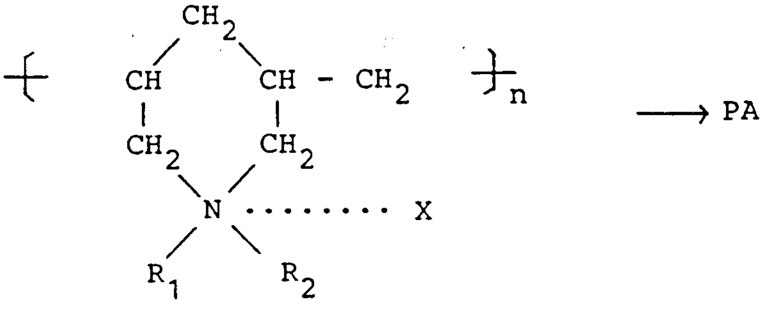


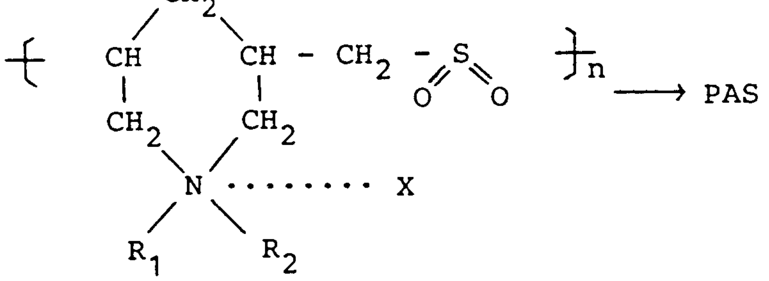
$$\left[R_4 - \overset{\displaystyle R_1}{\underset{\displaystyle R_3}{N}} - R_2 \right]^+ \cdots X^-$$

where R_1, R_2, R_3 and R_4 are each an alkyl group having 1 to 4 carbon atoms.

Some typical examples of the cationic polymers used in the present invention will be illustrated below.

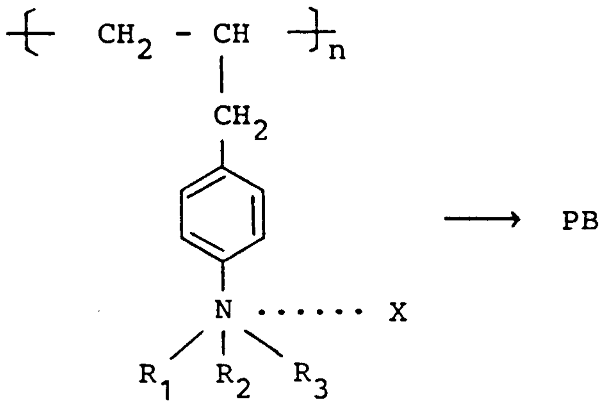
(1) Polymers obtained from diallylamine:



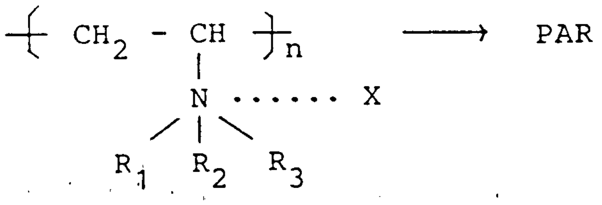


wherein R_1 and R_2 are each a lower alkyl group (CH_3, C_2H_5, C_3H_7, and C_4H_9), and X stands for Cl^-, HSO_4^-, $H_2PO_4^-$, $R\text{-}SO_3^-$ (R is an alkyl having 1 to 4 carbon atoms) and anion of NO_3^-.

(2) Polymers obtained from vinylbenzyl.



(3) Allylaminepolymers



wherein R_1, R_2 and R_3 are each an alkyl group (CH_3, C_2H_5, C_3H_7, or C_4H_9) and X represents anions of Cl^-, HSO_4^-, $H_2PO_4^-$, $R\text{-}SO_3^-$ (R is an alkyl group having 1 to 4 carbon atoms) or NO_3^-.

In addition to the above quaternary amine polymers, polymers of primary, secondary and tertiary amines may also be used for promoting the precipitation of Cr although they are less effective.

Regarding the amount of the primer coating, 10 to 50 g/m^2 is enough for assuring the desired corrosion resistance, and unavoidable impurities such as Pb, Sn, Ag, In, Bi, Cu, Sb, As, Al, Ti, Na, P and S may be present in a minor amount in the primer coating without degrading the desired properties of the present coated products.

For improving the spot weldability of the coated steel sheets according to the present invention, the iron-group metal, such as Fe, Ni and Co, is co-precipitated in the primer coating in an amount of 1 to 10 % by weight. The Zn-Cr electro-plated coating containing no iron-group metal show inferior spot weldability as compared with the conventional Zn-Ni and Zn-Fe alloy coatings. Although not theoretically clarified, the reason for the inferior spot weldability may be attributed to the following facts that as compared with the conventional Zn-Ni and Zn-Fe coatings the Zn-Cr coating containing no iron-group metal has a lower electric resistance and is more easily heated and fused by the current passage and further the coating itself is softer and is easily deformed by the pressure exerted thereon by a welding tip so that the current can hardly be concentrated on the welding spot.

When the Zn-Cr coating contains the iron-group metal, such as Fe, Ni and Co, the electric resistance is enhanced and the coating itself is hardened so that the spot weldability is definitely improved. With the iron-group metal content in an amount less than 1 % by weight is not effective for the purpose, while in excess of 10 % by weight, the coating is influenced largely by the nature of the iron-group metal so that corrosion resistance is, in some cases, deteriorated.

When the iron-group metal is present in the electro-plating bath, it produces favorable effect that the ions of this metal adsorbs on the fine particles of oxide, if present, to facilitate the precipitation of the oxide. However if the total amount of the iron-group metal in the coating is excessively increased, the workability of the coating is deteriorated despite the favorable effect of the co-precipitation of the cation polymer. Therefore, it is desirable to maintain the total content of Cr and the iron-group metal in the coating not more than 30 % by weight. As the iron-group metal, Ni is most desirable because it can further improve the corrosion resistance of the coating.

The fine particles of oxide contained in the coating contribute to further stabilize the corrosion products of Zn-Cr by intrusion thereinto and strong combination therewith through oxygen bonding, and the fine particles of oxide act as a barrier against corrosive factors. In this way the corrosion resistance of the coated steel sheet, particularly the corrosion resistance at and around the worked portions, is improved.

For the above purpose, it is desirable that the fine particles of oxide are contained in the coating in an amount from 0.1 to 10 % by weight. Less than 0.1 %, no substantial improvement of corrosion resistance is obtained and more than 10 %, workability is deteriorated. From aspects of both corrosion resistance and workability, 0.1 to 5 % by weight of the fine particles of oxide is more preferable.

As the fine particles of oxide usable in the present invention, many metal oxides and semi-metal oxides may be used, but oxides of Si, Al, Zr, Cr, Mo and W are most preferable. These oxides can be used in single or in combination. The particle size of these oxides is preferably not larger than 1 μm in average. The particle size larger than 1 μm is hard to co-precipitate in the coating.

The primer coating according to the present invention may be of homogeneous or heterogeneous structure. Thus within the scope of the coating composition as defined hereinabove, one or more specific components may be dispersed or condensed in a layer form, or the concentration of specific component or components may vary in gradient across the coating thickness.

The coated steel sheets having the primer coating described hereinabove may further be coated with a Zn or Zn-alloy coating such as Zn-Fe and Zn-Ni coatings in a small amount.

Further, instead of the Zn or Zn-alloy coating, the primer coating may be subjected to a chromate treatment and then further coated with an organic coating.

When the Zn or Zn-alloy coating is applied on the primer coating, 1 to 5 g/m^2 of such coating is preferred to improve the corrosion resistance after paint coating under a wet environment as under a salt spray test condition.

The chromate film applied on the primer coating is effective to enhance the adhesion with the organic coating.

As the Zn-Cr coating is highly reactive with an acidic treating solution containing Cr^{6+} and/or Cr^{3+}, any of the conventional chromate treatments, such as the spray type chromate treatment, the reaction type chromate treatment, and the electrolytic type chromate treatment may be applied.

For the spray type chromate treatment, and the reaction type chromate treatment, inorganic colloids, acids such as phosphoric acid, fluoride, water-soluble or emulsion type organic resin may be added to the treating solution in addition to Cr^{6+} and Cr^{3+} as conventionally done.

For example, as the solution containing the phosphoric acid and the fluoride, the solution may be composed of 30 g/l of chromic acid, 10 g/l of phosphoric acid, 4 g/l of potassium titanate fluoride, and 0.5 g/l sodium fluoride. As the treating solution containing the silica, the solution may be composed of 50 g/l of chromic acid (including 40 % of trivalent chromium) and 100 g/l of SiO_2.

As the inorganic colloids, preferred examples are colloids of SiO_2, Al_2O_3, TiO_2 and ZrO_2; colloids containing one or more of oxyacids such as molybdic acid, tungstic acid, vanadic acid, and their salts; phosphoric acids such as phosphoric acid and polyphosphoric acid which form hard-to-dissolve salts by reaction with Zn of the coating; and silicofluorides titanium, and phosphates which form hard-to-dissolve salts by reaction such as hydrolysis.

These colloids are found to be effective to fix a small amount of hexavalent chromium in the chromate film and also phosphoric acids and fluorides mentioned above in particular are found to be effective to promote the reaction between the primer coating and the chromate.

The amount of these inorganic colloids to be added may vary depending on their natures; in the case of phosphoric acids, 1 to 200 g/l is desirable, and in the case of SiO_2, 1 to 800 g/l is desirable, for example.

In some cases, organic resins, such as acrylic resin, which are consistently mixable with the chromate may be added.

As the electrolytic chromate treatment, any conventional treatment can be applied, such as one in which sulfuric acid, phosphoric acid, and halogen ions are added in addition of chromic acid, or inorganic colloids such as SiO_2 and Al_2O_3 are added, or cations such as Co and Mg are added. Normally the electrolysis is performed by the cathodic electrolysis, but the anodic electrolysis and alternate current electrolysis may be additionally used.

The amount of chromate film formed on the primer coating is preferably from 10 to 150 mg/m^2 in the term of total chromium. With a chromate film of less than 10 mg/m^2, the adhesion of the organic film is not satisfactory, while a chromate film of more than 150 mg/m^2, the weldability and press formability deteriorate. Therefore, from the practical point, 20 to 100 mg/m^2 is more desirable.

In order to avoid the contamination of the chemical conversion treating solution with chromium dissolving from the chromate film, and the complicated handling of the waste liquid, it is advantageous to form a chromate film which contains not more than 5 % of water-soluble component. For forming this hard-to-dissolve chromate film, the electrolytic chromate treatment is better suited.

On the chromate film, an organic coating of 0.3 to 3 µm in thick may be applied for improving the corrosion resistance. With an organic coating less than 0.3 µm the desired improvement of corrosion resistance cannot be assured, and with an organic coating exceeding 3 µm, weldability and press formability may sometimes deteriorate. A more preferable range is from 0.5 to 2 µm.

The organic coating may be either a solvent type or a water soluble type, and epoxy and acrylic resins, polyester, urethane and acrylic olefins etc., and their copolymer derivatives may be used, for example.

For heat-curing type organic coatings containing rust preventive pigments such as SiO_2 and $BaCrO_4$, various additives such as curing agent and lubricant for further improving the press formability may be added.

One preferred embodiment of the organic coating usable in the present invention is illustrated below.

Main resin:	bisphenol type epoxy resin (average molecular weight: 300 to 100,000), 30 % or more by weight in the coating.
Curing Agent:	block polyisocyanate compound: 1/10 to 20/10 by weight ratio to the main resin.
Rust preventive pigment:	dry silica (average primary particle size 1 to 100 µm); 5 to 50 % by weight to the coating.
Lubricant:	polyethylene wax; 0.1 to 10 % by weight to the coating.
Solvent:	ketone

The organic coating may be applied by any conventional methods, such as roll coating, spray coating, and curtain flow coating.

According to the present invention, the coated steel sheet may be coated only one side, and the other side may be uncoated or coated with the Zn-Cr coating alone depending on the final applications the coated steel sheet is intended for.

For producing the coated steel sheet according to the present invention, the electo-plating may be performed in a plating bath containing Zn^{2+} ions, Cr^{3+} ions, and 0.01 to 20 g/l of water soluble cation polymer, such as copolymers of tertiary amines as mentioned hereinbefore, having a pH value ranging from 0.5 to 3 at a bath temperature ranging from 40 to 70 ° C with a current density of 20 A/dm^2 or higher.

As the case requires, the iron-group metals, and fine particle oxides, such as SiO_2, TiO_2 and Al_2O_3 are added to the bath. Further the addition of salts of Na^+, K^+, and $NH_4{}^+$ ions are advantageous for improving the electric conductivity of the bath.

The Zn coating or Zn-alloy coating to be formed on the primer coating may be done by a conventional plating method. In this case, however, it is most desirable to completely remove the dragout containing Cr ions and cation polymer taken out from the primer coating bath with water prior to the coating.

As for the substrate for the coated steel sheet according to the present invention, a dull-finished rolled soft steel sheet is normally used. However, a bright-finished rolled steel sheet may be used, and the steel composition may be a high tensile steel containing larger amounts of Mn, S and P or may be a corrosion resistant steel containing larger amounts of Cr, Cu, Ni and P.

Fig. 1 is a drawing showing the shape of welding tip used for evaluating the spot-weldability.

Fig. 2 is to show the correlation between the surface brightness and the Cr content and the ratio of Cr^{6+}/Cr^{3+} and in a typical plating bath used in the present invention, showing that the ratio of Cr^{6+}/Cr^{3+} not more than 0.1 is essential.

The present invention will be described in more detail in connection with the following examples.

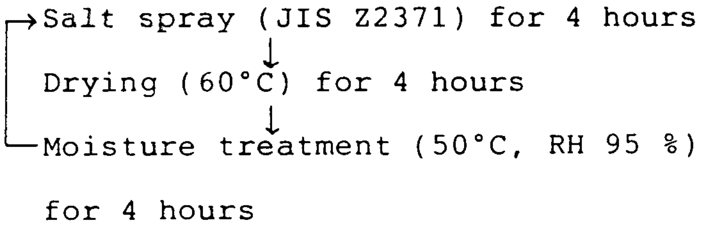
Example 1

A cold rolled steel sheet with a thickness of 0.8 mm was subjected to alkali degreasing, acid pickling with the use of 5 % sulfuric acid solution and washing in succession, and then the resultant steel sheet was electro-plated in an acidic bath of sulfuric acid at pH 2 at a bath temperature of 60 ° C, with a flow rate of the solution of 90 m/min by pump stirring, and the distance between the electrodes of 10 mm. The plating bath was composed of 70 g/l of Zn^{2+} ion, 1 - 30 g/l of Cr^{3+} ion, 0.01 - 20 g/l of cationic polymer (polyamine polymer (PA) with molecular weight of 10,000 or polyamine-sulfone polymer (PAS) with molecular weight of 120,000) and 16 g/l of Na^+. The contents of Cr and cationic polymer were controlled by their addition amounts and the electric current density. The plated amount was 20 g/m^2. In certain instances, further, Zn or Zn-alloy coating was applied in an amount of 3 g/m^2 as a topcoat by means of a known method.

The coating compositions and evaluation of corrosion resistance and workability of the electro-plated steel sheets produced in this way are shown in Table 1. By the way, Zn and Cr in the coating were analysed by means of the atomic absorption method and, as for the cationic polymer, C was analyzed by the combustion method and the amount of cationic polymer was recalculated therefrom. The methods for the evaluation of corrosion resistance and workability are as follows:

(1) Corrosion resistance of non paint-coated samples:

(a) Salt spray test (SST) (in accordance with JIS Z2371): Evaluated by the area of red rust formed after 672 hours.
less than 1 %: ◎
1 % - 10 %: ○
10 % - 30 %: △
more than 30 %: ×
(b) Cyclic corrosion test (CCT):



By taking the above three steps as one cycle, the results were evaluated by the loss of sheet thickness after 30 cycles.
less than 0.1 mm: ◎
0.1 mm - 0.2 mm: ○
0.2 mm - 0.3 mm: △
more than 0.3 mm: ×

(2) Corrosion resistance after paint coating:

The Zn-Cr coated samples were subjected successively to immersion type phosphoric acid treatment, cathodic electric coating of Zn with a thickness of 20 μm, intermediate coating, water polishing and topcoat paint coating to obtain a total thickness of coatings of 100 μm. The test pieces were given a crosscut reaching to the base metal and subjected to the 1,000 hour SST and the 60 cycle CCT as above mentioned, and the results were evaluated by means of the swollen width of the crosscut part.
less than 1 mm: ◎
1 mm - 3 mm: ○
3 mm - 5 mm: △
more than 5 mm: ×

(3) Workability

After cylindrical press forming with a size of 50 ø x 25 H, tape peeling tests were done on the worked surfaces, and the results were evaluated by the weight losses.
less than 2 mg: ◎
2 mg - 5 mg: ○
5 mg - 8 mg: △
more than 8 mg: ×

All the examples of the present invention were obviously excellent both in corrosion resistance and workability as compared with the comparison examples.

Table 1

	No.	Primer Coating Composition(weight %)					Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating		Corrosion Resistance after Paint Coating		Workability
		Zn	Cr	Cationic Polymer		Others		SST	CCT	SST	CCT	
Example	1	balance	5	PA	0.005			○	○	○	○	○
	2	〃	10	〃	0.005			◎	◎	○	◎	△
	3	〃	20	〃	1			◎	◎	○	◎	◎
	4	〃	30	〃	3			◎	◎	○	◎	○
	5	〃	5	PAS	0.005			○	○	○	○	○
	6	〃	10	〃	1			◎	◎	○	◎	◎
	7	〃	20	〃	3			◎	◎	○	◎	◎
	8	〃	30	〃	5			◎	◎	○	◎	○
	9	〃	7	〃	0.01			◎	◎	○	◎	○
	10	〃	7	〃	0.1			◎	◎	○	◎	◎
	11	〃	7	〃	1			◎	◎	○	◎	◎
	12	〃	15	〃	0.05			◎	◎	○	◎	○
	13	〃	15	〃	0.5			◎	◎	○	◎	◎
	14	〃	15	〃	5			◎	◎	○	◎	◎
	15	〃	7	〃	0.01		Zn	◎	◎	◎	◎	○
	16	〃	7	〃	0.1		Zn-11%Ni	◎	◎	◎	◎	◎
	17	〃	7	〃	1		Zn-80%Fe	◎	◎	◎	◎	◎
	18	〃	15	〃	0.05		Zn	◎	◎	◎	◎	○
	19	〃	15	〃	0.5		Zn-11%Ni	◎	◎	◎	◎	◎
	20	〃	15	〃	5		Zn-80%Fe	◎	◎	◎	◎	◎

Table 1 (Cont'd)

	No.	Primer Coating Composition(weight %)					Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating		Corrosion Resistance after Paint Coating		Workability
		Zn	Cr	Cationic Polymer		Others		SST	CCT	SST	CCT	
Comparison	21	100	-	-	-			×	×	×	×	○
	22	balance	-	-	-	Ni,12		×	×	△	△	◎
	23	〃	-	-	-	Fe,15	Zn-80%Fe	×	×	△	△	◎
	24	〃	5	-	-			○	○	○	○	×
	25	〃	1	PAS	0.03			△	×	△	×	○
	26	〃	40	PAS	0.5			◎	◎	○	◎	×
	27	〃	10	PAS	0.001			◎	◎	○	◎	×

Example 2

Except the addition of 10 - 150 g/l of iron group metal ion to the plating bath composition, plating was done under the same conditions as in Example 1.

The coating compositions and evaluation of corrosion resistance, spot weldability and workability of the electro-plated steel sheets produced in this way are shown in Table 2. Zn, Cr, Fe, Co and Ni in the coating were analyzed by means of the atomic absorption method and, for the cationic polymer, the amount of carbon was analyzed by the combustion method and the amount of cationic polymer was recalculated therefrom. The methods for evaluating corrosion resistance and workability were the same as in Example 1. Spot weldability was evaluated by the following method.

Spot Weldability:

The welding conditions were as below.

Electric current:	8 kA
Number of cycle:	10 cycles
Pressure applied:	200 kg
Shape of welding tip:	as shown in Fig. 1 (where A is 12 mmϕ, B is 6 mmϕ and θ is 30°)

After continuous shock of 5,000 times, the nugget diameter was measured and the results were evaluated as follows.
not less than 3.6 mm: ○
less than 3.6 mm: ×

Table 2

	No.	Primer Coating Composition(weight %)					Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating	Corrosion Resistance after Paint Coating		Spot Workability	Workability
		Zn	Cr	Iron-group Metal	Cationic Polymer			SST	SST	CCT		
Example 2	2- 1	balance	5	Ni:3	PA	0.01		◎	○	◎	○	◎
	2- 2	〃	5	Ni:3	〃	0.1		◎	○	◎	○	◎
	2- 3	〃	5	Fe:3	〃	0.01		○	○	○	○	○
	2- 4	〃	5	Co:3	〃	0.01		○	○	○	○	○
	2- 5	〃	7	Ni:10 Co:1	PAS	0.01		◎	○	◎	○	◎
	2- 6	〃	15	Ni:5 Fe:1	〃	0.01		◎	○	◎	○	△
	2- 7	〃	25	Ni:3	〃	3		◎	○	◎	○	○
	2- 8	〃	29	Ni:1	〃	5		◎	○	◎	○	○
	2- 9	〃	5	Ni:1	〃	0.005		○	○	○	○	○
	2-10	〃	5	Ni:2	〃	0.05		◎	○	◎	○	◎
	2-11	〃	5	Ni:5	〃	0.5		◎	○	◎	○	◎
	2-12	〃	10	Ni:1	〃	0.01		◎	○	◎	○	◎
	2-13	〃	10	Ni:5	〃	0.1		◎	○	◎	○	◎
	2-14	〃	10	Ni:10	〃	1		◎	○	◎	○	◎
	2-15	〃	5	Ni:1	〃	0.005	Zn	○	◎	○	○	○
	2-16	〃	5	Ni:2	〃	0.05	Zn-11%Ni	◎	◎	◎	○	◎
	2-17	〃	5	Ni:5	〃	0.5	Zn-80%Fe	◎	◎	◎	○	◎
	2-18	〃	10	Ni:1	〃	0.01	Zn	◎	◎	◎	○	◎
	2-19	〃	10	Ni:5	〃	0.1	Zn-11%Ni	◎	◎	◎	○	◎
	2-20	〃	10	Ni:10	〃	1	Zn-80%Fe	◎	◎	◎	○	◎

T a b l e 2 (Cont'd)

	No.	Primer Coating Composition(weight %)					Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating	Corrosion Resistance after Paint Coating		Spot Workability	Workability
		Zn	Cr	Iron-group Metal	Cationic Polymer			S S T	S S T	C C T		
Comparison 2	2-21	100	-	-	-	-		×	×	×	×	○
	2-22	balance	-	Ni:12	-	-		×	△	△	○	◎
	2-23	〃	-	Ni:15	-	-	Zn-80%Fe	×	△	△	○	◎
	2-24	〃	5	-	-	-		○	○	○	×	×
	2-25	〃	1	Ni:5	PAS	0.5		△	△	×	○	○
	2-26	〃	10	Ni:0.1	〃	1		●	○	●	×	◎
	2-27	〃	35	Ni:5	〃	3		●	○	●	○	×
	2-28	〃	10	Ni:5	〃	0.001		●	○	●	○	×

Example 3 (Zn plating + chromate treatment)

Except the addition of 0 - 30 g/l of iron-group metal to the plating bath composition, plating was done under the same conditions as in Example 1. To the plated steel sheets, chromate treatment and organic coating were further applied as shown below.

(1) Chromate treatment:

(a) Electrolysis-type chromate treatment:

By using a treating solution containing 3.0 g/l of chromic acid and 0.2 g/l of sulfuric acid, the plated steel sheet in the above was subjected to cathodic electrolysis with a current density of 10 A/dm^2 at a bath temperature of 40 ° C, and the resultant product was washed and dried. The amount of chromate to be formed was controlled by means of the amount of coulomb.

(b) Coating-type chromate treatment:

The coated steel sheets were immersed in a treating solution comprising 50 g/l of chromic acid (containing Cr^{3+} 40 %), 100 g/l of colloidal SiO_2 at a bath temperature of 40 ° C. The resultant coated steel sheets were dried for 1 min at 100 ° C after air-wipe treatment. The amount of chromate to be formed was controlled by means of the dilution ratio of the treating solution and the pressure at the air-wipe treatment.

(c) Reaction-type chromate treatment:

A treating solution containing 50 g/l of chromic acid, 10 g/l of phosphoric acid, 0.5 g/l of NaF and 4 g/l of K_2TiF_6 was sprayed on coated steel sheets at a bath temperature of 60 ° C, and the resultant coated steel sheets were dried at 60 ° C after washing. The amount of chromate was controlled by means of the dilution ratio of the treating solution and the duration of its spraying.

(2) Organic coating:

The coated steel sheets obtained by the above mentioned chromate treatment were further subjected to organic coating under the following conditions.

While the kind of resin as the main constituent is shown in Table 3, such agents as a rust preventing pigment, for instance SiO_2, curing agent, catalyst, lubricant and reformer against wetting were also added in the paint. The coated steel sheets to which chromate treatment was applied were further coated with the paint by means of a roll-coater, baked and dried. The baking condition differed in accordance with the type of resin used, but final sheet temperature was selected in the range of 100 - 200 ° C.

The construction of the thus obtained coated steel sheets having organic coating and the result of evaluation of their corrosion resistance, workability and weldability are shown in Table 3. The methods for evaluation are as below.

(a) Corrosion resistance of non worked portions:

The evaluation was done by the cycle corrosion test (CCT) as specified in Example 1.

(b) Corrosion resistance of worked portions

After cylindrical press forming with a size of 50 mmø x 25 mmH, the salt spray test (JIS Z2371) was done for 2,000 hours, and the evaluation was done with respect to the red-rust-suffering area in the worked portions.

less than 1 %: ◎
1 % - 5 %: ○
5 % - 10 %: Δ
more than 10 %: ×

(c) Press workability:

Evaluation was done by the workability evaluation method as specified in Example 1.

(d) Spot weldability:

Welding was done under the conditions shown in Example 2, and the evaluation was done by means of the number of times in continuous shock.

number of times more than 5,000: ◎
" 4,000 - 5,000: ○
" 3,000 - 4,000: △
" less than 3,000: ×

The results of these tests are shown in Table 3. As for comparison examples, the Cr content in the primer coating of No. 3-17 is too low, the iron group metal content (Ni) in the primer coating of No. 3-20 is too high, the organic coating film in No. 3-24 is too thin, and the primer coating in No. 3-26 contains no Cr, so that the corrosion resistance of these samples is not good. On the other hand, the Cr content in the primer coating of No. 3-18 is too high, No. 3-19 contains no cationic polymer in the primer coating, No. 3-21 contains an excessive amount of Cr and iron group metal (Ni) in total in the primer coating and No. 3-22 has too small amount of chromate film, and consequently their press workability is inferior and the corrosion resistance is also low. Further, since No. 3-23 has too much amount of chromate film, and No. 3-25 has too much organic coating film, their spot weldability is inferior.

In contrast to these comparison examples, as obvious from Table 3 all examples according to the present invention are excellent in all the points of corrosion resistance, workability and weldability.

Table 3

	No.	Primer Coating Composition (other than Zn)					Chromate Film		Organic Film		Corrosion Resistance before Working	Corrosion Resistance after Working	Press Formability	Spot Workability
		Cr (weight %)	Iron-group Metal		Cationic Polymer		Type	Amount of Cr Deposition (mg/m²)	Main Polymer Component	Thickness (μ)				
			kind	(weight %)	kind	(weight %)								
Example 3	3- 1	5	-	-	PAS	0.05	Electrolysis	20	Epoxy	1.0	◎	○	◎	○
	3- 2	10	-	-	PA	0.5	〃	40	Acrylic	1.2	◎	◎	◎	○
	3- 3	20	-	-	PAS	2	Reaction	50	Urethane	1.2	◎	◎	◎	○
	3- 4	30	-	-	〃	5	Spray	40	Acrylic-Olefinic	1.2	◎	◎	◎	○
	3- 5	5	Ni	2	〃	0.05	Electrolysis	40	Epoxy	1.0	◎	◎	◎	◎
	3- 6	5	Fe	2	PA	0.1	Reaction	80	Acrylic	0.7	◎	○	◎	◎
	3- 7	5	Co	2	PAS	1	Spray	30	Urethane	0.7	◎	○	◎	◎
	3- 8	7	Ni	3	〃	0.05	Electrolysis	40	Epoxy	2.0	◎	◎	◎	◎
	3- 9	7	Ni Fe	2 1	〃	0.005	〃	10	〃	1.0	◎	◎	◎	◎
	3-10	7	Ni Co	2 1	PA	0.2	〃	150	〃	1.0	◎	◎	○	○
	3-11	7	Ni	1	PAS	0.1	〃	40	〃	3.0	◎	◎	○	○
	3-12	10	Ni	3	〃	0.01	〃	50	〃	0.3	○	○	◎	◎
	3-13	10	Fe	5	〃	2	Reaction	100	Acrylic-Olefinic	0.7	◎	◎	◎	◎
	3-14	10	Co	5	PA	0.5	Spray	20	Epoxy	0.7	◎	◎	◎	◎
	3-15	20	Ni	2	PAS	1	Electrolysis	40	〃	1.5	◎	◎	◎	◎
	3-16	20	Ni	10	〃	5	〃	50	〃	0.5	◎	◎	◎	◎
Comparison 3	3-17	0.1	-	-	〃	0.05	〃	60	〃	1.0	×	×	○	○
	3-18	15	-	-	〃	3	〃	20	〃	1.0	◎	△	×	○
	3-19	5	-	-	-	-	〃	40	〃	1.0	◎	△	×	○
	3-20	10	Ni	10	PAS	0.5	〃	40	〃	1.0	△	△	◎	◎
	3-21	10	Ni	15	〃	1	〃	40	〃	1.0	◎	△	×	◎
	3-22	5	-	-	〃	0.05	〃	5	〃	1.0	○	△	×	○
	3-23	5	-	-	〃	0.05	〃	200	〃	1.0	◎	○	△	×
	3-24	5	Ni	2	〃	0.05	〃	40	〃	0.1	×	×	◎	◎
	3-25	5	Ni	2	〃	0.05	〃	40	〃	3.5	◎	◎	×	×
	3-26	-	Ni	11	-	-	〃	40	〃	1.0	△	×	◎	◎

Example 4

Except the addition of 0 - 50 g/l of iron group metal ion and 10 - 100 g/l of fine oxide particles (SiO_2, Al_2O_3, ZrO_2 and TiO_2 having a mean particle size of 0.02 - 0.05 μm, and Cr_2O_3 and WO_3 having a mean particle size of 0.1 - 0.5µm in the plating bath composition, plating was done under the same conditions as in Example 1.

The compositions of primer coatings and results of evaluation are as shown in table 4. By the way, the methods for determining metal constituents as well as the cationic polymers used are same as in Examples 1 and 2. The methods for evaluating corrosion resistance and workability are as below.

(1) Corrosion resistance of nonpaint-coated sample:

Salt spray test (exposed at Chiba district by spraying 5 % saline water once a week) was done, and the results were evaluated by the area where red rust formed after one year exposure.
less than 1 %: ◎
1 % - 10 %: ○
10 % - 30 %: Δ
more than 30 %: ×

(2) Corrosion resistance after paint coating:

The result was evaluated according to the method as specified in Example 1.

(3) Spot weldability:

The welding was done under the conditions as shown in Example 2, and the results were evaluated according to the following method, i.e., to measure the diameter of nugget after continuous shock of 3,000 times.
more than 4 mm: ◎
3 mm - 4 mm: ○
less than 3 mm: ×

(4) Workability:

Evaluated according to the method as specified in Example 1.

The results are shown in Table 4. All the examples according to the present invention are excellent in corrosion resistance and weldability as compared with the comparison examples. The examples containing iron group metal are particularly excellent in their spot weldability, and the examples having topcoat coating are also particularly excellent in the corrosion resistance after paint coating.

Table 4

	No.	Primer Coating Composition (weight %)								Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating	Corrosion Resistance after Paint Coating		Spot Workability	Workability
		Zn	Cr	Iron-group Metal		Fine Particle Oxide		Cationic Polymer			Exposure	S S T	Exposure		
Example 4	4- 1	balance	5	–	–	SiO_2	2	PA	0.1		◎	○	○	○	◎
	4- 2	〃	10	–	–	TiO_2	2	〃	0.5		◎	○	◎	○	◎
	4- 3	〃	20	–	–	ZrO_2	2	〃	1		◎	○	◎	○	◎
	4- 4	〃	29	–	–	Al_2O_3	2	PAS	5		◎	○	◎	○	○
	4- 5	〃	5	–	–	SiO_2 Al_2O_3	1 1	〃	0.5		◎	○	○	○	◎
	4- 6	〃	10	–	–	SiO_2	0.1	〃	0.5		◎	○	◎	○	◎
	4- 7	〃	15	–	–	〃	5	〃	1		◎	○	◎	○	◎
	4- 8	〃	5	–	–	〃	10	〃	0.01		◎	○	○	○	○
	4- 9	〃	15	–	–	〃	0.1	〃	2	Zn	◎	◎	◎	○	◎
	4-10	〃	5	–	–	〃	1	〃	0.05	Zn-12%Ni	◎	◎	◎	○	◎
	4-11	〃	10	–	–	〃	3	〃	0.1	Zn-85%Fe	○	◎	◎	○	◎
	4-12	〃	5	Ni	10	SiO_2	3	PA	0.1		◎	○	◎	◎	○
	4-13	〃	7	Ni Fe	5 1	Al_2O_3	3	〃	0.3		◎	○	◎	◎	◎
	4-14	〃	10	Ni Co	5 1	ZrO_2	3	〃	0.5		◎	○	◎	◎	◎
	4-15	〃	20	Co	5	WO_3	3	PAS	3		◎	○	◎	◎	○
	4-16	〃	7	Ni	3	SiO_2 TiO_2	2 1	〃	1		◎	○	◎	◎	◎
	4-17	〃	5	〃	3	SiO_2	0.1	〃	0.05		◎	○	◎	◎	◎

Table 4 (Cont'd)

	No.	Primer Coating Composition (weight %)								Kind of Upper Layer Coating	Corrosion Resistance before Paint Coating	Corrosion Resistance after Paint Coating		Spot Workability	Workability
		Zn	Cr	Iron-group Metal		Fine Particle Oxide		Cationic Polymer			Exposure	S S T	Exposure		
Example 4	4-18	balance	7	Ni	2	SiO_2	5	PAS	0.5		◎	○	◎	◎	◎
	4-19	〃	10	〃	4	〃	10	〃	0.5		◎	○	◎	◎	○
	4-20	〃	25	〃	5	〃	3	〃	5	Zn	◎	◎	◎	◎	○
	4-21	〃	7	〃	2	〃	3	〃	0.3	Zn-12%Ni	◎	◎	◎	◎	◎
	4-22	〃	10	〃	3	〃	3	〃	1	〃	◎	◎	◎	◎	◎
	4-23	〃	5	〃	10	〃	3	〃	0.01	〃	◎	◎	◎	◎	◎
	4-24	〃	7	〃	5	〃	3	〃	0.1	〃	◎	◎	◎	◎	◎
	4-25	〃	10	〃	3	〃	3	〃	2	Zn-85%Fe	○	◎	◎	◎	◎
Comparison 4	4-26	100	–	–	–	–	–	–	–		×	×	×	×	○
	4-27	balance	–	Ni	15	–	–	–	–		×	△	△	◎	◎
	4-28	〃	10	–	–	–	–	PAS	1		△	○	△	○	◎
	4-29	〃	0.1	Ni	3	SiO_2	3	〃	0.01		×	×	×	◎	○
	4-30	〃	35	–	–	Al_2O_3	2	〃	5		◎	○	◎	○	×
	4-31	〃	5	Ni	15	ZrO_2	3	〃	0.1		△	○	○	◎	×
	4-32	〃	10	〃	3	TiO_2	0.01	〃	1		△	○	△	○	◎
	4-33	〃	10	〃	3	Cr_2O_3	15	〃	1		◎	○	◎	◎	×
	4-34	〃	10	–	–	SiO_2	2	–	–		◎	○	○	○	×

Example 5

Plating was done under the same conditions as in Example 4, and the resultant coated steel sheets were subjected to chromate treatment and organic film coating treatment in succession under the same conditions as in Example 3.

The construction of thus produced composite coated steel sheets having organic film coating and their corrosion resistance, workability and weldability were evaluated as shown in Table 5. The methods for evaluation are as below.

(a) Corrosion resistance of flat sheet:

→Immersion in saline water (40°C, 5 % NaCl)
for 10 min.
↓
Drying (60°C) for 10 min.
↓
Moisture treatment (50°C, RH 95 %)
for 10 min.

By taking the above three steps as one cycle, the results were evaluated by the loss of sheet thickness after 3,000 cycles.
less than 0.1 mm: ◎
0.1 mm - 0.2 mm: ○
0.2 mm - 0.3 mm: Δ
more than 0.3 mm: ×

(b) Corrosion resistance of the worked portions:

After cylindrical press forming with a size of 50 mmø x 25 mmH, the salt spray test (JIS Z2371) was done for 3,000 hours, and the evaluation was done with respect to the red-rust-suffering area at the worked portions.
less than 1 %: ◎
1 % - 5 %: ○
5 % - 10 %: Δ
more than 10 %: ×

(c) Press workability:

Evaluation was done by the method as specified in Example 1.

(d) Spot weldability:

Welding and evaluation were done similarly as in Example 3.

The results of these tests are shown in Table 5. As for comparison examples, No. 5-20 is low in Cr content in the primer coating, No. 5-22 is too high in the content of iron group metal (Ni) in the primer coating, No. 5-23 and 5-24 contain no fine oxide particles in the primer coating, No. 5-28 is too thin in its organic coating film and No. 5-30 contains no Cr in the primer coating, so that they are all inferior in corrosion resistance. On the other hand, No. 5-21 contains too much Cr in the primer coating, No. 5-25 contains no cationic polymer in the primer coating, and No. 5-26 is too thin in its chromate film, and therefore their press workability, and accordingly, corrosion resistance at the worked portions are inferior. Further, since No. 5-27 has too much chromate film and No. 5-29 is too thick in its organic film, their press workability and spot weldability are not good.

In contrast to these comparison examples, all examples No. 5-1 to 5-19 according to the present invention are superior in corrosion resistance, workability and weldability.

Table 5

	No.	Primer Coating Composition								Chromate Film		Organic Film		Corrosion Resistance of Planar Portion	Corrosion Resistance of Worked Portion	Press Formability	Spot Workability
		Zn	Cr (weight %)	Iron-group Metal		Fine Particle Oxide		Cationic Polymer		Type	Amount of Cr Deposition (mg/m²)	Main Polymer Component	Thickness (μm)				
				kind	(weight %)	kind	(weight %)	kind	(weight %)								
Example 5	5- 1	balance	5	–	–	WO_3	2	PAS	0.05	Electrolysis	40	Urethane	3.0	◎	○	○	○
	5- 2	〃	7	–	–	SiO_2	10	〃	0.1	〃	60	Epoxy	1.0	◎	○	○	○
	5- 3	〃	10	–	–	〃	5	PA	0.5	〃	80	〃	0.3	○	○	◎	○
	5- 4	〃	20	–	–	〃	0.1	PAS	1	〃	20	〃	0.5	◎	○	◎	○
	5- 5	〃	30	–	–	SiO_2 TiO_2	1 1	〃	5	Spray	10	〃	1.0	◎	○	○	○
	5- 6	〃	5	Ni	2	SiO_2	2	〃	0.01	Electrolysis	60	〃	3.0	◎	◎	○	○
	5- 7	〃	5	Fe	2	〃	2	〃	0.5	〃	80	〃	1.0	◎	○	◎	◎
	5- 8	〃	5	Co	2	〃	2	PA	1	Spray	150	〃	1.0	◎	○	○	○
	5- 9	〃	7	Ni Fe	2 1	WO_3	3	PAS	0.05	Electrolysis	20	Acrylic-Olefinic	1.0	◎	◎	◎	◎
	5-10	〃	7	Ni Co	2 1	Cr_2O_3	3	〃	0.5	〃	100	Urethane	0.3	○	○	◎	◎
	5-11	〃	7	Ni	3	SiO_2	10	〃	0.01	〃	50	Epoxy	1.0	◎	◎	○	◎
	5-12	〃	7	Ni	5	〃	5	〃	1	〃	50	〃	0.5	◎	◎	◎	◎
	5-13	〃	7	Ni	3	〃	0.1	PA	0.1	〃	50	〃	1.0	◎	◎	◎	◎
	5-14	〃	10	Ni	2	TiO_2	2	PAS	0.01	〃	150	〃	1.0	◎	◎	○	◎
	5-15	〃	10	Fe	5	Al_2O_3	2	〃	1	Reaction	40	Acrylic	0.7	◎	○	◎	◎
	5-16	〃	10	Co	5	ZrO_2	2	〃	2	Electrolysis	50	Polyester	1.5	◎	◎	◎	◎
	5-17	〃	10	Ni	5	SiO_2 Al_2O_3	2	PA	0.1	〃	10	Epoxy	1.0	◎	◎	◎	◎
	5-18	〃	20	Ni	2	SiO_2	1	PAS	1	〃	50	〃	1.0	◎	◎	◎	◎
	5-19	〃	20	Ni	10	〃	2	〃	5	Spray	40	〃	1.0	◎	◎	◎	◎

Table 5 (Cont'd)

	No.	Primer Coating Composition								Chromate Film		Organic Film		Corrosion Resistance of Planar Portion	Corrosion Resistance of Worked Portion	Press Formability	Spot Workability
		Zn	Cr (weight %)	Iron-group Metal		Fine Particle Oxide		Cationic Polymer		Type	Amount of Cr Deposition (mg/m²)	Main Polymer Component	Thickness (µm)				
				kind	(weight %)	kind	(weight %)	kind	(weight %)								
Comparison 5	5-20	balance	0.1	-	-	SiO_2	2	PA	0.001	Electrolysis	50	Epoxy	1.0	×	×	○	○
	5-21	〃	35	-	-	Al_2O_3	2	〃	5	〃	50	〃	1.0	◎	△	×	○
	5-22	〃	5	Ni	15	ZrO_2	5	〃	0.5	〃	50	〃	1.0	△	△	×	◎
	5-23	〃	10	-	-	-	-	〃	1	〃	50	〃	1.0	△	△	◎	○
	5-24	〃	7	Ni	5	-	-	〃	0.5	〃	50	〃	1.0	○	△	◎	◎
	5-25	〃	5	-	-	TiO_2	2	-	-	〃	50	〃	1.0	○	△	×	○
	5-26	〃	5	Ni	3	SiO_2	3	PAS	0.5	〃	< 5	〃	1.0	○	×	×	◎
	5-27	〃	7	-	-	〃	2	〃	1	〃	200	〃	1.0	○	○	△	△
	5-28	〃	5	Ni	3	〃	3	〃	0.5	〃	50	〃	0.1	×	×	◎	◎
	5-29	〃	7	-	-	〃	2	〃	1	〃	50	〃	4.0	◎	○	×	×
	5-30	〃	-	Ni	12	-	-	-	-	〃	50	〃	1.0	△	×	◎	◎

Example 6

Preferred embodiments of electro-plating bath compositions and electro-plating conditions for obtaining the coated steel sheets according to the present invention are shown in Table 6.

Corrosion resistance was evaluated by the area of red rust after 500 hours salt spray test (JIS Z2371).
less than 1 %: ◎
1 % - 10 %: ○
10 - 30 %: △
more than 30 %: ×

Surface brightness was evaluated by brightness degree (JIS Z8741, G_s (60°), standard value of black glass plate: 93).

brightness degree not less than 50: ◎
" not less than 20: ○
" less than 20: △
turned black: ×

Among the coated products obtained by the examples of the present invention, those with the Cr content of not less than 5 wt.% are particularly excellent in corrosion resistance. All of the examples were excellent in the surface brightness.

As for comparison examples, No. 6-27 and 6-29 do not contain cationic polymer in the plating bath and thereby the current density is not sufficiently high, so that the Cr content in the coating is only in a trace amount and the corrosion resistance is not good. While No. 6-28 and 6-30, too, do not contain cationic polymer, since the current density is sufficiently high to increase, the Cr content and the corrosion resistance is excellent, but their surface appearance is inferior. In the comparison examples No. 6-31 and 6-32, since the ratio of Cr^{6+}/Cr^{3+} in the plating bath is high, the Cr content in the primer coating is low, corrosion resistance is insufficient and surface appearance, too, is inferior. By the way, as for the current efficiency, while all the examples of the present invention show the efficiency of more than 60 %, the efficiency of all the comparison examples is as low as 50 % or lower.

Table 6

	No.	Plating Bath Composition (g/l)			Anode:Pi/Ti electrode					pH	Remarks
		Zn^{2+}	Cr^{3+}	Cr^{6+}/Cr^{3+} ratio	Cationic Polymer		$Ni^{2+}, Fe^{2+}, Co^{2+}$	Fine Particle Oxide	Others		
Example 6	6-1	70	10	0	PAS-2	2	-	-	Na^+ : 16	2	Sulfate Bath
	6-2	20	10	0.001	〃	1	-	-	〃	〃	〃
	6-3	100	100	0.005	〃	2	-	-	〃	〃	〃
	6-4	50	5	0.01	〃	1	-	-	〃	〃	〃
	6-5	150	30	0.05	〃	1	-	-	〃	〃	〃
	6-6	70	10	0.1	〃	2	-	-	〃	〃	〃
	6-7	70	10	0	〃	2	Ni^{2+} : 20	-	〃	〃	〃
	6-8	20	10	0.001	〃	1	〃	-	〃	〃	〃
	6-9	80	100	0.005	〃	2	〃	-	〃	〃	〃
	6-10	50	5	0.01	〃	1	〃	-	〃	〃	〃
	6-11	100	30	0.05	〃	1	〃	-	〃	〃	〃
	6-12	70	10	0.1	〃	2	〃	-	〃	〃	〃
	6-13	70	10	0	PAS-1	2	-	-	〃	〃	〃
	6-14	70	10	0.003	〃	1	-	-	K^+ : 20	〃	Chrolide Bath
	6-15	70	10	0.007	PAS-3	2	-	-	NH^{4+} : 10	〃	Sulfate Bath
	6-16	70	20	0	PAR	10	-	-	Na^+ : 16	3	〃
	6-17	50	30	0.005	PAS-2	0.01	-	-	〃	2	〃
	6-18	50	30	0.005	〃	10	-	-	〃	〃	〃

Table 6 (Cont'd))

	No.	Plating Bath Composition (g/ℓ) Anode:Pi/Ti electrode								pH	Remarks
		Zn^{2+}	Cr^{3+}	Cr^{6+}/Cr^{3+} ratio	Cationic Polymer		$Ni^{2+}, Fe^{2+}, Co^{2+}$	Fine Particle Oxide	Others		
Example 6	6-19	50	50	0.005	PAS-2	20	–	SiO_2 : 10	Na^+ : 16	2	Sulfate Bath
	6-20	70	10	0.03	PAS-1	2	Ni^{2+} : 10	Al_2O_3 : 10	〃	〃	〃
	6-21	70	10	0.1	PAS-3	1	Fe^{2+} : 10	–	〃	〃	〃
	6-22	70	10	0.05	〃	2	Co^{2+} : 10	–	〃	〃	〃
	6-23	70	20	0.001	PB	10	Ni^{2+} : 30	–	〃	〃	〃
	6-24	50	30	0.005	PAS-2	0.01	Ni^{2+}:100、Co^{2+}:10	–	〃	〃	〃
	6-25	50	30	0.005	〃	10	Ni^{2+}:30、Fe^{2+}:10	–	〃	〃	〃
	6-26	50	50	0.005	〃	20	Ni^{2+} : 10	–	〃	〃	〃
Comparison 6	6-27	70	30	0	–	–	–	TiO_2 : 10	Na^+ : 16	2	Sulfate Bath
	6-28	70	30	0	–	–	–	–	〃	〃	〃
	6-29	70	30	0	–	–	Ni^{2+} : 20	ZrO_2 : 10	〃	〃	〃
	6-30	70	30	0	–	–	〃	–	〃	〃	〃
	6-31	70	10	0.2	PAS-2	2	–	–	–	〃	〃
	6-32	70	10	0.5	〃	2	Ni^{2+} : 20	–	–	〃	〃

Table 6 (Cont'd)

	No.	Plating Condition			Coating Composition (weight %)					Corrosion Resistance	Surface Brightness
		Current Density (A/dm²)	Bath Temperature (℃)	Relative Flow Velocity (m/min)	Zn	Cr	Ni,Fe,Co	Cationic Polymer	Fine Particle Oxide		
Example 6	6- 1	150	60	90	balance	10	–	0.1	–	◎	◎
	6- 2	20	〃	〃	〃	6	–	0.005	–	◎	◎
	6- 3	100	〃	〃	〃	7	–	0.05	–	◎	◎
	6- 4	250	〃	〃	〃	10	–	0.1	–	◎	◎
	6- 5	50	〃	〃	〃	10	–	0.01	–	◎	◎
	6- 6	200	〃	〃	〃	6	–	0.5	–	◎	○
	6- 7	150	〃	〃	〃	10	Ni : 3	0.1	–	◎	◎
	6- 8	20	〃	〃	〃	5	Ni : 3	0.005	–	◎	◎
	6- 9	200	〃	〃	〃	7	Ni : 3	0.05	–	◎	◎
	6-10	250	〃	〃	〃	10	Ni : 3	0.1	–	◎	◎
	6-11	50	〃	〃	〃	10	Ni : 3	0.01	–	◎	◎
	6-12	200	〃	〃	〃	5	Ni : 3	0.5	–	◎	○
	6-13	100	〃	〃	〃	7	–	0.05	–	◎	◎
	6-14	50	〃	〃	〃	7	–	0.01	–	◎	◎
	6-15	150	〃	〃	〃	7	–	0.1	–	◎	◎
	6-16	150	〃	〃	〃	10	–	0.02	–	◎	◎
	6-17	20	〃	〃	〃	6	–	0	–	◎	◎
	6-18	100	〃	〃	〃	20	–	2	–	◎	◎

Table 6 (Cont'd)

	No.	Plating Condition			Coating Composition (weight %)					Corrosion Resistance	Surface Brightness
		Current Density (A/dm²)	Bath Temperature (°C)	Relative Flow Velocity (m/min)	Zn	Cr	Ni,Fe,Co	Cationic Polymer	Fine Particle Oxide		
Example 6	6-19	200	60	90	balance	30	–	5	SiO_2 : 1	◎	◎
	6-20	200	40	〃	〃	7	Ni : 1	0.2	Al_2O_3 : 2	◎	◎
	6-21	50	50	〃	〃	5	Fe : 2	0.01	–	◎	○
	6-22	100	70	〃	〃	7	Co : 3	0.05	–	◎	◎
	6-23	150	60	200	〃	10	Ni : 5	0.02	–	◎	◎
	6-24	20	〃	90	〃	6	Ni : 10 Co : 1	0	–	◎	◎
	6-25	100	〃	〃	〃	20	Ni : 5 Fe : 1	2	–	◎	◎
	6-26	200	〃	〃	〃	29	Ni : 1	5	–	◎	◎
Comparison 6	6-27	100	60	90	balance	0.01	–	–	TiO_2 : 1	×	○
	6-28	300	〃	〃	〃	7	–	–	–	◎	×
	6-29	100	〃	〃	〃	0.01	Ni : 2	–	ZrO_2 : 3	×	○
	6-30	300	〃	〃	〃	5	Ni : 3	–	–	◎	×
	6-31	150	〃	〃	〃	3	–	0.1	–	△	×
	6-32	150	〃	〃	〃	1	Ni : 3	0.1	–	△	×

Example 7

Continuous electro-plating was done in a plating bath having the composition as in Example No. 6-1 by using an anode of Pb-5 % Sn. The ratio of Cr^{6+}/Cr^{3+} in the bath was measured periodically and the current density was controlled to 150 A/dm^2 so as to obtain a coating of 20 g/m^2. Until the ratio of Cr^{6+}/Cr^{3+} in the bath reached to 0.1, the Cr content in the coating obtained was not less than 6 wt.% and the coating was excellent in surface brightness, but when said ratio exceeded 0.1, the Cr content in the coating was decreased and the surface brightness also deteriorated remarkably or further the surface was turned to black. At the time when the Cr^{6+}/Cr^{3+} ratio in the bath reached to 0.5, the plating solution was circulated through a bath filled with Zn metal, and then the Cr^{6+}/Cr^{3+} ratio was decreased. After the Cr^{6+}/Cr^{3+} ratio was lowered to 0.1, the plating was done again under the above mentioned condition, and the coating with the Cr content of 7 wt.% and having excellent surface brightness could be obtained. Continuous electro-plating was done thereafter by passing the plating solution occasionally through the tank filled with metallic Zn and repeating the measurement of the Cr^{6+}/Cr^{3+} ratio in the bath periodically. Thus, a coating with the Cr content of not less than 6 wt.% and excellent surface brightness could be obtained under the condition that the Cr^{6+}/Cr^{3+} ratio in the bath was not more than 0.1.

Example 8

With an anode of Pb-5% Sn and using a plating bath same as in Example No. 6-7, electro-plating was done under the condition of Example 7. The result was the same as in Example 7 until the Cr^{6+}/Cr^{3+} ratio did not exceed 0.1. By adding Fe^{2+} ion in an amount of 5 g/l to the bath at the time when the Cr^{6+}/Cr^{3+} ratio reached to 0.5, the Cr^{6+}/Cr^{3+} ratio lowered to 0.05, and a coating with the Cr content of 10 wt.% and having excellent surface brightness could be obtained.

As above described, it is possible according to the present invention to produce a composite electro-plated steel sheet having a primer coating comprising Zn as main constituent, containing simultaneously a large quantity of Cr and having excellent surface brightness which has been very difficult to produce by the conventional arts. The coated products according to the present invention are very suitable for the production of a rust preventing steel sheet for such uses as in automobiles, home electric appliances and constructions in which high corrosion resistance and excellent surface brightness are required.

Claims

1. A coated steel sheet having a primer coating comprising 5 to 30 % by weight of Cr and 0.005 to 5 % by weight of a cationic polymer, and optionally comprising not less than 1 % by weight of iron-group metal and/or 0.1 to 10 % by weight of fine particles of oxide, with the balance being Zn.

2. A coated steel sheet according to claim 1 wherein the total amount of Cr and the iron-group metal is not more than 30 % by weight.

3. A coated steel sheet according to claim 1 or 2, wherein the primer coating comprises 1 to 10 % by weight of an iron-group metal.

4. A coated steel sheet according to any one of claims 1 to 3, wherein the content of the iron-group metal is in a range from 1/10 to 1/2 of the Cr content.

5. A coated steel sheet according to any one of claims 1 to 4, wherein the oxide is selected from the group consisting of oxides of Si, Al, Zr, Ti, Cr, Mo and W.

6. A coated steel sheet according to any one of claims 1 to 5, wherein the cationic polymer is a quaternary amine polymer.

7. A coated steel sheet according to any one of claims 1 to 6, which further comprises a Zn or Zn-alloy coating formed on the primer coating.

8. A coated steel sheet according to any one of claims 1 to 6 which further comprises a chromate film formed on the primer coating in an amount of 10 to 150 mg/m^2 in total chromium, and an organic coating formed on the chromate film in a thickness of 0.3 to 3 μm.

9. A process for producing a coated steel sheet having a primer coating comprising 5 to 30 % by weight of Cr and 0.005 to 5% by weight of a cationic polymer and having excellent corrosion resistance and surface brightness, said process comprising performing electro-plating in an acidic Zn plating bath containing Cr ions and a cationic polymer, with the ratio of Cr^{6+} ions/Cr^{3+} ions being not more than 0.1.

10. A process according to claim 9, in which the acidic bath contains Ni^{2+}, Fe^{2+} and/or Co^{2+}.

11. A process according to any one of claims 9 and 10, in which the acidic bath further contains at least one oxide of Si, Al, Zr, Ti, Cr, Mo and W.

12. A process according to any one of claims 9 to 11, in which the cationic polymer is a quaternary amine polymer.

Patentansprüche

1. Beschichtetes Stahlblech mit einer Grundierungsbeschichtung, die 5 bis 30 Gew.-% Cr und 0.005 bis 5 Gew.-% eines kationischen Polymers aufweist und gegebenenfalls mindestens 1 Gew.-% eines Metalls der Eisengruppe und/oder 0.1 bis 10 Gew.-% feiner Oxidteilchen aufweist, wobei der Rest Zn ist.

2. Beschichtetes Stahlblech gemäß Anspruch 1, wobei die Gesamtmenge von Cr und dem Metall der Eisengruppe höchstens 30 Gew.-% beträgt.

3. Beschichtetes Stahlblech gemäß Anspruch 1 oder 2, wobei die Grundierungsbeschichtung 1 bis 10 Gew.-% eines Metalls der Eisengruppe aufweist.

4. Beschichtetes Stahlblech gemäß einem der Ansprüche 1 bis 3, wobei der Gehalt des Metalls der Eisengruppe in einem Bereich von 1/10 bis 1/2 des Cr-Gehalts liegt.

5. Beschichtetes Stahlblech gemäß einem der Ansprüche 1 bis 4, wobei das Oxid aus der Gruppe, die aus den Oxiden von Si, Al, Zr, Ti, Cr, Mo und W besteht, ausgewählt wird.

6. Beschichtetes Stahlblech gemäß einem der Ansprüche 1 bis 5, wobei das kationische Polymer ein quarternäres Aminpolymer ist.

7. Beschichtetes Stahlblech gemäß einem der Ansprüche 1 bis 6, welches ferner eine auf der Grundierungsbeschichtung ausgebildete Beschichtung aus Zn oder einer Zn-Legierung umfaßt.

8. Beschichtetes Stahlblech gemäß einem der Ansprüche 1 bis 6, welches ferner einen Chromatfilm, der auf der Grundierungsbeschichtung mit einer gesamten Chrommenge von 10 bis 150 mg/m^2 ausgebildet ist, und eine organische Beschichtung umfaßt, die mit einer Dicke von 0.3 bis 3 μm auf dem Chromatfilm ausgebildet ist.

9. Verfahren zur Herstellung eines beschichteten Stahlblechs mit einer Grundierungsbeschichtung, die 5 bis 30 Gew.-% Cr und 0.005 bis 5 Gew.-% eines kationischen Polymers aufweist, und mit ausgezeichneter Korrosionsbeständigkeit und ausgezeichnetem Oberflächenglanz, wobei das Verfahren die Durchführung einer Elektroplattierung in einem säurehaltigen galvanischen Zn-Bad umfaßt, das Cr-Ionen und ein kationisches Polymer enthält, wobei das Verhältnis von Cr^{6+}-Ionen/Cr^{3+}-Ionen höchstens 0.1 beträgt.

10. Verfahren gemäß Anspruch 9, bei dem das säurehaltige Bad Ni^{2+}, Fe^{2+} und/oder Co^{2+} enthält.

11. Verfahren gemäß einem der Ansprüche 9 und 10, bei dem das säurehaltige Bad ferner mindestens ein Oxid von Si, Al, Zr, Ti, Cr, Mo und W enthält.

12. Verfahren gemäß einem der Ansprüche 9 bis 11, bei dem das kationische Polymer ein quarternäres Aminpolymer ist.

Revendications

1. Tôle d'acier revêtue ayant un revêtement d'apprêt constitué de 5 à 30 % en poids de Cr et de 0,005 à 5 % en poids d'un polymère cationique, et comportant en option pas moins de 1 % en poids d'un métal du groupe fer et/ou 0,1 à 10 % en poids de fines particules d'oxyde, le reste étant Zn.

2. Tôle d'acier revêtue selon la revendication 1, dans laquelle la quantité totale de Cr et du métal du groupe fer n'est pas supérieure à 30 % en poids.

3. Tôle d'acier revêtue selon la revendication 1 ou 2, dans laquelle le revêtement d'apprêt comprend 1 à 10 % en poids d'un métal du groupe fer.

4. Tôle d'acier revêtue selon l'une quelconque des revendications 1 à 3, dans laquelle la teneur en métal du groupe fer est dans la gamme 1/10 à 1/2 de la teneur en Cr.

5. Tôle d'acier revêtue selon l'une quelconque des revendications 1 à 4, dans laquelle l'oxyde est choisi dans le groupe constitué des oxydes de Si, Al, Zr, Ti, Cr, Mo et W.

6. Tôle d'acier revêtue selon l'une quelconque des revendications 1 à 5, dans laquelle le polymère cationique est un polymère d'amine quaternaire.

7. Tôle d'acier revêtue selon l'une quelconque des revendications 1 à 6, qui comprend en outre un revêtement en Zn ou en alliage de Zn formé sur le revêtement d'apprêt.

8. Tôle d'acier revêtue selon l'une quelconque des revendications 1 à 6, qui comprend en outre un film de chromate formé sur le revêtement d'apprêt dans une quantité de 10 à 150 mg/m^2 en chrome total, et un revêtement organique formé sur le film de chromate suivant une épaisseur de 0,3 à 3 μm.

9. Procédé pour fabriquer une tôle d'acier revêtue ayant un revêtement d'apprêt comprenant 5 à 30 % en poids de Cr et 0,005 à 5 % en poids d'un polymère cationique et présentant une excellente résistance à la corrosion et brillance de la surface, ledit procédé comportant l'exécution d'un revêtement électrolytique dans un bain acide de revêtement en Zn contenant des ions Cr et un polymère cationique, le rapport ions Cr^{6+}/ions Cr^{3+} n'étant pas supérieur à 0,1.

10. Procédé selon la revendication 9, dans lequel le bain acide content Ni^{2+}, Fe^{2+} et/ou Co^{2+}.

11. Procédé selon l'une quelconque des revendications 9 et 10, dans lequel le bain acide comprend en outre au moins un oxyde de Si, Al, Zr, Ti, Cr, Mo et W.

12. Procédé selon l'une quelconque des revendications 9 à 11, dans lequel le polymère cationique est un polymère d'amine quaternaire.

FIG.1

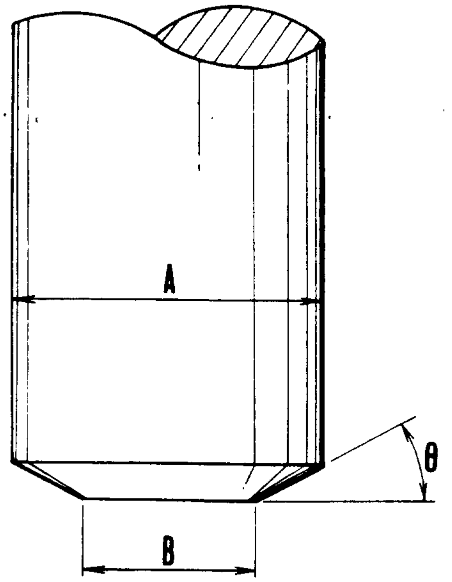
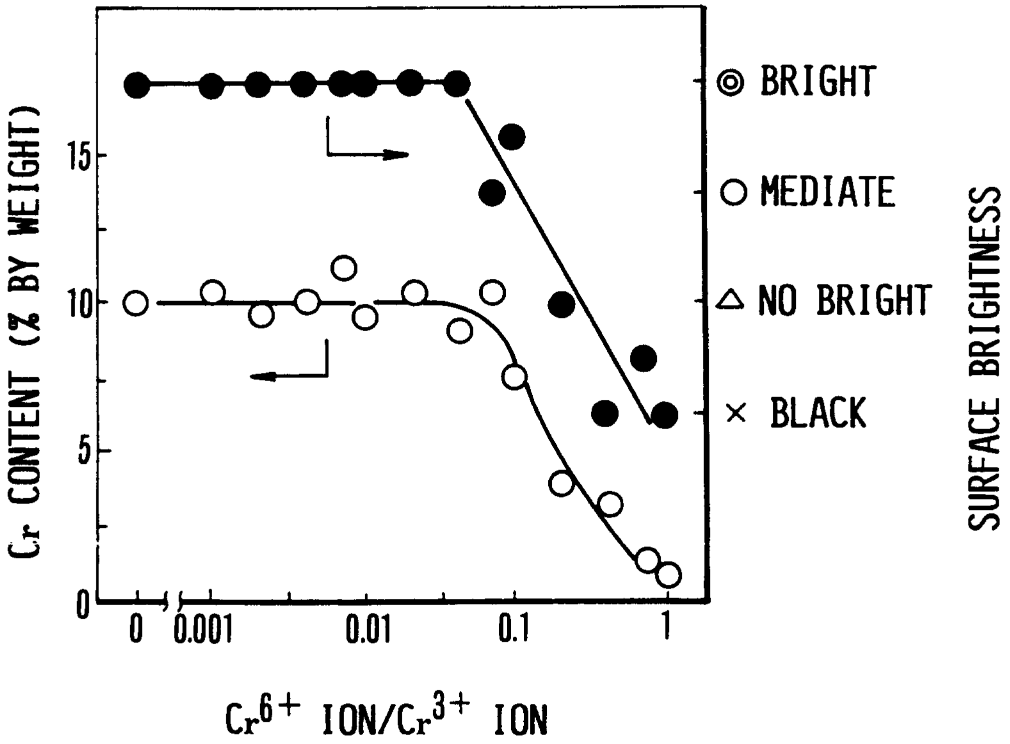

A
B
θ

FIG.2


Cr CONTENT (% BY WEIGHT)
15
10
5
0
0
0.001
0.01
0.1
1
Cr6+ ION/Cr3+ ION
◎ BRIGHT
○ MEDIATE
△ NO BRIGHT
× BLACK
SURFACE BRIGHTNESS