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PATENT ABSTRACTS OF JAPAN, vol. 6, no. 149 (C-118)[1027], 10th August 1982; & JP-A-57 70 249

This invention relates to a colored zinc coating technique applied onto the surface of an iron or steel material, and particularly to a colored zinc coating method with the use of Ti-Zn or Ti-Mn-Zn system alloys by which the development of new colors not obtained by conventional techniques and clearer color developments compared to conventional ones are permitted. According to this invention, the developments of gold and dark red colors which could not have yet obtained are permitted and simultaneously yellow color, green color, blue color, purple color etc. may be more clearly developed. Thus, this invention provides colored zinc coated materials which are applicable to wider variety of fields and have coloring more suitable to the environment where they are placed.

Background of the invention

Hot-dip galvanized iron and steel materials, coated by dipping in molten zinc, are used for corrosion protection purposes in a wide range of application, forming parts and facilities in the fields of building and construction, civil engineering, agriculture, fisheries, chemical plants, electric power supply and communications, and so forth.

For pylons and other towers, lighting poles, guard-rails, temporary stands and frames for various operations and displays, shells and planks, and the like, there has been growing demand in recent years for colored hot-dip galvanized materials that present attractive appearances matching the environments involved, in preference to the classic hot-dip galvanized steels with metallic lusters. With the spread of the aesthetic sense the colored hot-dip galvanized articles show promise, with extensive potential demand in architecture, civil engineering, industrial plants, electric power supply and communications, transportations, agriculture, marine products and other industries.

Coloration of hot-dip galvanized steels has usually been by the application of paints. The method has the disadvantage of the paint film eventually coming off the coated surface. This results from the activity of Zn in the coating of the hot-dip galvanized steel that causes gradual alkali decomposition of the fatty acid constituting the oily matter in the paint, leading to the formation of zinc soap that hampers the adhesion of the paint film to the underlying surface.

In an effort to eliminate the disadvantage, a complex procedure has had to be followed. A steel article is first galvanized by dipping in a molten zinc bath. The coated steel is exposed to the air for one to three weeks so that corrosion products such as Zn(OH)₂, ZnO, ZnCO₃, ZnCl₂ and the like deposit on the coated steel surface. The surface is then cleaned and colored.

Aside from the coating method described above, another approach that depends on the color-developing action of the oxide film in the hot-dip galvanizing is known in the art. Particularly, US-A-3 630 792 discloses a process for the production of zinc coatings that uses a hot-dip bath of a zinc alloy containing at least one element selected from manganese, titanium and vanadium, and optionally also one or more elements selected from niobium, zirconium, thorium, mischmetal, cadmium, arsenic, copper, lead and chromium, and in an amount sufficient to form on the coating, upon reaction of the surface of the coating with oxygen, a colored oxide film. It is indicated that the preferred range for the alloy compositions is from 0.1 to 0.45 % both for manganese and for titanium. In experiments actually described the manganese content of zinc-manganese alloys providing for yellow-, red- and blue-colored coatings is from 0.02 to 0.15 %, and the titanium content of zinc-titanium alloys providing for yellow-, bronze-, red-, blue- or silver blue-colored coatings is from 0.008 to 0.15 %. When using a zinc-titanium alloy containing 0.15 % Ti and bath temperature of 500 °C the final coating color was yellow or red dependent on the gauge of the coated sheet material. At a bath temperature of 550 °C an alloy of zinc and 0.15 % Ti resulted in a bronze or yellow-colored coating of the dipped panel. The coated article may be post-heated, for example by induction heating, and the coated article is allowed to air cool or is quenched with cold air blasts. It is indicated that the tests were made with commercial Special High Grade zinc and that the other commercial grades of zinc, e.g. Prime Western which contains up to 1.5 % Pb, can be used provided that the aluminum content is limited to below 0.002 %. However, the hot-dip galvanized coatings obtained by the disclosed technique have been found to be generally very thin and light, with tendencies of rapid color fading and film separation with time. The desired color development is difficult to control precisely, often bringing out dim, indefinite hues. For such reasons, even though many years have lapsed since its development, hot-dip galvanized coloring technique has not put into practical use.
FR-A-1 115 121 discloses a method for coating ferrous metal objects in which a layer of aluminum, zinc or another non-ferrous metal is applied, e.g. by a gun. Upon this metallization a layer of a waterglass-type plastic material, e.g. potassium silicate, or of glycerophthalate is applied. Then the coated object is heat-treated at a temperature of about 350 °C, the final temperature being dependent on the melting point of the applied non-ferrous metal.

There is still a steady demand in the art for many improvements such as:
(a) the development of new colorings which have not yet been obtained in past;
(b) the obtainance of the color developments which are more beautiful and clearer than ones previously obtained;
(c) the enhanced stability of color development;
(d) that the inherent corrosion resistance of galvanized zinc coating is not sacrificed;
(e) less change with the lapse of time; and
(f) to provide easy and stable operation.

Object of the invention

The object of this invention is to establish colored zinc coating technique by which the above mentioned improvements may be attained using Ti-Zn or Ti-Mn-Zn zinc alloys.

Summary of the invention

In conformity with one aspect thereof the invention provides for a method of forming a golden colored zinc coating on an iron or steel surface, comprising coating said iron or steel surface at a bath temperature of 450 to 470 °C in a hot-dipping bath of a galvanizing zinc alloy containing 0.10 to 0.5 wt % Ti in a distilled water.

According to another aspect the invention provides for a method of forming a purple colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting substantially of 0.10 to 0.5 wt % Ti - bal. Zn at a bath temperature of 500 to 550 °C for at least one minute, either allowing the coated surface to cool in the air for 10 to 50 seconds or heating it in an atmosphere at 500 to 520 °C for 10 to 20 seconds, and thereafter cooling it with cold or warm water.

The present invention further provides for a method of forming a zinc coating having a color selected from the group of yellow, dark red and green on an iron or steel surface, comprising coating said iron or steel surface at a temperature of 590 to 620 °C for 1 to 3 minutes in a hot-dipping bath of a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti, and cooling the coated surface after heating it to a temperature of 450 to 550 °C, the color of the coating being selected by controlling the extent of the oxidation of the coating.

The subject invention also provides for a method of forming a zinc coating having a color selected from the group of gold, purple, blue, yellow, dark red and green on an iron or steel surface, comprising coating said iron or steel surface at a temperature of 490 to 620 °C in a hot-dipping bath of:
(a) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti and 1.3 to 5.9 wt % Pb,
(b) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti, 1.2 to 1.3 wt % Pb and 0.1 to 0.2 wt % Cd, or
(c) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti, 1.0 to 1.2 wt % Pb, 0.05 to 0.2 wt % Cd and 0.01 to 0.05 wt % of at least one element selected from the group consisting of Cu, Sn, Bi, Sb and In,
and cooling the coated surface after heating it to a temperature of 450 to 550 °C, the color of the coating being selected by controlling the extent of the oxidation of the coating.

Another aspect of the invention is a method of forming a dark red colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting essentially of 0.2 to 0.5 wt % Ti - 0.05 to 0.15 wt % Mn - bal. Zn at a bath temperature of 580 to 600 °C, heating the coated work in an atmosphere at 500 to 520 °C for 30 to 70 seconds, and thereafter cooling it with cold or warm water.

The subject invention also provides for a method of producing a green colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping which contains from 0.2 to 0.5 wt % Ti and from 0.05 to 0.15 wt % Mn at a bath temperature between 600 and 620 °C, heating the coated work in an atmosphere at from 500 to 520 °C for from 50 to 60 seconds, and thereafter cooling the same with cold or warm water or with a coolant gas.

In conformity with a further aspect thereof the invention provides for a method of forming a yellow colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use
of a zinc alloy for hot dipping containing from 0.2 to 0.5 wt % Ti and from 0.05 to 0.15 wt % Mn at a bath temperature between 560 and 600 °C, heating the coated work in an atmosphere at 500 to 520 °C for from 20 to 30 seconds, and thereafter cooling it with cold or warm water or with a coolant gas.

Furthermore, according to the subject invention a method of forming a blue colored zinc coating on an iron or steel surface, comprises coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting essentially of 0.1 to 0.5 wt % Ti - 0.05 to 0.15 wt % Mn - bal. Zn at a bath temperature of 530 to 550 °C, allowing the coated surface to cool in the air for 15 to 25 seconds, and thereafter cooling it with cold or warm water.

The present invention further provides for a method of forming a colored zinc coating on an iron or steel surface, comprising thermally spraying by a spray gun a zinc alloy containing 0.1 to 2.0 wt % Ti and optionally 0.01 to 4.0 wt % of at least one more element selected from Mn, Cu, Cr and Ni, in the form of a sprayable wire or rod or powder, and then heating the thermally sprayed surface until the given color is developed.

In the colored hot-dip galvanizing, the composition of the plating bath and the conditions of producing an oxidized film delicately combine to present coloring effects by light interference. By ingeniously controlling these factors, in Ti-Zn alloys, the invention successfully attained the development of golden color which had been thought that such trial is beyond the range of possibilities, and succeeded in developing dark red color which has strongly been desired. In addition, it became possible to stably attain the development of clearer yellow, purple, green or other colors compared to ones previously obtained. Further, in Ti-Mn-Zn alloys, the method of the present invention allows to develop a strongly needed dark red color, and to stably attain yellow, green and blue colors clearer than previous ones.

It was also found that colored zinc coating may be applied by a thermal spraying method and that a change of the colored zinc coating with the lapse of time may be suppressed by painting thereon.

Detailed explanation of the invention

Zinc alloy hot dipping is carried out by melting a zinc alloy in a coating bath and immersing a member to be coated thereinto.

A-1) The development of golden color with Ti-Zn alloy

It is possible to form a colored coating with a golden hue on an iron or steel surface by plating the base metal using a bath of a zinc alloy for hot dipping of a composition comprising 0.1 - 0.5 wt % Ti - bal. Zn at a bath temperature of 450 - 470 °C, allowing the plated work to stand in air for 5 - 20 seconds, and thereafter cooling it with cold or warm water.

The metallic zinc bullion to be used in forming the zinc alloy for hot dipping is typically one of the grades conforming to JIS H2107, for example, distilled zinc 1st grade (at least 98.5 % pure), purest zinc (at least 99.99 % pure), and special zinc grades. The impurities inevitably contained in these zinc materials are, for example, in the distilled zinc 1st grade, all up to 1.2 wt % Pb, 0.1 wt % Cd, and 0.020 wt % Fe. For the purposes of the invention a metallic zinc with a total impurity content of less than 1.5 wt % is desirable. Particularly, distilled zinc is preferred because it permits to effect plating with the use of ordinary flux and color strength produced becomes higher.

In the embodiment, the plating is carried out using a molten zinc alloy bath of the composition 0.1 - 0.5 wt % Ti - bal. Zn, obtained by adding 0.1 - 0.5 wt % Ti to the above-mentioned zinc. A bath of a molten zinc alloy containing 0.3 wt % Ti is particularly desirable.

In order to produce the golden colored coating from the hot-dip zinc alloy bath of the above composition, a base metal of iron or steel is immersed in the plating bath at 450 - 470 °C for at least one minute, the base metal is pulled out of the bath and allowed to cool in air for about 5 - 20 seconds, and then is immediately cooled with cold or warm water to form thereon an oxide film with a golden hue.

Thus, in producing a golden colored coating, it is essential to immerse the iron or steel base metal in the bath of molten zinc alloy of the composition 0.1 - 0.5 wt % Ti - bal. Zn at a bath temperature of 450 - 470 °C and then allow it to cool in air for a very short period of 5 - 20 seconds, preferably for 10 - 20 seconds. If the conditions are outside the ranges specified above, the desired golden hue will not result. For example, if the heating temperature is above 470 °C and the period of time for which the plated works in allowed to cool in air exceeds 20 seconds, the hue of the coating will turn purplish.

As stated hereinafter, a colored coating with a uniform, stable golden hue can be formed on a base metal of iron or steel by plating it under specific conditions using a molten zinc alloy of the specific composition. It thus provides a corrosion-resistant material for the components and facilities for uses where
they are required to be golden in color from the aesthetic viewpoint. The iron or steel products with colored coatings of the invention are highly corrosion-resistant and are of value in a wide range of use.

A-2) The development of clear purple color with Ti-Zn alloy

It is possible to form a colored coating with a purple hue on an iron or steel surface by plating the base metal using a bath of a zinc alloy for hot dipping of a composition comprising 0.1 - 0.5 wt % Ti - bal. Zn at a bath temperature of 500 - 550 °C, either allowing the plated work to cool in air for 10 - 50 seconds or heating it in an atmosphere at 500 - 520 °C for 10 - 20 seconds, and thereafter cooling it with cold or warm water. With regard to a zinc bulletin, the same explanation as in A-1) is applied hereto.

The plating is carried out using a molten zinc alloy bath of the composition 0.1 - 0.5 wt % Ti - bal. Zn, obtained by adding 0.1 - 0.5 wt %, preferably 0.3 wt %, Ti to the above-mentioned zinc.

In order to produce the purple colored coating from the hot-dip zinc alloy bath of the above composition, a base metal of iron or steel is immersed in the plating bath at 500 - 550 °C, preferably at 500 - 520 °C, for at least one minute, the base metal is pulled out of the bath and allowed to cool in air for 10 - 50 seconds, preferably for 40 - 50 seconds, and then is immediately cooled with cold or warm water to form thereon an oxide film with a purple hue. Alternatively, the work taken out of the bath is heated in an atmosphere at 500 - 520 °C for 10 - 20 seconds and then is cooled with cold or warm water to form a purple colored oxide film thereon.

Thus, in producing a purple colored coating, it is essential to immerse the iron or steel base metal in the bath of molten zinc alloy of the composition 0.1 - 0.5 wt % Ti - bal. Zn at a bath temperature of 500 - 550 °C, preferably of 500 - 520 °C, and then either allow it to cool in air for a very short period of 10 - 50 seconds, preferably of 40 - 50 seconds or heat it in an atmosphere at 500 - 520 °C for 10 - 20 seconds and then cool it with cold or warm water. If the conditions are outside the ranges specified above, the desired purple hue will not result.

As stated hereinafter, a colored coating with a uniform, stable purple hue can be formed on a base metal of iron or steel by plating it under specific conditions using a molten zinc alloy of the specific composition. It thus provides a corrosion-resistant material for the components and facilities for uses where they are required to be purple in color from the aesthetic viewpoint.

The iron or steel products with colored coatings of the invention are highly corrosion-resistant and are of value in a wide range of use.

A-3) Selective development of yellow-dark red-green color with Ti-Zn alloy

There is provided a zinc alloy for colored hot-dip galvanizing capable of developing yellow, dark red, and green colors selectively as desired, composed of 0.2 - 0.7 wt % Ti and the balance zinc and inevitable impurities. An iron or steel surface is coated at a temperature of 590 to 620 °C in a hot-dipping bath of such an alloy. The coated surface is cooled after heating it to a temperature of 450 to 550 °C. The color of the coating is selected by controlling the extent of the oxidation of the coating.

It has further been found that the following alloys, made by adding the ingredients as follows to the above Ti-Zn alloy, are useful in uniform coloring in yellow, dark red, and green:

(a) A zinc alloy for colored hot-dip galvanizing capable of developing yellow, dark red, and green colors selectively as desired, composed of 0.2 - 0.7 wt % Ti, 1.3 - 5.9 wt % Pb, and the balance zinc and inevitable impurities.

(b) A zinc alloy for colored hot-dip galvanizing capable of developing yellow, dark red, and green colors selectively as desired, composed of 0.2 - 0.7 wt % Ti, 1.2 - 1.3 wt % Pb, 0.1 - 0.2 wt % Cd, and the balance zinc and inevitable impurities.

(c) A zinc alloy for colored hot-dip galvanizing capable of developing yellow, dark red, and green colors and desired, composed of 0.2 - 0.7 wt % Ti, 1.0 - 1.2 wt % Pb, 0.05 - 0.2 wt % Cd, 0.01 - 0.05 wt % of at least one element selected from the group consisting of Cu, Sn, Bi, Sb, and In, and the balance zinc and inevitable impurities.

A base material of iron or steel is galvanized by immersion in a molten zinc bath of such an alloy at a temperature of 490 to 620 °C, and the coated metal is cooled in the air after heating it to a temperature of 450 to 550 °C. Through proper control of the conditions, it is possible to bring out yellow, dark red, and green colors selectively at will. Even with an alloy based on a purest metallic zinc (at least 99.995% pure) or special zinc (at least 99.99 % pure), galvanizing with good wettability and uniformity in hue can be achieved.
Zinc alloy hot dipping is carried out by melting a zinc alloy in a coating bath and immersing a work to be galvanized in the bath. The zinc alloy is prepared by adding a specific alloying additive to a metallic zinc. In the practice of the invention, a metallic zinc bullion with a high purity of at least 99.9 %, typified by a pure zinc (99.995 % pure) and special zinc (at least 99.99 % pure) as defined in JIS H2107, in used. This prevents any adverse effects the variable introduction of impurities (Pb, Cd, Fe, etc.) can have upon the controllability of color development. Nevertheless, the use of such a high purity zinc brings shortcomings while it eliminates variations in the coating conditions due to the presence of impurities. For example, when an iron or steel material is galvanized by immersion in a coating bath (Fe saturated) containing predetermined amounts of Ti and Mn, the formation of an oxide film on the bath surface is rapid and large in amount. These and other factors tend to produce color shading, such as partial two-color mixing of the colored oxide film of the coating layer.

Under the circumstances the present inventors have found that the addition of 0.2 - 0.7 wt % Ti is effective in giving a yellow, dark red, or green color clearly and brightly without partial lackness of plating or unevenness in color.

If the Ti content in the coating bath is less than 0.2 wt %, the formation of a colored oxide film in the coating layer of the galvanized metal is inadequate, and the hue is low and ununiform, thus reducing the marketable value of the colored galvanized product. If the Ti content is above 0.7 wt %, the oxide film forms too rapidly and the change in hue of the colored oxide film becomes too fast to control.

Moreover, too much oxide formation on the coating bath reduces the wettability of the bath with respect to the base metal to be galvanized.

For the further improvement in the coating wettability, various alloys, prepared by adding Pb, Cd, Sn, Bi, Sb, In, and/or the like to the 0.2 - 0.7 wt % Ti - bal. Zn alloy, were investigated. As a result, the zinc alloys (a), (b), and (c) referred to above have now been found particularly useful. These three alloys will be described below.

a) Alloy containing 1.3 - 5.9 wt % Pb in addition to Ti:-

If the Pb content is less than 1.3 % the wettability-improving effect is limited. In colored coating at a bath temperature of 470 - 500 °C partial uncoating will result. Especially in the bath temperature range of 470 - 490 °C cross deposition on the coating film will frequently occur. In the 500 - 600 °C range too holidays and color shading in the colored oxide film will result. The Pb addition proves increasingly effective up to the limit of its solubility. Since the Pb solubility in molten zinc at a bath temperature of 600 °C is 5.9 wt %, the value is taken as the upper limit.

b) Alloy containing 1.2 - 1.3 wt % Pb and 0.1 - 0.2 wt % Cd in addition to Ti:-

Where Pb and Cd are combinedly used, small additions can prove effective. If the Pb content is less than 1.2 wt %, partial uncoating occurs in the colored coating at a bath temperature of 470 - 600 °C, even in the presence of Cd. In the temperature range of 470 - 490 °C the possibility of cross deposition on the coating film will be greater. Even when the Pb content is within the specified range, similar troubles will take place if the Cd content is less than 0.1 wt %. If the Pb content exceeds 1.3 wt % or the Cd content is more than 0.2 wt %, the oxide formation on the coating bath becomes so much that the rate of uncoating rises.

c) Alloy containing, besides Ti, 1.0 - 1.2 wt % Pb, 0.05 - 0.2 wt % Cd, and 0.01 - 0.05 wt % of at least one or more element selected from Cu, Sn, Bi, Sb, and In:-

The addition of at least one element selected from Cu, Sn, Bi, Sb, and In promotes the wettability-improving effect of Pb and Cd. If the Pb content is less than 1.0 wt % and the Cd content below 0.05 wt %, partial uncoating results from colored galvanizing at a bath temperature of 470 - 600 °C. Especially in the bath temperature range of 470 - 490 °C the cross deposit on the coating film will increase. On the other hand, if the Pb content is more than 1.2 wt % and the Cd exceeds 0.2 wt %, much oxide formation on the coating bath surface is observed. The addition of 0.01 - 0.05 wt % of at least one of Cu, Sn, Bi Sb, and In retards the rate of oxide film formation on the bath surface and improves the wettability for the work to be galvanized.

The addition elements thus prevent uncoating, color shading, dross deposition, and other troubles, render it easy to control the hue of the colored oxide film, and increase its color depth or strength.

In the hot dip galvanizing with such a zinc alloy, the work to be galvanized is degreased, for example by the use of an alkaline bath, descaled by pickling or the like, and then treated with a flux to be ready for
galvanizing. The flux treatment is effected, for example, by a dip for a short time in a ZnCl₂-KF solution, ZnCl₂-NH₄Cl solution, or other known flux solution.

After the pretreatment, the works is immersed in a coating bath at a specific controlled temperature for 1 to 3 minutes. The coated metal is pulled out of the bath and, through proper control of the degree of oxidation, a yellow, dark red, or green color is selectively obtained at will.

After the coated work has been pulled out of the bath, it is held in an atmosphere at 450 - 550 ° C for a predetermined period of time, so that the degree of its oxidation can be controlled. The holding temperature, holding time, and subsequent cooling method are chosen as desired.

As the degree of oxidation is increased, yellow, dark red, and green colors are developed successively in the order of mention.

An example of the oxidation degree control is as follows:

Yellow: After the work has been pulled out of the coating bath at a bath temperature of 590 °C, it is held in an atmosphere at 500 °C for 15 - 20 seconds and then is cooled with warm water.

Dark red: The bath temperature is increased by 5 - 10 °C, and either the atmosphere temperature is raised or the holding time is prolonged by 5-10 seconds.

Green: The bath temperature is made even higher by 5 - 10 °C, and either the atmosphere temperature is further increased or the holding time is extended by a further period of 5 - 10 second.

With the alloys of the invention, i.e., (a) the Ti - 1.3 - 5.9 wt % Pb - bal. Zn alloy, (b) Ti - 1.2 - 1.3- wt % Pb - 0.1 - 0.2 wt % Cd - bal. Zn alloy, and (c) Ti - 1.0 - 1.2 wt % Pb - 0.05 - 0.2 wt % Cd - 0.01 - 0.05 wt % (Cu, Sn, Bi, Sb, and/or In) - bal. Zn alloy, the color development is controllable in the order of golden, purple, and blue hues. In the order of increasing degrees of oxidation, gold, purple, blue, yellow, dark red, and green colors are brought out.

B-1) The development of dark-red color with Ti-Mn-Zn alloy

It is possible to form a colored coating with a dark red hue on a base metal of iron or steel by plating the base metal using a bath of a molten zinc alloy of a composition comprising 0.2 - 0.5 wt % Ti - 0.05 - 0.15 wt % Mn - bal. Zn at a bath temperature of 580 - 600 °C, heating the plated work in an atmosphere at 500 - 520 °C for 30 - 70 seconds, and thereafter cooling it with cold or warm water.

The metallic zinc to be used in forming the zinc alloy for hot dipping is typically one of the grades conforming to JIS H2107, for example, distilled zinc 1st grade (at least 98.5 % pure), purest zinc (at least 99.99 % pure), and special zinc grades. The impurities inevitably contained in these zinc materials are, for example in the distilled zinc 1st grade, all up 1.2 wt % Pb, 0.1 wt % Cd, and 0.020 wt % Fe. For the purposes of the invention a metallic zinc with a total impurity content of less than 1.5 wt % is desirable. Among these zinc varieties, distilled zinc is preferred practically because it can be plated with ordinary flux and the concentration is high.

Under this embodiment the plating is carried out using a bath of molten zinc alloy made by adding 0.2 - 0.5 wt %, preferably 0.3 wt %, Ti and 0.05 - 0.15 wt %, preferably 0.1 wt %, Mn to the above-mentioned zinc.

In order to produce the dark red colored coating from the hot-dip zinc alloy bath of the above composition, a base metal of iron or steel is immersed in the plating bath at 580 - 600 °C for at least one minute, the base metal is pulled out of the bath and held in an atmosphere at 500 - 520 °C (for example in an oven) for 30 - 70 seconds, and then is immediately cooled with cold or warm water to form thereon an oxide film with a dark red hue.

Thus, in producing a colored coating with a specific dark red hue, it is important to plate the iron or steel base metal using the bath of the molten zinc alloy of the specific composition at the specific bath temperature, heat it under specific temperature conditions, and then cool it with cold or warm water. If the conditions are outside the ranges specified above, no coating with the desired dark red hue be obtained.

B-2) The development of green color with Ti-Mn-Zn alloy

Using a zinc alloy for hot dipping to form on a base surface a green colored coating containing 0.2 - 0.5 wt % Ti and 0.05 - 0.15 wt % Mn, it is possible to produce a green colored coating on an iron or steel surface by coating the base metal with the zinc alloy for hot dipping at a bath temperature of 600 - 620 °C, heating the coated work in an atmosphere at 500 - 520 °C for 50 - 60 seconds, and thereafter cooling it with cold or warm water or with a coolant gas.

The zinc to be used is in accordance with B-1).
The coating is carried out using a molten zinc alloy bath of the above-mentioned zinc with the addition of 0.2 - 0.5 wt % Ti and 0.05 - 0.15 wt % Mn. The use of a hot-dip bath of a zinc alloy containing 0.3 wt % Ti and 0.1 wt % Mn is particularly desirable for forming a green coloured coating.

In order to produce the green colored coating from the hot-dip bath of the zinc alloy containing the above-specified percentages of Ti and Mn, a base metal of iron or steel is immersed in the molten zinc alloy bath at 600 - 620 °C for at least one minute, the base metal is then pulled out of the bath and heated in an atmosphere (for example, in an oven) at 500 - 520 °C for 50 - 60 seconds. After the heating, the work is cooled with cold or warm water or with coolant gas to form thereon a colored coating of an oxide with a green hue.

As described above, a colored coating, stable green hue can be obtained by conducting the plating by the use of a hot-dip bath of molten zinc alloy containing 0.2 - 0.5 wt % Ti and 0.05 - 0.15 wt % Mn under the specified condition. If the Ti and Mn contents in the zinc alloy are outside the ranges specified, the green hue of the resulting colored coating will be uneven and the oxide film will show poor wettability with respect to the coated base metal.

Also if the bath temperature and subsequent heating temperature and time as hot-dip conditions are not within the specific ranges, other hues can mix in, rendering it impossible to give a coating with a uniform green hue.

Thus, in producing a green colored coating uniform in hue, important roles are played by the Ti and Mn contents in the molten zinc alloy for the hot-dip bath, the subsequent heating conditions. It is only by the combination of such specific conditions that the objective green colored coating is obtained.

The colored coating formed excellently resists corrosive attacks with the so-called corrosion weight loss by far the less than that of coatings using ordinary molten zinc alloys.

B-3) The development of yellow color with Ti-Mn-Zn alloy

It is possible to form a colored coating with a yellow hue on an iron or steel surface by plating the base metal with a zinc alloy for hot dipping containing 0.2 - 0.5 wt % Ti and 0.05 - 0.15 wt % Mn at a bath temperature of 580 - 600 °C, heating the plated work in an atmosphere at 500 - 520 °C for 20 - 30 seconds, and thereafter cooling it with cold or warm water or with coolant gas.

The zinc to be used is according to B-1).

The plating is carried out using a molten zinc alloy bath of the above-mentioned zinc with the addition of 0.2 - 0.5 wt % Ti and 0.05 - 0.15 wt % Mn. A bath of a molten zinc alloy containing 0.3 wt % Ti and 0.1 wt % Mn is particularly desirable.

In order to produce the yellow colored coating from the hot-dip bath of the zinc alloy containing the above-specified amounts of Ti and Mn, a base metal of iron or steel is immersed in the plating bath at 580 - 600 °C for at least one minute, the base metal is then pulled out of the bath and heated in an atmosphere (for example, in an oven) at 500 - 520 °C for 20 - 30 seconds. After the heating, the work is water-cooled for about 10 seconds to form thereon a colored coating of an oxide with a yellow hue.

Thus, in producing a yellow colored coating, it is especially important to perform the plating by the use of the bath of molten zinc alloy of the specific composition under the specific conditions and then heat the plated work in an atmosphere at 500 - 520 °C for 20 - 30 seconds. If the heating after the plating is done under conditions outside the ranges specified above, no uniform yellow hue will be attained. For example, if the heating time exceeds 30 seconds the color hue will be mixed with green, and the desired yellow colored coating will no longer be obtained.

The colored coating obtained is excellent in its corrosion resistance.

B-4) The development of blue color with Ti-Mn-Zn alloy

It is possible to form a colored coating with a blue hue on an iron or steel surface by plating the base metal using a bath of a zinc alloy for hot dipping of a composition comprising 0.1 - 0.5 wt % Ti - 0.05 - 0.15 wt % Mn - bal. Zn at a bath temperature of 530 - 550 °C, allowing the plated work to cool in air for 15 - 25 seconds, and thereafter cooling it with cold or warm water.

The zinc to be used is in accordance with B-1).

The plating is carried out using a bath of molten zinc alloy made by adding 0.1 - 0.5 wt %, preferably 0.3 wt %, titanium (Ti) and 0.05 - 0.15 wt %, preferably 0.1 wt %, manganese (Mn) to the above-mentioned zinc.
In order to produce the blue colored coating from the hot-dip zinc alloy bath of the above composition, a base metal of iron or steel is immersed in the plating bath at 530 - 550 °C, for at least one minute, the base metal is pulled out of the bath and allowed to cool in air for about 15 - 25 seconds, and then is immediately cooled with cold or warm water to form thereon an oxide film with a blue hue.

Thus, in producing a blue colored coating, it is essential to plate the iron or steel base metal using the bath of molten zinc alloy of the composition comprising 0.1 - 0.5 wt % Ti - 0.05 - 0.15 wt % Mn - bal. Zn at a bath temperature of 530 - 550 °C, and then allow it to cool in air for a short period of 15 - 25 seconds. If the conditions are outside the ranges specified above, no coating with the desired blue hue will result.

The colored coating obtained is excellent in its corrosion resistance.

C) After-treatment

The colored oxide film formed on the colored, hot-dip galvanized material tends to discolor or fade with time, with changes in hue due to the progress of deterioration, depending on the environmental conditions including the sunlight, temperature, and humidity. Although the deterioration of the colored oxide film, of course, does not adversely affect the corrosion resistance of the hot-dip galvanized steel itself, the original beautiful appearance is unavoidably marred.

As a simple measure for protecting the colored oxide film on the colored hot-dip galvanized material to suppress the discolor or fade with time, surprisingly, painting has been found appropriate for realizing the object. As noted already, painting of the coated surface of ordinary (uncolored) hot-dip galvanized steel poses the problems of inadequate adhesion or separation of the paint film on short-period exposure. Partly responsible for them is the deposits on the galvanized steel surface of oxides (zinc white rust) and flux such as ammonium chloride used for the galvanizing. Presumably responsible too is the basic zinc dissolution product formed between zinc and the water that has permeated through the paint film. It is presumed that this product acts to decompose the resinous content (oily fatty acid) of an oily paint or long oil alkyd resin paint, causing the decomposition product to react with the zinc to produce zinc soap along the interface between the zinc surface and the paint film, thereby substantially reducing the adhesion of the paint.

A common belief has been that the colored oxide film layer formed on the surface of the colored hot-dip galvanized steel does not provide an adequate barrier between the zinc surface and the surrounding air. The pessimistic view that painting over the oxide film would, after all, be the same as direct paint application to the galvanized surface has been predominant. Contrary to these predictions, it has now been found that the colored oxide film has good affinity for and adhesion to paints, allowing the applied paint to permeate through the film to show high separation resistance, and is sufficiently capable of preventing water permeation to inhibit the reaction of the zinc layer with water and therefore the formation of zinc soap.

In accordance with the invention, the hot-dip galvanized materials thus colored may be coated with a paint having excellent adhesion, weather resistance, durability, and environmental barrier properties.

For the painting of ordinary hot-dip galvanized steels, pretreatment is essential and the types of paints that may be employed are limited. With colored, hot-dip galvanized steels, by contrast, there is no need of pretreatment and various paints may be used. Since the heating for oxidation that follows the galvanized step produces a film of oxide such as TiO₂ or MnO on the galvanized surface, the coating on the galvanized steel is so clean that there is no necessity of treating the surface before painting.

The paint to be used may be any type which does not unfavorably affect, but protect, the colored oxide film layer to be painted. Typically a synthetic resin paint is used. Among synthetic resin paints, those superior in protective effects are polyurethane resin, acrylic resin, epoxy resin, and chlorinated rubber paints. The paint is properly chosen in consideration of the price, environments to be encountered, ease of application, and other factors.

Where the color of the colored oxide film is to be shown as it is, a clear paint is the best choice, and where the color tone is to be modified, an aqueous paint is the easiest to handle. In any case, the paint can be applied by brushing, spraying, or dipping.

In certain situations multicoating is not impractical. For instance, where the environments are very severe or adverse, multiple painting may be taken into account. An example is the application of an aqueous paint as the base coat and a clear paint as the intermediate and top coats. Alternatively, an epoxy resin paint durable against the alkali attacks that result from zinc elution may form the undercoat and a chlorinated rubber or polyurethane paint excellently resistant to water, chemicals, and weather may form the intermediate and surface coats.

Even if the paint degrades with time, leading to chipping or flaking of the coat, the beautiful appearance of the galvanized steel will remain unaffected thanks to the colored oxide film on the steel surface. Under the invention, such chipping or flaking seldom takes place because the paint permeated through and binds
solidly with the colored oxide film. The paint that had permeated the oxide film keeps off water and the like by its water-repelling action and thereby protects the film.

D) Spraying

For the colored hot-dip galvanizing it is prerequisite that the work to be coated be dipped in a molten zinc alloy bath. In the practice, therefore, there are sometimes met the following limitations:

1. The process is difficult to apply to shapes too large to be dipped in the bath.
2. The coating of assembly parts and structures is sometimes difficult.
3. Localized coloring is cumbersome. Although masking and other techniques may be resorted to, they involve much complexities and difficulties. The techniques are difficult to cope with the trend toward more frequent situations requiring pattern drawing for decorative purposes.
4. For repairs of installations and the like the process is difficult to practice at sites.
5. There are tendencies that the larger the content of such an alloying element as Ti and Mn, the worse the wettability of the bath and the more the number of holidays and other coating defects. Although an increase in the content of the additive element improves the durability of the resulting coating accordingly, such addition is sometimes difficult from the standpoint of the coating technology.
6. The process sometimes brings failure of coating and other coating defects.

The colored zinc coating by metal spraying basically involves spraying a zinc alloy, which is otherwise used for a coating bath, in the form of wire, rod, or powder, over the object. Surprisingly, the oxidation reaction of the additional element had been found to proceed more favorably than expected during the spraying process, achieving at least as satisfactory effects as the colored hot-dip galvanizing.

Thus, in the present invention, a colored zinc coating may be attained by spraying a coloring, oxidizing zinc alloy over a base surface by a metal spraying process, whereby a colored oxide film is formed on the base surface. After the spraying, the color development of the colored oxide film may be controlled by cooling and/or heating.

Metal spraying comprises heating a sprayable material to a half-molten state and spraying it over a base surface to form a coating tightly bonded to the surface. The sprayable material takes the form of a wire, rod, or powder, any of which may be employed under the invention.

The sprayable material may be any of the zinc alloys in common use for colored hot-dip galvanizing. It may, for example, be a Ti-Zn, or Ti-Mn-Zn alloy with or without the further addition of Cu, Ni and/or Cr. In the case of hot dipping, a work high in Ti, Mn or the like is not readily wetted when dipped in the bath, leaving holidays on the surface. The possibility of uncoating puts limitations to the amounts of the additive ingredients. Metal spraying is free from the wettability problem, and larger proportions of the additional elements can be used. Accordingly, the range of color development is wider and the hues have longer life.

The desirable sprayable material is a zinc alloy containing 0.1 - 2.0 wt % Ti and optionally 0.01 - 4.0 wt % of at least one selected from Mn, Cu, Cr, and Ni. With good workability the zinc alloy can be easily made into a wire or rod or powdered by crushing or melt dropping.

The sprayer that may usually be used is of the type known as a gas flame spray gun. An arc type spray gun may be employed as well.

The sprayable material is melted by the sprayer and sprayed over the base surface to be coated. The corners and intricate portions of the work difficult to coat by hot dipping can be completely coated by aiming the spray gun to those portions. Localized coatability permits figures and other patterns to be made easily. Another major advantage of metal spraying is the ability of coating iron and steel structures or the like at the sites.

After the spraying, the degree of surface oxidation is controlled so as to develop a desired color. A variety of colors, e.g., yellow, dark red, green, golden, purple, and blue colors, can be selectively developed as desired, depending on the degree of oxidation. For the oxidation control, the cooling rate of the sprayed coat can be adjusted by the use of natural cooling in the air or forced cooling with water or air. Also, the spray coat may be heated for a variable period with flame, infrared lamp, oven (where usable) or the like, and the subsequent cooling may be controlled. Proper combination of the sprayable material composition and surface oxidation conditions renders it possible to bring out a desired hue.

In this way a zinc sprayed coating with both corrosion resistance and colorability is produced.

The painting described above may be applied onto the sprayed coating.

The functional effects of the spraying are summarized as follows:

1. Applicable to large components that cannot be hot-dipped.
2. Capable of easily coating the portions of assembly parts and structures difficult to hot-dip.
3. Permits localized color development and display of a desired figure or other pattern thus enhancing the decorative value of the coating.
4. Possibility of coating at the site.
5. Ability to use high-melting alloys.
6. Ease of forming a thick coat suited for providing long-term corrosion protection.
7. A high Ti content in the alloy enhances the corrosion resistance and enriches the color hue.
8. The coating film, with a rough and porous surface, is suited as a base to be painted, and painting with a clear paint or various colored dyes can improve the durability of the colored oxide film of the coating. Other than spraying process, vapor deposition process, sputtering process, ion plating process or other surface coating process may be applied in this invention.

The Examples will be described below: The Examples A to D correspond to the items A to D described in the detailed explanation.

Example A - 1 (development of golden color with Ti-Zn alloy)

A test piece of steel sheet, SS41, 50 mm wide, 100 mm long, and 3.2 mm thick, was degreased by immersion in an alkaline bath at 80 °C for 30 minutes. It was washed with warm water, and then derusted by immersion in a 10% hydrochloric acid bath at ordinary temperature for 30 minutes. Next, the steel sheet was washed with warm water and was fluxed by a dip in a solution containing 35% ZnCl₂-NH₄Cl at 60 °C for 30 seconds.

The steel sheet thus pretreated was plated by immersion in a plating bath of the composition comprising 0.3 wt % Ti - bal. Zn at 450 - 470 °C for one minute. It was pulled out of the bath, allowed to cool in air for 10 - 20 seconds, and was immediately cooled with water at ordinary temperature. The steel surface so obtained had a coating of oxide with a lustrous, uniform golden hue.

The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 72 g/m².

By way of comparison, ordinary plated steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example A - 2 (development of purple color with Ti-Zn alloy)

The steel sheet pretreated in the same manner as the previous example was plated by immersion in a plating bath of the composition comprising 0.3 wt % Ti - bal. Zn at 500 - 520 °C for one minute. It was pulled out of the bath, allowed to cool in air for 40 - 50 seconds, and was immediately cooled with water at ordinary temperature.

The steel surface so obtained had a coating of oxide with a uniform purple hue.

The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 63 g/m².

By way of comparison, ordinary plated steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example A - 3 (development of yellow - dark red - green color and additional development of gold - purple - blue color)

The individual pieces pretreated as described previously were immersed in coating baths of the compositions given in Table 1 for one minute and then were pulled out at a rate of about 6 meters per minute. The steel pieces thus taken out of the baths were heated in an atmosphere at 500 °C for given periods of time, and cooled with warm water to form the following colored oxide films.

The treating conditions were as follows:
Yellow: Bath temperature 590°C
    Holding at 500°C for 15 - 20 seconds

Dark red: Bath temperature 600°C
    Holding at 500°C for 25 - 30 seconds

Green: Bath temperature 610°C
    Holding at 500°C for 35 - 40 seconds
Using alloys Nos. 2 to 5 of Examples, golden, purple, and blue colors were successfully developed under the following conditions:

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Zinc alloy ingredient (wt %)</th>
<th>Holiday</th>
<th>Color shading</th>
<th>Dross deposition</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>This invention</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>o</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>o</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>1.2</td>
<td>0.1</td>
<td>-</td>
<td>o</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>1.2</td>
<td>0.1</td>
<td>Cu 0.01</td>
<td>o</td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>1.1</td>
<td>0.1</td>
<td>Cu 0.02</td>
<td>o</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>In 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sn 0.04</td>
<td></td>
</tr>
<tr>
<td>Comparative Example</td>
<td>6</td>
<td>0.17</td>
<td>1.3</td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>7</td>
<td>0.35</td>
<td>1.1</td>
<td>0.05</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

o No x Yes
Golden: Bath temperature 490°C (1 min)↓
Holding at 500°C for 1 - 2 seconds

Purple: Bath temperature 500°C (1 min)↓
Holding at 500°C for 10 - 15 seconds

Blue: Bath temperature 520°C (1 min)↓
Holding at 500°C for 15 - 20 seconds

Thus, in the same manner as in Examples, the oxidation conditions were gradually intensified to provide a wide variety of colors, as many as six, i.e., golden → purple → blue → yellow → dark red → green, in succession in a controllable way. No holiday or color shading took place.

Example B - 1 (development of dark red color with Ti-Mn-Zn alloy)

A test piece of steel sheet, SS41, 50 mm wide, 100 mm long, and 3.2 mm thick, was degreased by immersion in an alkaline bath at 80 °C for 30 minutes. It was washed with warm water, and then derusted by immersion in a 10 % hydrochloric acid bath at ordinary temperature for 30 minutes. Next, the steel sheet was washed with warm water and was fluxed by a dip in a solution containing 35 % ZnCl₂-NH₄Cl at 60 °C for 30 seconds.

The steel sheet thus pretreated was plated by immersion in a plating bath of the composition comprising 0.3 wt% Ti - 0.1 wt % Mn - bal. Zn at 580 - 600 °C for one minute. It was pulled out of the bath, held in an oven at 500 - 520 °C for 30 - 70 seconds, taken out of the oven, and was immediately cooled with warm water at 40 - 60 °C.

The steel surface so obtained had a coating of oxide film with a dark red hue.

The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 60 g/m².

By way of comparison, ordinary plated steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example B - 2 (development of green color with Ti-Mn-Zn alloy)

The steel sheet thus pretreated as described was plated by immersion in a plating bath of the composition given below at 600 - 620 °C for one minute. It was pulled out of the bath, held in an oven at 500 - 520 °C for 50 - 60 seconds, taken out of the oven, and cooled with warm water by a dip in the bath for 10 seconds.

Composition of the bath:
0.3 wt % Ti - 0.1 wt % Mn - bal. Zn.

Zinc used was distilled zinc 1st grade.

The sequential steps of plating, heating, and cooling with warm water gave a uniformly colored coating layer with a bright green hue on the steel sheet.

The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 61 g/m².

By way of comparison, ordinary steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example B - 3 (development of yellow color with Ti-Mn-Zn alloy)

The steel sheet pretreated as previously described was plated by immersion in a plating bath of the composition comprising 0.3 wt % Ti - 0.1 wt % Mn - bal. Zn at 580 - 600 °C for one minute. It was pulled out of the bath, held in an oven at 500 - 520 °C for 20 - 30 seconds, taken out of the oven, and was immediately cooled by dipping in warm water at 40 - 60 °C for 10 seconds.
The steel surface so obtained had a coating of oxide with a bright yellow hue. The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 48 g/m². By way of comparison, ordinary steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example B - 4 (development of blue color with Ti-Mn-Zn alloy)

The steel sheet pretreated as previously described was plated by immersion in a plating bath of the composition comprising 0.3 wt % Ti - 0.1 wt % Mn - bal. Zn at 530 - 550 °C for one minute. It was pulled out of the bath, allowed to cool in air for 15 - 25 seconds, and was immediately cooled with water at ordinary temperature. The steel surface so obtained had a coating of oxide film with a uniform blue hue. The test piece of steel sheet with color coating thus obtained was subjected to a salt spray corrosion test for 240 hours. The corrosion weight loss was 70 g/m². By way of comparison, ordinary plated steel sheets hot-dip galvanized with distilled zinc were likewise tested. The corrosion weight loss amounted to as much as 120 - 150 g/m².

Example C (After-treatment)

Test pieces of steel sheet, measuring 50 mm wide, 100 mm long, and 3.2 mm thick, were either conventionally hot-dip galvanized or colored, hot-dip galvanized (with a Zn-Ti alloy). The galvanized pieces were coated with a clear polyurethane resin (resin : hardener = 5 : 1) or a colored, aqueous acrylic resin paint by brushing or dipping. The coated pieces, together with uncoated ones, were subjected to outdoor weathering tests. The tests were conducted within a plant under the possession of the present applicant. The degrees of degradation after test periods of three months, six months, and one year were visually inspected. The results are tabulated below in Table 2.

Conventionally hot-dip galvanized pieces became defective in only three months after the painting. Among the colored, hot-dip galvanized pieces, the golden-colored piece had a thinner oxide film than the rest because of the immature oxidation. Without a paint coat, therefore, the golden-colored piece degraded in three months and the blue-colored in one year. Painting could retard the degradation. Needless to say, an increase in the thickness of the paint coat, multicoating, or other similar step would prove effective in further retarding the degradation.
<table>
<thead>
<tr>
<th>Test piece condition</th>
<th>Outdoor weathering test</th>
<th>3 months</th>
<th>6 months</th>
<th>1 year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-dip acrylic galvanized</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Colored Blue</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Yellow</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Green</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Golden</td>
<td></td>
<td>o</td>
<td>Δ</td>
<td>x</td>
</tr>
<tr>
<td>Blue</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Yellow</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Green</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Olive</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
</tbody>
</table>

o: Good       Δ: Rather poor       x: Poor

Example D - 1 (Spraying)

A rod of zinc alloy containing 1.9 wt % Ti and 0.3 wt % Mn was used as a sprayable material. It was sprayed over a steel material by means of an oxy-acetylene gas flame type spray gun. The sprayed surface was allowed to cool, heated to 500 °C for 30 seconds, and again allowed to cool in the air.

A green colored coating was obtained.

Example D - 2 (Spraying)

Under the same conditions as in Example 1 but by the use of a zinc alloy rod containing 1.0 wt % Ti, spraying and afterheat treatment were carried out.

A blue colored coating resulted.
Claims

1. A method of forming a golden colored zinc coating on an iron or steel surface, comprising coating said iron or steel surface at a bath temperature of 450 to 470 °C in a hot-dipping bath of a galvanizing zinc alloy containing 0.10 to 0.5 wt % Ti in a distilled zinc, allowing the coated surface to cool in air for 5 to 20 seconds, and thereafter cooling it with cold or warm water.

2. A method of forming a purple colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting substantially of 0.10 to 0.5 wt % Ti - bal. Zn at a bath temperature of 500 to 550 °C for at least one minute, either allowing the coated surface to cool in the air for 10 to 50 seconds or heating it in an atmosphere at 500 to 520 °C for 10 to 20 seconds, and thereafter cooling it with cold or warm water.

3. A method of forming a zinc coating having a color selected from the group of yellow, dark red and green on an iron or steel surface, comprising coating said iron or steel surface at a temperature of 590 to 620 °C for 1 to 3 minutes in a hot-dipping bath of a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti and cooling the coated surface after heating it to a temperature of 450 to 550 °C, the color of the coating being selected by controlling the extent of the oxidation of the coating.

4. A method of forming a zinc coating having a color selected from the group of gold, purple, blue, yellow, dark red and green on an iron or steel surface, comprising coating said iron or steel surface at a temperature of 490 to 620 °C in a hot-dipping bath of
   (a) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti and 1.3 to 5.9 wt % Pb,
   (b) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti, 1.2 to 1.3 wt % Pb and 0.1 to 0.2 wt % Cd,
   or
   (c) a galvanizing zinc alloy containing 0.2 to 0.7 wt % Ti, 1.0 to 1.2 wt % Pb, 0.05 to 0.2 wt % Cd and 0.01 to 0.05 wt % of at least one element selected from the group consisting of Cu, Sn, Bi, Sb and In,
   and cooling the coated surface after heating it to a temperature of 450 to 550 °C, the color of the coating being selected by controlling the extent of the oxidation of the coating.

5. A method of forming a dark red colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting essentially of 0.2 to 0.5 wt % Ti - 0.05 to 0.15 wt % Mn - bal. Zn at a bath temperature of 580 to 600 °C, heating the coated work in an atmosphere at 500 to 520 °C for 30 to 70 seconds, and thereafter cooling it with cold or warm water.

6. A method of producing a green colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping which contains from 0.2 to 0.5 wt % Ti and from 0.05 to 0.15 wt % Mn at a bath temperature between 600 and 620 °C, heating the coated work in an atmosphere at from 500 to 520 °C for from 50 to 60 seconds, and thereafter cooling the same with cold or warm water or with a coolant gas.

7. A method of forming a yellow colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping containing from 0.2 to 0.5 wt % Ti and from 0.05 to 0.15 wt % Mn at a bath temperature between 580 and 600 °C, heating the coated work in an atmosphere at 500 to 520 °C for from 20 to 30 seconds, and thereafter cooling it with cold or warm water or with a coolant gas.

8. A method of forming a blue colored zinc coating on an iron or steel surface, comprising coating a base metal of iron or steel by the use of a zinc alloy for hot dipping of a composition consisting essentially of 0.10 to 0.5 wt % Ti -0.05 to 0.15 wt % Mn - bal. Zn at a bath temperature of 530 to 550 °C, allowing the coated surface to cool in the air for 15 to 25 seconds, and thereafter cooling it with cold or warm water.

9. A method of forming a colored zinc coating on an iron or steel surface, comprising thermally spraying by a spray gun a zinc alloy containing 0.1 to 2.0 wt % Ti and optionally 0.01 to 4.0 wt % of at least one more element selected from Mn, Cu, Cr and Ni, in the form of a sprayable wire or rod or powder, and
then heating the thermally sprayed surface until the given color is developed.

10. A method according to any one of claims 1 to 9 wherein the colored zinc coating is directly coated with a paint, with no use of any pretreatment.

11. A method according to claim 10 wherein the paint is selected from among synthetic resin paints.

12. A method according to claim 11 wherein the synthetic resin paint is selected from among polyurethane resin, acrylic resin, epoxy resin, and chlorinated rubber paints.

Patentansprüche

1. Verfahren zum Ausbilden einer goldfarbenen Zinkbeschichtung auf eine Eisen- oder Stahloberfläche, bei dem die Eisen- oder Stahloberfläche bei einer Badetemperatur von 450 bis 470 °C in einem Heißtauchbad aus einer Galvanisierzinklegierung beschichtet wird, die 0,10 bis 0,5 Gew. % Ti in einem destillierten Zink enthält, und bei dem man die beschichtete Oberfläche in Luft 5 bis 20 Sekunden lang abkühlen laßt sowie danach mit kaltem oder warmem Wasser abkühlt.

2. Verfahren zum Ausbilden einer purpurfarbenen Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem ein Grundmetall aus Eisen oder Stahl unter Verwendung einer Heißtauch-Zinklegierung mit einer Zusammensetzung im wesentlichen bestehend aus 0,10 bis 0,5 Gew.% Ti-Rest Zn bei einer Badetemperatur von 500 bis 550 °C mindestens eine Minute lang beschichtet wird, und bei dem man die beschichtete Oberfläche entweder in Luft 10 bis 50 Sekunden lang abkühlen läßt oder 10 bis 20 Sekunden lang in einer Atmosphäre bei 500 bis 520 °C erhitzt und danach mit kaltem oder warmem Wasser abkühlt.

3. Verfahren zum Ausbilden einer Zinkbeschichtung mit einer aus der aus Gelb, Dunkelrot und Grün bestehenden Gruppe ausgewählten Farbe auf einer Eisen- oder Stahloberfläche, bei der die Eisen- oder Stahloberfläche ein bis drei Minuten lang bei einer Temperatur von 590 bis 620 °C in einem Heißtauchbad aus einer Galvanisierzinklegierung beschichtet wird, die 0,2 bis 0,7 Gew.% Ti enthält, und bei dem die beschichtete Oberfläche nach Erhitzen auf eine Temperatur von 450 bis 550 °C abgekühlt wird, wobei die Farbe der Beschichtung ausgewählt wird, indem der Grad der Oxidation der Beschichtung gesteuert wird.

   (a) einer Galvanisierzinklegierung, die 0,2 bis 0,7 Gew.% Ti und 1,3 bis 5,9 Gew.% Pb enthält,
   (b) einer Galvanisierzinklegierung, die 0,2 bis 0,7 Gew.% Ti, 1,2 bis 1,3 Gew.% Pb und 0,1 bis 0,2 Gew.% Cd enthält, oder
   (c) einer Galvanisierzinklegierung, die 0,2 bis 0,7 Gew.% Ti, 1,0 bis 1,2 Gew.% Pb, 0,05 bis 0,2 Gew.% Cd und 0,01 bis 0,05 Gew.% mindestens eines Elements enthält, das aus der aus Cu, Sn, Bi, Sb und In bestehenden Gruppe ausgewählt ist, beschichtet wird, und bei dem die beschichtete Oberfläche nach Erhitzen auf eine Temperatur von 450 bis 550 °C abgekühlt wird, wobei die Farbe der Beschichtung ausgewählt wird, indem das Ausmaß der Oxidation der Beschichtung gesteuert wird.

5. Verfahren zum Ausbilden einer dunkelrot gefärbten Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem ein Grundmetall aus Eisen oder Stahl unter Verwendung einer Heißtauch-Zinklegierung mit einer Zusammensetzung im wesentlichen bestehend aus 0,2 bis 0,5 Gew.% Ti - 0,05 bis 0,15 Gew.% Mn - Rest Zn bei einer Badetemperatur von 580 bis 600 °C beschichtet wird, und bei dem das geschichtete Werkstück 30 bis 70 Sekunden lang in einer Atmosphäre bei 500 bis 520 °C erhitzt und danach mit kaltem oder warmem Wasser abgekühlt wird.

6. Verfahren zum Ausbilden einer grün gefärbten Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem ein Grundmetall aus Eisen oder Stahl unter Verwendung einer Heißtauch-Zinklegierung, die 0,2 bis 0,5 Gew.% Ti und 0,05 bis 0,15 Gew.% Mn enthält, bei einer Badtemperatur zwischen 600 und 820
7. Verfahren zum Ausbilden einer gelbfarbenen Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem ein Grundmetall aus Eisen oder Stahl unter Verwendung einer Heißtauch-Zinklegierung, die 0,2 bis 0,5 Gew.% Ti und 0,05 bis 0,15 Gew.% Mn enthält, bei einer Badtemperatur zwischen 580 und 600 °C beschichtet wird, und bei dem das beschichtete Werkstück 20 bis 30 Sekunden lang in einer Atmosphäre bei 500 bis 520 °C erhitzt und danach mit kaltem oder warmem Wasser oder mit einem Kühlgas abgekühlt wird.

8. Verfahren zum Ausbilden einer blaufarbenen Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem ein Grundmetall aus Eisen oder Stahl unter Verwendung einer Heißtauch-Zinklegierung mit einer Zusammensetzung im wesentlichen bestehend aus 0,10 bis 0,5 Gew.% Ti - 0,05 bis 0,15 Gew.% Mn - Rest Zn bei einer Badtemperatur von 530 bis 550 °C beschichtet wird, und bei dem man die beschichtete Oberfläche in Luft 15 bis 25 Sekunden lang abkühlen läßt und danach mit kaltem oder warmem Wasser abkühlt.

9. Verfahren zum Ausbilden einer gefärbten Zinkbeschichtung auf einer Eisen- oder Stahloberfläche, bei dem eine Zinklegierung, die 0,1 bis 2,0 Gew.% Ti und gegebenenfalls 0,01 bis 4,0 Gew.% mindestens eines weiteren Elements enthält, das aus der aus Mn, Cu, Cr und Ni bestehenden Gruppe ausgewählt ist, in Form eines spritzbaren Drahtes oder Stabes oder Pulvers mittels einer Spritzpistole thermisch gespritzt wird, und bei dem dann die thermisch gespritzte Oberfläche erhitzt wird, bis die betreffende Farbe entwickelt ist.

10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem die gefärbte Zinkbeschichtung ohne Anwendung irgendeiner Vorbehandlung unmittelbar mit einer Farbe beschichtet wird.


Revendications

1. Procédé de formation d'un revêtement à base de zinc, de couleur dorée, sur une surface de fer ou d'acier, comprenant le revêtement de ladite surface de fer ou d'acier à une température de bain de 450 à 470 °C dans un bain d'immersion à chaud constitué d'un alliage de zinc de galvanisation contenant 0,10 à 0,5 % en poids de Ti dans un zinc distillé, le refroidissement de la surface revêtue dans l'air pendant 5 à 20 secondes, puis le refroidissement de cette surface avec de l'eau froide ou chaude.

2. Procédé de formation d'un revêtement à base de zinc, de couleur pourpre, sur une surface de fer ou d'acier, comprenant le revêtement d'un métal de base consistant en fer ou acier au moyen d'un alliage de zinc pour immersion à chaud, ayant une composition consistant essentiellement en 0,10 à 0,5 % en poids de Ti, le reste étant du Zn, à une température du bain de 500 à 550 °C pendant au moins 1 minute, le refroidissement de la surface revêtue dans l'air pendant 10 à 50 secondes ou le chauffage de cette surface dans une atmosphère à une température de 500 à 520 °C pendant 10 à 20 secondes, puis le refroidissement de cette surface avec de l'eau froide ou chaude.

3. Procédé de formation d'un revêtement de zinc ayant une couleur choisie dans le groupe comprenant le jaune, le rouge foncé et le vert sur une surface de fer ou d'acier, comprenant le revêtement de ladite surface de fer ou d'acier à une température de 590 à 620 °C pendant une à trois minutes dans un bain d'immersion à chaud constitué d'un alliage de zinc de galvanisation contenant 0,2 à 0,7 % en poids de Ti, et le refroidissement de la surface revêtue après son chauffage à une température de 450 à 550 °C, la couleur du revêtement étant choisie en ajustant le degré d'oxydation du revêtement.

4. Procédé de formation d'un revêtement de zinc ayant une couleur choisie dans le groupe comprenant l'or, le pourpre, le bleu, le jaune, le rouge foncé et le vert sur une surface de fer ou d'acier, comprenant
le revêtement de ladite surface de fer ou d'acier à une température de 490 à 620 °C dans un bain d'immersion à chaud constitué

(a) d'un alliage de zinc de galvanisation contenant 0,2 à 0,7 % en poids de Ti et 1,3 à 5,9 % en poids de Pb,
(b) d'un alliage de zinc de galvanisation contenant 0,2 à 0,7 % en poids de Ti, 1,2 à 1,3 % en poids de Pb et 0,1 à 0,2 % en poids de Cd, ou
(c) d'un alliage de zinc de galvanisation contenant 0,2 à 0,7 % en poids de Ti, 1,2 à 1,3 % en poids de Pb, 0,05 à 0,2 % en poids de Cd et 0,01 à 0,05 % en poids d'au moins un élément choisi dans
le groupe consistant en Cu, Sn, Bi, Sd et In,

et le refroidissement de la surface revêtue après son chauffage à une température de 450 à 550 °C, la couleur du revêtement étant choisie en ajustant le degré d'oxydation du revêtement.

5. Procédé de formation d'un revêtement de zinc de couleur rouge foncé sur une surface de fer ou d'acier, comprenant le revêtement d'un métal de base consistant en fer ou acier au moyen d'un alliage de zinc pour immersion à chaud, ayant une composition consistant essentiellement en 0,2 à 0,5 % en poids de Ti, 0,05 à 0,15 % en poids de Mn, le reste consistant en Zn, à une température du bain de 580 à 600 °C, le chauffage de la pièce revêtue dans une atmosphère à une température de 500 à 520 °C pendant 30 à 70 secondes, puis son refroidissement avec de l'eau froide ou chaude.

6. Procédé de production d'un revêtement de zinc de couleur verte sur une surface de fer ou d'acier, comprenant le revêtement d'un métal de base consistant en fer ou acier au moyen d'un alliage de zinc pour immersion à chaud qui contient 0,2 à 0,5 % en poids de Ti et 0,05 à 0,15 % en poids de Mn à une température du bain de 600 à 620 °C, le chauffage de la pièce revêtue dans une atmosphère à une température de 500 à 520 °C pendant un temps de 50 à 60 secondes, puis le refroidissement de cette pièce avec de l'eau froide ou chaude ou bien avec un gaz de refroidissement.

7. Procédé de formation d'un revêtement de zinc de couleur jaune sur une surface de fer ou d'acier, comprenant le revêtement d'un métal de base consistant en fer ou acier au moyen d'un alliage de zinc pour immersion à chaud contenant 0,2 à 0,5 % en poids de Ti et 0,05 à 0,15 % en poids de Mn à une température du bain de 580 à 600 °C, le chauffage de la pièce revêtue dans une atmosphère à une température de 500 à 520 °C pendant un temps de 20 à 30 secondes, puis son refroidissement avec de l'eau froide ou chaude ou bien avec un gaz de refroidissement.

8. Procédé de formation d'un revêtement de zinc de couleur bleue sur une surface de fer ou d'acier, comprenant le revêtement de métal de base consistant en fer ou acier au moyen d'un alliage de zinc pour immersion à chaud, ayant une composition consistant essentiellement en 0,10 à 0,5 % en poids de Ti, 0,05 à 0,15 % en poids de Mn, le reste consistant en Zn, à une température du bain de 530 à 550 °C, le refroidissement de la surface revêtue dans l'air pendant 15 à 25 secondes, puis son refroidissement avec de l'eau froide ou chaude.

9. Procédé de formation d'un revêtement de zinc coloré sur une surface de fer ou d'acier, comprenant la pulvérisation thermique au moyen d'un pistolet pulvérisateur d'un alliage de zinc contenant 0,1 à 2,0 % en poids de Ti et, facultativement, 0,01 à 4,0 % en poids d'au moins un élément supplémentaire choisi entre Mn, Cu, Cr et Ni, sous forme d'un fil, d'une baguette ou d'une poudre pulvérisable, puis le chauffage de la surface ayant subi une pulvérisation thermique jusqu'à développement de la couleur donnée.

10. Procédé suivant l'une quelconque des revendications 1 à 9, dans lequel le revêtement de zinc coloré est revêtu directement avec une peinture, sans l'utilisation d'un quelconque prétraitement.

11. Procédé suivant la revendication 10, dans lequel la peinture est choisie entre des peintures à base de résines synthétiques.

12. Procédé suivant la revendication 11, dans lequel la peinture à base de résine synthétique est choisie entre des peintures à base de résines de polyuréthane, des peintures à base de résines acryliques, des peintures à base de résines époxy et des peintures à base de caoutchoucs chlorés.