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(54) METHOD FOR PRODUCTION OF CORROSION-RESISTANT STEEL STRIP

(57) A method for production of a pre-painted steel strip is proposed, which ensures forming a monolithic coating with improved corrosion resistance and mechanical strength, the method comprising steel strip surface treatment in a 10-50 g/l pickling solution in the pickling bath at 60 °C, with a strip temperature of 20-25 °C; passing the pickled steel strip through a bath with molten metal, comprised of: 1.0-1.4 wt% of metallic aluminium, 1.0-1.4 wt% of metallic magnesium, up to 0.5 % of impurities and the balance being metallic zinc, thus forming a metallic coating; treating the metallic coating with an aqueous suspension of 15 - 40 g/l alkaline salt at the pH= 10-12 in the degreasing bath at 60 °C, with the strip temperature of 20-25 °C, the solution comprising a 1 - 7 g/l of a surfactant; applying a Ti-containing conversion layer of dihydrogen hexafluortitanate on the metallic coating; successively applying a thermoset primer layer and a thermoset polymer top coat layer on the surface of the conversion layer; bringing the steel strip temperature down to a room temperature when curing of the thermoset primer and the thermoset polymer top coat is completed; wherein the thermoset primer and thermoset top coat compositions are selected to have a difference between their curing temperatures within 0-5 °C; wherein the curing time difference of the thermoset primer and the thermoset polymer top coat after their application to the conversion layer surface is 0-10 seconds.

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Description

[0001] The invention refers to the steel industry, particularly to the continuous process of steel strip production, and can be used by steel companies for producing pre-painted steel strips with polymer coatings that have longer durability and better corrosion resistance.

[0002] Steel strips with multi-layer anti-corrosion coating is utilized in various areas, such as construction, automotive industry, manufacturing of equipment hulls, buildings' interior and exterior panels, etc. Zinc coatings or multi-layer coatings, where zinc, primer and top coat are applied consecutively, are traditionally used to protect steel against corrosion. The main reasons for using zinc as a base of a protective metallic coating is high technological effectiveness of zinc application process together with low zinc electrolytic potential with respect to iron, which provides for anti-corrosion protection of a steel sheet even in cases when the coating integrity gets damaged.

[0003] The corrosion resistance of the coating itself can be improved by alloying zinc with other metals such as magnesium, aluminium, nickel, etc. Decreasing of zinc content in a coating may negatively affect the steel cathode protection on uncoated areas (e.g. edges, welds). On the other hand, the addition of magnesium and aluminium to the zinc coating improves its corrosion resistance by formation of a strong oxide layer during the interaction of magnesium and aluminium with the environment.

[0004] There is a known method for producing a steel strip with corrosion resistant coating described in WO2013160567A1 (dd. 25 April 2012, Arcelormittal Investigacion Y Desarrollo, SL) which is the closest analogue to the present invention. According to the known method, the metal coating comprises zinc, aluminium and magnesium alloy in the following ratio: 0.1-20 wt % of aluminium, 0.1-10 wt % of magnesium, with the balance being zinc.

[0005] The method comprises of the following steps:

1. prior to depositing a coating, preparation of the steel surface with chemical etching solutions;

2. application of a metallic coating by hot dip galvanizing ;

3. cooling of the steel strip;

4. removing layers of magnesium oxide or magnesium hydroxide off the metallic coating surfaces by step-wise treatment with alkali solutions followed by treatment with conversion acid solutions with pH between 1 and 4;

5. painting the Zn-based coating surface with melamine-cross-linking polyesters, isocyanate-cross-linking polyesters, polyurethanes and halogenated derivatives of vinyl polymers.

[0006] The main disadvantage of the proposed method is its low flexibility, not allowing use of the production lines intended for implementation of the known method of making a steel strip with various metallic and colour coatings that differ from the one disclosed in the patent application. For example, according to the known method, magnesium hydroxide which is inevitably formed on the surface of a steel strip during implementation of the method, is to be necessarily removed. Another disadvantage of the known method is low quality of the coating. Oxidation of aluminium and magnesium on a steel strip during its transportation from the place of treatment with alkali and acid solutions to the painting line can cause formation of local areas with loose oxide films, and thus appearance of unprotected areas and cause delamination of top coat and primer at those areas due to poor adhesion between Zn-based metallic coating and polymer layers.

[0007] Furthermore a wide range of metal concentrations in a HDG bath can be considered as a disadvantage of the proposed method. Continuous holding of constant concentration in the bath during production of industrial volumes of coils makes it difficult to achieve uniform composition and consequently uniform properties and phase composition of ZnAlMg coating along the strip length. This uncertainty leads to possibility to have extremely different corrosion resistant properties over the strip length.

[0008] The objective and technical result achieved by the claimed technical solution is production of a steel strip with enhanced anti-corrosion properties and higher strength. The improved anti-corrosion effect achieved by combining methods of corrosion protection on the steel surface in such a way that the successively located anti-corrosion layers have as high adhesion to each other as possible, and wherein the process parameters at all stages of the method cause forming the anti-corrosion layers all having as high quality as possible with no negative influence on the initial mechanical properties of the steel strip.

[0009] The method for producing a steel strip with colour coating is proposed to address the issues mentioned above and to achieve the technical effect. The method comprises of:

pickling a steel strip surface with a pickling fluid at 60 °C in the degreasing bath, with the strip temperature of 20-25 °C, and solution concentration of 10-50 g/l;

after preliminary heating in a continuous annealing furnace up to 405-415 °C, the pickled steel strip is dipped through a bath with a melt comprising 1.0-1.4 wt % of metallic aluminium, 1.0-1.4 wt % of metallic magnesium, up to 0.5 wt % of impurities and the balance being metallic zinc, as a result of which operation a metallic coating is formed on both sides of the strip after cooling the strip;

treatment of the metal coating with an aqueous suspension of alkaline salt with a pH = 10-12 in a degreasing bath at the solution temperature of 60 °C, with the strip temperature of 20-25 °C, where the alkaline salt concentration in the solution is 15-40 g/l and concentration of a surfactant in the solution is 1-7 g/l;

application of a Ti-based conversion layer comprising dihydrogen hexafluortitanate on the degreased metallic coating of the strip to ensure titanium deposition thereon;

successive application of a thermoset polymeric primer layer and a thermoset polymer top coat layer on the surface of the conversion layer; and

bringing the steel strip to a room temperature after completion of curing of the thermoset polymeric primer layer and the thermoset polymer top coat layer;

wherein the thermoset primer and the thermoset polymer top coat are selected to have a difference between the curing temperatures of the thermoset primer and the thermoset polymer top coat is within 0-5 °C;

wherein the difference between the curing time of the thermoset primer polymer layer and the thermoset top coat polymer layer after their deposition on the conversion layer surface is 0-10 seconds.

[0010] In some embodiments of the present invention the strip to be treated using the proposed method is a strip of cold-rolled annealed steel, cold-rolled full-hard steel or hot-rolled structural steel.

[0011] According to the proposed method, the steel strip temperature is preferably brought to 20-25 °C before applying the thermoset primer layer on the conversion layer.

[0012] During the metallic coating deposition the following components can be added to the bath with the melt while the melt is consumed for forming the coating: 1.2-3.0 wt% of Mg, 1.2-2.0 wt% of Al, up to 0.5 wt % of impurities and the balance being Zn.

[0013] The alkaline salt aqueous suspension used in the method can comprise 1.0-7.0 g/l of an anionic surfactant. When applying the conversion layer, 3-12 mg/m^2 of Ti can deposit into the conversion layer. A decorative enamel based on polyester, melamine-cross-linking polyester, polyurethane, PVDF, including polyurethane and polyesters with a wrinkled or textured structure as well as comprising acrylate and/or epoxy resins, can be used as a top coat polymer paint composition. The Ti-based conversion layer can comprise 2-10 mg/m^2 of dihydrogen hexafluortitanate and 2-10 mg/m^2 of hexafluorozirconic acid.

[0014] Four steps of protective coating formation on the surface of the steel strip can be used in this method.

[0015] At the first step, a ZnAlMg coating is applied on the steel strip which is preliminarily degreased and cleaned off oxide films. The coating is applied in the bath of molten Zn (97.2-98.0 wt%) + Al (1-1.4 wt%) + Mg (1-1.4 wt%) at a temperature of 420-460 °C and at a speed of the strip through the bath of 40-165 m/min. The initial temperature of the steel strip before dipping in the bath and the residence time of the strip in the bath is defined by a required thickness of the protective coating. When the strip leaves the bath, a layer of crystallized melt is preferably formed on the surface due to removal of excessive melt by air knives (air or nitrogen) and cooling the melt on the strip surface with the use of air or water cooling systems.

[0016] Concentration of Zn, Al and Mg in the melt bath is monitored every 1.0-3.0 hours by an atomic-absorption spectroscopy method or by inductively coupled plasma mass spectrometer. The melt composition is maintained in a stable condition by adding ingots of Zn with 1.2-3.0 wt% of Mg and 1.2-2.0 wt% of Al. After going through the bath, air knives (air or nitrogen) remove excessive liquid metal away from the strip surface, which allows forming a metallic coating with a thickness of 4-15 μm. The coating thickness can be controlled via both the speed of the strip passing the bath and via changing intensity of blowing off the strip with gas after the strip leaves the bath.

[0017] Then the strip with the applied coating is cooled down at a speed of 1-20 °C/second, and a final crystalline structure of the coating is formed.

[0018] The coating formed represents a Al/Zn/$MgZn_2$ matrix (up to 10 wt%) with a Zn phase (over 90 wt%) distributed therein in the form of separate grains or continuously associated grains. The high zinc content in the coating provides steel sheet cathode protection even in the areas where integrity can be damaged or where the coating would be perforated during operation activity. Corrosion products of Al and Mg formed during operation of the steel strips form layered double hydroxides, which function as an additional barrier protection between corrosive medium and the ZnAlMg coated steel strip. Corrosion resistance of the steel strip with such coating, tested in a salt spray chamber (NSST) according to the official standard procedure GOST 30630.2.5-2013 (ISO 9227:2012), is 3-10 times higher than that of a steel sheet with standard zinc coating of the same thickness. A coating with the content of Al and Mg below the specified ranges is not beneficious as compared to the traditional pure zinc coating, while an excess content of Mg and Al above the specified ranges significantly increases the costs and can lead to formation of loose oxide films on the surface that promotes peeling of the polymer coating.

[0019] At the second step, the coated steel surface is cleaned of possible organic contaminations with removal of oxides from the subsurface layer. A composition of a 15-40 g/l alkaline salts aqueous suspension and 1.0-7.0 g/l anionic surfactant is used for performing this cleaning operation 50-70°C. Application of said composition with alkaline pH $\approx$ 10-12 allows to ensure an efficient surface cleaning and avoid noticeable metal dissolving and dragging-out from the ZnAlMg coating. Furthermore, the cleaned steel strip surface does not require any additional surface cleaning prior to the deposition of the conversion layer.

[0020] At the third step, the ZnAlMg coated steel strip is treated with the conversion chemical compositions based on dihydrogen hexafluortitanate or a combination of dihydrogen hexafluortitanate and hexafluorzirconic acid.

[0021] During the deposition of the conversion layer a layer of insoluble titanium-based and zirconium-based compounds is formed on the surface of the ZnAlMg coating. This layer comprises a metal-oxide hydrated film containing TiO_2*2H_2O or $TiO_2*2H_2O+ZrO_2*2H_2O$.

[0022] This film provides an additional barrier protection against corrosion as well as improvement of the strip wettability resulting in better adhesion to the organic coating layers that are going to be deposited on the next step. The concentration of the active components and the strip treatment time in the conversion solution is selected in such a way that the amount of Ti distributed in the conversion layer to be at the level of 3-12 mg/m^2. The Ti content below 3 mg/m^2 results in a deterioration of the coating corrosion properties, while the Ti content of over 12 mg/m^2 causes reducing mechanical properties of the coating, e.g. decreasing of the bending strength.

[0023] At the fourth step, the steel strip is successively coated with the thermoset polymer primer and the thermoset polymer top coat that are applied by roll coaters. First, the polymer primer is applied followed by the finishing top coat. In one embodiments of the invention, the finishing coating can be applied as a single layer (monolayer). Depending on the product type and order requirements, it is possible that either one side or both sides of the steel strip are covered with the primer and a finishing enamel or with the monolayer coating.

[0024] Compounds with similar curing time at the selected curing temperatures should be selected as the primer or the finishing enamel. The difference in the curing temperatures should be no more than 0-5 °C, while the difference in the curing time should be no more than 0-10 sec. Selection of such parameters is based on the fact that when the polymer coatings with bases having different thermophysical properties are successively applied, there is an increased risk that such defects as blisters and pits are formed during the application of the organic layers. These defects have a negative impact on the corrosion resistance and mechanical properties of the finished pre-painted steel strip.

[0025] In addition, selection of similar curing times and temperatures allows using identical process modules for performing the curing operation and make possible to apply a constant speed of the strip across the successive processing areas.

[0026] The primers and finishing enamels are selected from the paints and varnishes based on polyesters, melamine-cross-linking polyesters, polyurethanes, PVDF, including wrinkled or textured polyurethanes and polyesters, as well as hot-curing epoxy resins with the curing temperature of 320-385 °C, peak metal temperature of 200-250 °C and curing dwell time in a pre-painting line of 21-34 seconds.

[0027] Furthermore the primer and the finishing enamel composition may include particles of fillers and pigments based on such minerals as TiO_2, $BaSO_4$, SiO_2, $CaCO_3$, talc, kaolinite, wollastonite, ferromanganese spinel and others.

[0028] The method according to the invention as described above has the following advantages:

- the method allows to improve corrosion resistance due to combining several types of corrosion protection: cathode type, barrier type and inhibition type;

- stability of physical and mechanical properties as well as chemical composition of the coating along the entire strip length due to constant monitoring and maintaining the metals concentration in the molten metal bath;

- prior to the application of the conversion layer the surface is cleaned using an aqueous suspension of alkaline salts (pH = 10-12), which in contrast to acidic solutions (pH < 7) excludes damaging of the ZnAlMg coating and therefore its decreasing in thickness;

- the method comprises application of the conversion layer having a certain mass-area ratio which ensures optimum combination of corrosion resistance and mechanical properties after application of the organic coating;

- when producing the coated steel product, no cancer inducing components are used containing chrome (Cr^{6+} and Cr^{3+}), identified as toxic and prohibited for use in the EU and USA;

- use of paints and varnishes with similar thermophysical properties results in reduction of potential rejects, minimizes the defects formation during the exploitation life of the products made of the coated steel produced using the claimed method, and also improves the performance of the painting lines.

[0029] The invention is further illustrated by the following example:

Example

[0030] A pilot batch of steel products coated with ZnAlMg coating at Hot Dip Galvanizing Lines (HDGL) and Prepainting Lines (PPL) produced at a production site of NLMK Group.

Application of ZnAlMg coating

[0031] A steel strip with the ZnAlMg coating was produced in the bath of Hot Dip Galvanizing Line (HDGL) according to the following process. A melt containing 97.6 ± 0.4 wt % of Zn, 1.2±0.2 wt% of Al and 1.2±0.2 wt % of Mg was prepared. Al and Mg concentrations were monitored hourly via atomic-absorption spectroscopy and were maintained within the range 1.1-1.3 wt% of Al and 1.1-1.3 wt% of Mg by adding ingots of Zn with 1.2-3.0 wt% of Mg and 1.2-2.0 wt % of Al as far as the metal in the bath is being consumed. Melt temperature was maintained at 430±5 °C.

[0032] The DC04 grade steel strip was degreased and cleaned of oxide films, annealed in preheated continuous furnace up to the temperature at the furnace exit of 435 °C, and then was dipped in the bath of molten metal at the running speed of 165 m/min in the HDGL, where the ZnAlMg coating was deposited on strip surface. Coating thickness at the output of the bath was maintained within the range of 8-10 μm by blowing the melt excess away by air knives. Then the steel strip was cooled down at the speed of 15±2 °C/s in a continuous cooling chamber. Further oiling in an oiling machine is possible to protect coils from white rust during their storage.

Preparation of the strip surface to painting

[0033] Preparation of the strip surface to painting comprises the following steps:

- Pressure treatment in a skin pass mill in order to obtain roughness Ra between 0.5 and 1.5 μm.
- The surface was degreased and surface oxides were removed by an alkali-based composition (pH=11) of a 25 g/l alkaline salt aqueous suspension (D1) and a 3 g/l anionic surfactant (S1).

[0034] Application of the conversion layer. In order to apply the conversion layer a composition based on a combination of dihydrogen hexafluortitanate with hexafluorzirconic acid (Bonderite 1455) was used. The amount of titanium distributed in the strip surface layer was 10 mg/m^2.

Painting

[0035] The polyester-based primer (P1) in accordance with GOST R 52146-2003 or EN 10169-2010 and the polyester-based topcoat (trade mark Beckrupol 3000) were used as the topcoat. The topcoat had an assumed viscosity 50 sec according to GOST 8420-74, nonvolatile-matter content 55 % and peak metal temperature of 240 °C. The primer and the finish enamel were deposited one after another by a roll coater of a painting line. Top side: primer application, then primer drying in a continuous furnace at 340 °C within 25 seconds, then cooling, then top coat application, then paint drying in the continuous furnace at 340 °C during 25 seconds, and cooling. Back side: one-layer coating application, then drying in the continuous furnace at 340 °C within 25 seconds, and cooling.

[0036] Painted steel strip manufactured according to the above method was coiled and shipped to stock.

[0037] The properties of the steel strip were tested according to standards EN 10169, EN 13523-7, EN 13523-8 and 13523-26. The test results are given in Table 1.

Table 1. Coating properties according to standards.

Coating composition					**Properties**			
Metal Coating	Degreasing bath	Conversion coating	Primer	Top coat	Neutral salt spray - 360 hours V-notch (lamination)	Condensation resistance - 40 °C 1500 hours	T-bend test (flexibility)	T-bend test (adhesion)
Zn + 1.2Mg + 1.2Al	D1 25 g/l + 3g S1	7 mg/m^2 1455T	(PI)	Beckrypol 3000 RAL 9010	0 mm	OK	1.75T	0T
						OK	1.5T	0T

Claims

1. A method for producing a polymer coated steel strip, comprising:

   pickling a steel strip surface with a pickling fluid at 60 °C in a degreasing bath, with the strip temperature of 20-25 °C and the pickling fluid concentration of 10-50 g/l;

   dipping the pickled steel strip through a bath with a molten alloy comprising 1.0-1.4 wt% of metallic aluminium, 1.0-1.4 wt% of metallic magnesium, up to 0.5 wt% of impurities and the balance being metallic zinc, for forming a metallic coating;

   treating the metallic coating with an aqueous suspension of an alkaline salt with pH = 10-12 in a degreasing bath at 60 °C, with the strip temperature of 20-25 °C, wherein the alkaline salt concentration in the solution is 15-40 g/l and concentration of a surfactant in the solution is 1-7 g/l;

   applying a Ti-based conversion layer comprising dihydrogen hexafluortitanate on the metallic coating of the steel strip to ensure deposition of the metallic titanium thereon;

   applying successively a thermoset primer layer and a thermoset polymer top coat layer on the surface of the conversion layer; and

   bringing the temperature of the steel strip to a room temperature when curing of the thermoset primer the and thermoset polymer top coat is completed;

   wherein the thermoset primer and the thermoset polymer top coat are selected to have a difference between their respective curing temperatures within 0-5 °C;

   wherein the difference between the curing times of the thermoset primer and the thermoset polymer top coat after their deposition to the conversion layer surface is 0-10 seconds.

2. The method according to Claim 1, wherein the temperature of the steel strip is brought to 20-25 °C before applying the primer to the conversion layer surface.

3. The method according to Claim 1, wherein the steel strip is made of cold-rolled annealed steel, cold-rolled full-hard steel or hot-rolled structural steel.

4. The method according to Claim 1, wherein Zn alloy ingots comprising 1.2-3.0 wt% of magnesium, 1.2-2.0 wt % of aluminium, up to 0.5 wt % of impurities and the balance being zinc, are added into the bath with molten metal as far as it is being consumed for forming the coating.

5. The method according to Claim 1, wherein the alkaline salt aqueous suspension comprises 0.1- 3.0 g/l of an anion surfactant.

6. The method according to Claim 1, wherein the deposited conversion layer comprises 3-12 mg/m^2 of titanium.

7. The method according to Claim 1, wherein the polymer top coat layer comprises a decorative top coat material selected from polyester, melamine-cross-linking polyesters, polyurethane, PVDF, including wrinkled or textured polyurethane or polyester.

8. The method according to Claim 1, wherein the Ti-based conversion layer comprises 2-10 mg/m^2 of dihydrogen

hexafluortitanate and 2-10 mg/m^2 of hexafluorozirconic acid.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 15 5025

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	8 June 2021	Slembrouck, Igor

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X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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