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(54) Heavy-metal-free pre-treatment process for pre-painted galvanised steel coils

(57) Disclosed is a process of prepaint surface conversion on galvanised steel coils, as an alternative to the conventional alkaline passivation (or oxidation) treatment, characterised by a conversion treatment in an aqueous solution free from heavy metal, particular free from cobalt and nickel-free, and containing ferric ions, trivalent chromium ions, zirconium salts, a complexing agent and a base.

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Description

[0001] The present invention relates to a heavy metal such as cobalt and nickel-free pre-treatment process for pre-painted galvanised steel coils, characterised by an alkaline conversion treatment in the presence of ferric ions, trivalent chromium ions, zirconium salts and suitable complexing agents.

BACKGROUND OF THE INVENTION

1.1 COIL-COATING

[0002] The treatment of flat laminates in the form of coils can consist of hot laminates (carbon and stainless steels) pickling to eliminate the oxides that cover them, or of their (steels, galvanised steels and aluminium) surface conversion treatment, generally to prepaint, but also with direct protective purposes.

[0003] The three applications (pickling, prepainting surface conversion and passivating surface conversion) obviously differ in terms of their purposes and the technologies used, but have at least the following characteristics in common:

- the need to unwind the coils on entry to the treatment unit and rewind them on exit,
- the need for high speeds and very short treatment times,
- the availability of material in the form of flat laminate with very simple geometry; this means that brushes can be used to administer mechanical energy at the degreasing step, and squeezing rollers to eliminate excess solution or rinsing water.

1.2 PREPAINT

[0004] Flat painted laminates are said to be ***prepainted*** because painting precedes the subsequent operations required for the manufacture of the finished product. In order to withstand these mechanical operations without damage, the paint must have excellent "mechanical" properties of adhesion, flexibility and elongation, which must not be jeopardised in any way by the pre-treatment. Pre-treatment is obviously also required to give the paint suitable resistance to the propagation of subcorrosion.

1.3 METHOD OF CONTACT BETWEEN SOLUTION AND SURFACE

[0005] Solution-surface contact is facilitated by the planar geometry of the metal strip, but must take account of the very short reaction times (about 10 seconds at most). The different types of plant found on the market are generally one of three models, called "spray coating", "reaction cell" and "roll coating".

[0006] Spray coating is a spray application lasting about two seconds, generally with fairly high pressures and strong spraying, followed by a flash-off time (or "reaction zone") lasting 5-10 seconds.

[0007] The reaction cell is an immersion application wherein a high volume of solution is pumped into an auxiliary container which can take the form of an approximately parallelepipedal tank, with or without a lid, lacking two opposite long, narrow sides through which the metal strip runs; the solution is pumped into the container in the opposite direction to the advance of the metal strip, and exits from the strip entry and exit areas, which act as overflow.

[0008] The roll coater is a system of two cylinders whose rotation is induced by the advance of the metal strip: the first collects the solution and transfers it to the rubber applicator roller, which in turn deposits it on the metal strip in the form of a thin, even film.

[0009] The spray coater and reaction cell are normally used in standard treatments which involve rinsing after surface conversion. The roll coater is used for "dry-in-place" applications, followed by heat treatment at a moderate temperature (generally < 100°C) to allow water evaporation and chemical reactions with the metal surface, without rinsing.

[0010] A coil-coating line can treat up to 200 m of sheet metal a minute, and must never stop.

2. PRE-TREATMENT OF GALVANISED STEEL

[0011] There are three main types of galvanised steel treatment (obtained by hot or electrolytic galvanisation): crystalline phosphating, alkaline passivation (or oxidation) and finally, chromating, which is much more rare and tending to fall out of use for environmental and safety reasons, but is preferred when the zinc is alloyed with aluminium. Preliminary degreasing is generally unnecessary when galvanising and painting are performed in the same factory but on different lines. However, if degreasing is required, the use of strongly alkaline solutions (which are very effective but corrosive) is preferable in view of the very short contact times, and brushing is widespread.

[0012] Crystalline phosphating is widely used not only immediately before a painting treatment, but also when the galvanised sheet metal is to be subsequently cut, formed and assembled as part of a structure (such as vehicle bodywork or the casing of a household appliance) which is to be painted after assembly.

[0013] Chromating can performed on galvanised steel for pre-painting purposes, especially if aluminium is also treated in the same unit.

2.1 ALKALINE PASSIVATION (or OXYDATION)

[0014] Alkaline passivation is an oxidation process which takes place in alkaline solution, in the presence of metals such as iron, nickel and cobalt kept in solution by complexing agents. The coating formed, based on mixed Zn, Fe, Ni and Co oxides, must be further passivated in order to protect against corrosion. The passivating product, once based on chromium and today replaced for years by chromium-free products based on titanium, zirconium, vanadium, molybdenum and/or silica, is designed to protect the surface against oxidation before painting.

[0015] The coating formed gives the surface a slightly brown colour, and is very thin: the cobalt deposited on the surface is generally between 3 and 20 mg/m^2.

[0016] Alkaline passivation is a process which has been known for decades, and is well established. See, for example, US 3,444,007 and US 3,515,600 (1970s) and US 4,381,203 (1983).

[0017] A more recent patent (2003), EP 1 484 432, again refers to alkaline passivation but introduces new elements, disclosing the use of chelating agents such as tartaric, malic, oxalic, malonic, succinic, citric, adipic and glyoxylic acids, alone or combined with one another, and indicates that the pH of the process must be between 0.5 and 4, preferably between 2 and 3.

[0018] As alkaline passivation process will be subject to major limitations on use as a result of new legislation that requires restrictive labelling regarding the use of cobalt and nickel, which are potentially carcinogenic, attempts are being made to replace it with products that are easy to handle and more environment-friendly.

[0019] There are two current trends: the first is based on simple replacement and/or elimination of nickel and cobalt, while the second is based on the use of conversion processes with an acid base which create a coating based on trivalent chromium on the galvanised steel surface.

[0020] Processes of this second type are described in EP 1,995,348, which relates to surface treatment of zinc with aqueous solutions containing trivalent chromium ions, chelating agents able to form water-soluble complexes of trivalent chromium, zinc ions, a sulphated compound and phosphite ions. The pH of the solution must be acid: between 0.5 and 4, preferably between 1 and 3. The chelating agents are the same as those described in EP 1,484,432, in particular oxalic acid.

[0021] US 2009/0020185 describes surface treatment of zinc with aqueous solutions similar to the preceding ones but containing phosphoric or phosphorous esters instead of phosphites. Once again, the pH of the solution must be between 0.5 and 4, preferably between 1 and 3.

DESCRIPTION OF THE INVENTION

[0022] The invention relates to a process of prepaint surface conversion on galvanised steel coils, as an alternative to the conventional alkaline passivation treatment.

[0023] The process to which the invention relates produces:

- A low environmental impact, due to the elimination of heavy metals such as cobalt and nickel.
- Maintenance of alkaline process conditions, compared with other substitutes for alkaline passivation process, which require an acid environment.
- An improvement in anticorrosion performance and mechanical properties.
- Greater stability of the pre-treatment solution, even in the event of pollution by zinc.
- A drastic reduction in the quantity of sludge formed, estimated at not less than 70%.
- A reduction in deposits/scales in the feed pipes and heat exchangers.

[0024] The process according to the invention therefore produces a significant reduction in operating costs and greater operational safety, and is more environment-friendly.

[0025] The process according to the invention is characterised by a conversion treatment in an aqueous solution containing ferric ions, trivalent chromium ions, zirconium salts, a complexing agent and a base. The complexing agent is preferably sodium gluconate, and the base is preferably sodium hydroxide. The pH of the solution is between 11 and 13, preferably 12 ± 0.5. The concentration of ferric ions can range between 100 and 300 ppm, and that of trivalent chromium ions between 100 and 600 ppm. The corresponding nitrates will preferably be used. Zirconium ions can range between 100 and 300 ppm.

[0026] The conversion treatment according to the invention is preferably preceded by a step of degreasing with alkaline aqueous solution and by one or more washing steps.

[0027] When the conversion treatment has been performed, the coils are usually washed with demineralised water before undergoing the final no-rinse chromium-free and heavy metal-free passivation treatment.

[0028] The degreasing step serves to eliminate all trace of oils, fats, cleaning paste, oxides and any other impurities from the coil surface, to ensure that the metal surface is perfectly clean before the subsequent treatments. Normally, said degreasing is performed with aqueous solution at an alkaline pH (10-14). The use concentration is between 1% and 10%, and the temperature of the working bath is between 60°C and 80°C, for a treatment time of between 5 and 20 seconds, with spray pressures of between 1 and 4 bars.

[0029] The main constituents of the degreasing bath are listed in Table 1.

Table 1

Compound	Concentration
KOH or NaOH	2 - 20 g/l
P_2O_5	2 - 20 g/l
Surfactants	200 - 3000 ppm
Sequestering additives	1 - 10 g/l
P_2O_5 is present as orthophosphates (monosodium, disodium or trisodium phosphate) or polyphosphates (tripolyphosphate or neutral pyrophosphate), all in the form of sodium or potassium salts.	

[0030] The surfactants most commonly used belong to the chemical families of ethoxylated fatty alcohols with alcohol chain C9-C 11, C12-C13 or C12-C18 with different degrees of ethoxylation, ie. containing different numbers of ethylene oxide moles.

[0031] The sequestering additives are organic compounds chosen from nitriloacetic acid, sodium gluconate, gluconic acid, ethylenediaminetetraacetic acid disodium, ethylenediaminetetraacetic acid trisodium, phosphonates, acrylates and polyacrylates.

[0032] Washing with water, not necessarily demineralised, serves to eliminate all trace of the preceding step; the temperature is usually between 30°C and 60°C, with times ranging between 2 and 20 seconds, and the application is by spraying, with water renewal.

[0033] The conversion treatment according to the invention is the decisive step of the pre-treatment process, and serves to ensure good anchorage to the subsequent coat of paint, which must maintain excellent "mechanical" characteristics of adhesion, flexibility and elongation, together with good resistance to the propagation of subcorrosion.

[0034] The solution of ferric ions, trivalent chromium and zirconium salts replaces the solutions conventionally used in alkaline passivation treatment, the composition of which is set out in Table 2.

Table 2

Compound	Concentration
Heavy metals (nickel, cobalt, iron)	200 - 700 ppm for each metal
KOH or NaOH	12 - 18 g/l
Sequestering additives	6 - 8 g/l

[0035] The solutions of ferric ions, trivalent chromium and zirconium salts can be used according to the invention in concentrations of between 1% and 10%. The temperatures of the working bath are between 60°C and 80°C, with a treatment time of between 5 and 20 seconds and spray pressures of between 1 and 4 bars.

[0036] The sequestering additives are organic compounds selected from nitriloacetic acid, sodium gluconate, gluconic acid, phosphonates, acrylates and polyacrylates, preferably sodium gluconate.

[0037] After the conversion treatment, the coils are usually washed with demineralised water to eliminate all trace of undesirable deposits from the surface of the material; as in the preceding cases, the temperature is generally between 30°C and 60°C, with times ranging between 2 and 20 seconds, and application is by spraying.

[0038] The final passivation step is designed to protect the surface temporarily against oxidation during transport and storage periods. Until a few years ago it was almost always performed with solutions containing hexavalent chromium, whereas aqueous solutions of chromium-free products with an acid pH (2 - 4) are used today. The use concentration is between 1% and 10%, and the temperature of the working bath is between 30°C and 50°C, for a treatment time of between 5 and 20 seconds, with spray pressures of between 1 and 4 bars. The application is the no-rinse type.

[0039] The main constituents of the chromium-free passivation bath are listed in Table 3.

Table 3

Compound	Concentration
Zirconium and/or titanium salts	0.3 - 2 g/l, for each metal
Vanadium	100 mg/l
Colloidal silica	200 mg/l
Al (from alumina)	50 mg/l
NH_3	50 ppm
Modified acrylic or phenolic organic polymer	1000 mg/l

[0040] The zirconium salts are preferably chosen from fluozirconic acid, ammonium zirconium carbonate and potassium fluozirconate.

[0041] The titanium compounds comprise, for example, fluotitanic acid, titanium oxalate, titanium oxide and potassium fluotitanate.

[0042] The vanadium is inserted as ammonium vanadate, while the colloidal silica is a normal silica in dispersion.

[0043] The invention is described in greater detail in the examples below.

Example 1 - Process

Step a) Degreasing:

[0044]

Compound	Concentration
KOH or NaOH	4 g/l
P_2O_5 from neutral potassium pyrophosphate	5 g/l
Surfactants with chain C9-C11 + 5 and 6 moles of EO	500 ppm
Sodium gluconate	3 g/l
Use concentration of product	3 - 5%
Temperature	60 - 70°C
Treatment time	5 sec
Spray pressure	2 bar

Step b) First wash

[0045]

Continuously renewed demineralised water	-
Temperature	25°C
Treatment time	3 sec

(continued)

Continuously renewed demineralised water	-
Spray pressure	2 bar

Step c) Second wash

[0046]

Continuously renewed demineralised water	-
Temperature	25°C
Treatment time	3
Spray pressure	2 bar

Step d) Conversion treatment

[0047]

	Concentration
Trivalent iron (from iron nitrate)	200 ppm
Trivalent chromium (from chromium nitrate)	500 ppm
Zirconium (from zirconium nitrate)	100 ppm
Sodium gluconate (as complexing agent)	6 - 10 g/l
NaOH	12 - 18 g/l
Use concentration of product	50 - 150 g/l
pH of the solution	12,0
Temperature	60 - 70°C
Treatment time	5 sec
Spray pressure	2 bar

Step e) Washing with demineralised water

[0048]

Continuously renewed demineralised water	-
Temperature	25°C
Treatment time	3
Spray pressure	2 bar

Step f) No-rinse final passivation

[0049]

Compound	Concentration
Zr (from fluozirconic acid)	500 mg/l

(continued)

Compound	Concentration
Ti (from fluotitanic acid)	300 mg/l
Vanadium	100 mg/l
Al (from alumina)	50 mg/l
NH_3	50 ppm
Modified acrylic or phenolic organic polymer	500 - 2000 mg/l
Use concentration of product	2-3%
Temperature	50°C
Treatment time	2 sec
pH	3 - 6

[0050] The articles were dried with hot air at a temperature of between 60 and 80°C.

Example 2 - Comparative tests of corrosion resistance and mechanical adhesion characteristics

[0051] The results obtained with the process described in example 1 were compared with those of a conventional alkaline passivation cycle and of a cycle similar to the process according to the invention, but performed in an acid environment (pH of treatment bath 2.2-2.4).

[0052] Versions of the novel product based on chromium nitrate only and based on an iron nitrate / chromium nitrate / zirconium nitrate mixture, and versions with oxalic acid as complexing agent in one case and sodium gluconate in the other, were tested under both test conditions (acid environment and alkaline environment).

[0053] For the sake of convenience, Table 4 summarises the test conditions used, with the codes of the corresponding strips:

Table 4

PROCESS	pH	METALS	COMPLEXING AGENT	CODE
ALKALINE PASSIVATION TRADITIONAL PROCESS	alkaline	nickel, cobalt, iron	sodium gluconate	**N**
NOVEL PROCESS, NaOH-FREE	acid	chromium	oxalic acid	**AC/C/O**
			sodium gluconate	**AC/C/G**
		chromium, iron, zirconium	oxalic acid	**AC/CFZ/O**
			sodium gluconate	**AC/CFZ/G**
NOVEL PROCESS, WITH NaOH	alkaline	chromium	oxalic acid	**AL/C/O**
			sodium gluconate	**AL/C/G**
		chromium, iron, zirconium	oxalic acid	**AL/CFZ/O**
			sodium gluconate	**AL/CFZ/G**

[0054] Hot-dip galvanised (HDG) steel strips were used; after the cycles had been performed, the strips were painted with 2 types of paint according to the normal conditions of industrial application.

[0055] The treated and painted strips were then subjected to:

- corrosion resistance test in salt-fog chamber, in accordance with Standard ASTM B117, checking for the appearance of the first signs of corrosion on panels in which a deep cross was cut down to the basic metal, with protected edges

- mechanical adhesion test according to UNI 8900.

[0056] For the sake of convenience, Table 5 shows the results obtained, expressed as follows:

- for the corrosion test in salt-fog chamber: hours that elapsed until the appearance of the first signs of blistering 2+2 mm from the crosscut
- for adhesion: percentage of paint that adheres to the backing.

Table 5

STRIP CODE	PAINT	RESULTS OF CORROSION TEST	RESULTS OF ADHESION TEST
N	1	950	95
	2	900	100
AC/C/O	1	550	80
	2	600	75
AC/C/G	1	600	80
	2	650	75
AC/CFZ/O	1	700	70
	2	700	75
AC/CFZ/G	1	700	80
	2	750	85
AL/C/O	1	700	80
	2	650	80
AL/C/G	1	700	90
	2	750	85
AL/CFZ/O	1	750	85
	2	800	80
AL/CFZ/G	1	1000	95
	2	950	100

[0057] In view of the results obtained, two processes, **AL/CFZ/O** and **AL/CFZ/G**, were further tested to evaluate their behaviour in the event of pollution of the bath due to increasing accumulations of zinc and aluminium (present as an element in the alloy of some galvanised steels), and the quantity of sludge formed.

[0058] Table 6 shows the evaluations compared with the conventional alkaline passivation process.

Table 6

PROCESS	POLLUTION TEST *	QUANTITY OF SLUDGE **
N	OK up to Zn 1 g/l	100
AL/CFZ/O	OK up to Zn 1.5 g/l	70
AL/CFZ/G	OK up to Zn 2 g/l	30
* In this case, only mechanical adhesion tests were conducted ** Not absolute but relative values		

[0059] The laboratory tests described above were confirmed on an industrial coil-coating line, using a conventional alkaline passivation product.

[0060] This industrial test demonstrates that compared with the traditional product:

- the quality of items treated is equal, if not greater.

- there is a 90% reduction in online sludge, which is also more friable and almost impalpable.
- the process according to the invention offers improved performance in terms of corrosion resistance and adhesion of the film of paint.
- the product is less sensitive to problems of bath pollution with zinc.
- the product is cheaper, involves lower electricity consumption, less maintenance of the tanks and lower sludge disposal costs.

Claims

1. A chemical surface conversion coating process before painting for galvanised steel coils, **characterised by** a conversion treatment in an aqueous solution containing ferric ions, trivalent chromium ion, zirconium salts, a complexing agent and a base, in the absence of cobalt and nickel ions.

2. A process as claimed in claim 1 wherein the complexing agent is sodium gluconate and the base is preferably sodium hydroxide.

3. A process as claimed in claim 1 or 2 wherein the concentration of the ferric ions ranges from 100 to 300 ppm, that of the trivalent chromium ion ranges from 100 to 600 ppm and that of zirconium ion ranges from 50 to 150 ppm.

4. A process as claimed in any one of claims 1 to 3 wherein the conversion treatment is preceded by a degreasing step with an aqueous solution of alkaline degreasing agent in one or more washing steps.

5. A process as claimed in any one of claims 1 to 3 wherein the conversion treatment is followed by washing with purified water and final no-rinse passivation treatment free from chromium and heavy metals.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 18 7843

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 240 943 A2 (METALLGESELLSCHAFT AG [DE]) 14 October 1987 (1987-10-14)	1-3	INV. C23C22/60 C23C22/83
Y	* page 2, line 1 - page 3, line 26 * -----	4,5	
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			C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 December 2011	Hoyer, Wolfgang

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 11 18 7843

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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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