

(12) **UK Patent Application** (19) **GB** (11) **2 239 196** (13) **A**

(43) Date of A publication 26.06.1991

(21) Application No **8928757.7**

(22) Date of filing **20.12.1989**

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(51) INT CL⁵
B05D 1/36, B32B 15/08 15/18 27/40

(52) UK CL (Edition K)
**B2E ECD EQ E1307 E1748 E409S E413S E414S
E418T E418U E436U E489T E614T E614U**

(56) Documents cited
None

(58) Field of search
**UK CL (Edition K) B2E
INT CL⁵ B05D
WPI.**

(54) **Chromate-organic pre-treated steel for high corrosion resistance and improved paintability**

(57) A process of applying additional coatings to zinc coated steel or zinc alloy coated steel to improve at least the corrosion resistance and paintability of zinc or zinc alloys coated steel, comprises:

applying to the zinc or zinc alloy coated steel a first composition comprising an aqueous emulsion of an organic acrylic polymer in a chromic acid solution to form a first additional coating; and

subsequently applying to the steel a second, aqueous composition, comprising a polyurethane polymer, one or more crosslinking agents and one or more silicates, to form a second additional coating.

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1982.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1982.

GB 2 239 196 A

1 - STATE OF THE ART

During last years a great deal of concern about corrosion prevention has arised, especially in the domaine of long lasting goods exposed to very detrimental atmosphere, being automobil industry an excellent example.

At present time, car manufacturing industry is, slowly but progressively, replacing cold rolled steel for Zinc coated steel, because of the excellent corrosion resistance apported by Zinc to steel. In accordance, materials such as electrogalvanized, hot dip galvanized and galvanized steel are increasing their use in the construction of car bodies. In Germany, for example, the use of such materials for this purpose is in the order of 40 % of total steel sheet assembled in a car.

More recently, other pre-coated steel compositions are becoming more popular, as for example Zinc-Nickel alloy, due to its extremely high corrosion resistance.

The highest anticorrosion demand from the automotive industry is consequence of the need for supplying cars with a 10 years perforating corrosion guaranty.

The significant improvement in corrosion resistance of the above described materials, as compared to cold rolled steel, however it does not mean that its use by enterely satisfactory and acceptable in every situation.

It is well known that Zinc developes very thick mass of oxidized products under agressive environment, and this is responsible for the disbonding of paint coatings applied onto its surface, and furtherly increasing the rate of corrosion of the steel base.

Consequently is obvious than passivating or protecting Zinc is necessary to maintain its beneficial action onto steel, and furthermore to present good adhesion to paints.

Another question which demands practical solutions is the evidence that, when pre-forming Zinc coated steel, little dust is loosen from the metal sheet, making stamping process more difficult.

Passivating or protecting Zinc is a delicate process, also requiring special techniques, since too thin protective coating would be insufficient, whereas too thick layers would prevent from good welding.

2 - BACKGROUND

In the process described in U.S. Patent 4.006.041, a phosphate-chromate plus organic resin treatment for steel, Zinc and alloy surfaces is disclosed, where passivation of metal is achieved in a single non-rinse process. This process having shown on the grounds of industrial application a relevant improvement on preventing white rust formation and paintability of Zinc coated steel and more precisely hot dip galvanized strip, electrogalvanized, and Zinc-Aluminium alloys.

Following U.S. Patent 4.006.041, and introducing some new specific improvements claimed in this patent, a new two coating system for improved corrosion resistance and paintability of Zinc coated steel is described here after.

In view of the demanded characteristics for special pre-coated steels by the car industry, as summarised in page . . . , many attempts have been made by chemical manufactures to have an effective protection for Zinc coated steel plates. Then, a process is described in GB Patent 2096488, where a two layer system is used, being the first coating an inorganic chromate treatment and the second coating containing organic resins, silyane compounds and silica. However the complexity of the process, adhesion to further painting by electrodeposition seems to be insufficient.

GB Patent 2147826 A is an improvement of such adhesion problem, and modifications are disclosed on the second coating composition, then containing epoxy resin and silica, known to be favourable for good paint adhesion. The process needing a drying-curing temperature of about 250° C, altering, under this condition, the required paint-bake hardenability of the steel.

A further step as shown in GB Patent 2195560 A, means an improvement as decreasing curing temperature is concern. For this purpose, an especific

epoxy two component resin is disclosed, as well as compositions including epoxy-polyurethane systems. Finally, the process consisting of a first coating composed by an especial chromate film and a second coating consisting of a solvent based organic film.

3 - DESCRIPTION OF THE PROCESS

As mentioned before, the interaction of a phospho-chromate solution in contact with an organic polymer and deposited together onto a Zinc coated surface, is responsible for an excellent improvement on the prevention of white rust formation.

This process, protected by several patents as :

US 4006041
 GB 1482457
 RF 2248330
 D 2449967 (Germany)
 J 1072410 (Japan)
 RB 821346 (Belgium)

is already exploited on industrial lines, to protect materials such as, EC, HDG and Zn-Al alloy coated steel strip.

Zinc coated steel pannels, treated with this process, show high corrosion resistance, such as :

<u>Salt spray test</u>	
EC :	100 - 200 h. }
HDG :	200 - 250 h. }
Zn-Al :	200 - 300 h. }

Before white rust formation

Improved paintability, and an important reduction on friction coefficient, producing a non-galling material, are other benefits provided by the product.

On the other hand, weldability is not affected by the treatment, due to the extreme thin layer deposited, in the range of 0,6 gr./sq.mt. equivalent to less than 0,5 μ .

In spite of the qualities shown by this process, they were not sufficient to meet the high standard specifications required by automobile industry. Consequently a further development and improvement was necessary.

A new process, as described herein, was developed aiming to fulfill all the characteristics in accordance with motor-car requirements :

- High corrosion resistance
- Weldability
- Easy formability
- No Zinc dusting
- Resistance to chemicals : Alkaline - Acidic
- Conductivity (electropaint deposition)
- No crater formation
- Paintability (adhesion, flexibility)
- Ability to be applied on low-bake hardenable steel

The new process, then consists of a two coating system applied onto the Zinc coated steel by squeeze-rollers and/or roll coater, and after low temperature drying a thin coating is obtained. The new process is valid for improvement of the behaviour of different type of Zinc coated materials, such as electrozinc coated steel, hot dip galvanized, galvanized and most especially new electro Zinc alloys as Zinc-Nickel, where highest performances are achieved.

The first layer to be applied, is consisting of a phospho-chromate solution and an organic resin applied in one step, and forming an unique Zinc passivating film which acts in two ways : by inhibiting the metal surface from reacting with aggressive environment due to the presence of chromates, and sealing the surface from porosities by the organic polymer, providing a barrier to water-vapours, oxygen and other corrosive vapours. At this respect, it is important to outline that this process differs completely from other patents, where the first coating is composed essentially of chromate film without the presence of organic compound in itself, as is

claimed (claim nº 1) in GB 2195560 patent, where the first protective coating is deposited via inorganic solutions, with more or less especial chromate compositions, but without the presence and benefits of introducing an organic polymer in the film.

Within the same general context, the composition of this first layer may be slightly modified on its composition depending on the base material nature to be treated, whether it is EC. or HDG., for example.

Thickness of deposited film is very important, too low thick film will not give sufficient corrosion resistance, to high thick film would prevent from good welding and flexibility.

Best general performance is obtained at thickness in the order of $0,5 \mu$, this corresponding to 0,8 gr./sq.mt. with a chromium content of 60-80 mg./sq.mt.

In the first layer, chromium is present in the form of hexa and trivalent, and after drying, the ratio of Cr^{+6} / Cr^{+3} is between 30/70 to 5/95.

Lower Cr^{+3} content films show a tendency to redissolution (leaching), whereas extreme high Cr^{+3} content have unsatisfactory corrosion resistance.

The conversion of chromium, which is present in the liquid composition in the form of hexavalent chromium almost exclusively, is performed inside the film during the drying-curing step.

The presence of a resin in this composition is a key parameter for its high performance, and makes all the difference from other granted patents in the art.

The nature and characteristics of the polymer can be defined as an acrylic emulsion with an average particle size lower than $0,2 \mu$ and a molecular weight above 1.000.000.

The resin emulsion is prepared by a standard emulsion polymerization method and with standard equipment. The polymer is obtained from a selection of monomers amongst : methyl methacrylate, ethyl acrylate, buthyl acrilate, styrene, acrylic acid, hydroxiethyl methacrylate, glycidyl methacrylate, etc., which produce a polymer of a Glass Transition Temperature of $T_g = 15 - 65^{\circ} \text{C}$. A selective range of surfactans, anionic and no-ionic, are used in order to obtain best chemical and mechanical stability of the emulsion.

Acrylic resins with some free radicals are capable of reacting and consequently crosslinking with some polyvalent metals. A chemical reaction of this type occurs in the deposited film during the drying-precuring stage, and it is believed that the subsequent crosslinking is responsible for the high water resistance of the polymer.

From the practical and environment point of view, the process (first coating) presents the following advantages :

- a) The product is completely water based, with no presence of any type of solvent. Absolutely free from solvent contamination and fire risk.
- b) The application of this chromating coating does not include any rinsing after deposition of film. Consequently there are not chromate containing waters to decontaminate before disposal.
- c) Despite the presence of hexavalent chromium in the solution, the application method does not involve any high pressure impact to the metal surface, generating no-mist, neither any high temperature reaction, as other chromating processes do, and reducing considerably room ambient contamination.

On the other hand, the fact of applying an organic resin at the same time, it helps also to reduce evaporation, due to the sealing effect of the polymer.

This first coating of the present new process, will be applied onto the Zinc coated material, either :

- a) By dip or flow, followed by roll squeezing (to control film thickness) and immediate dry-curing at 140^o C, PMT, in EC or HDG galvanizing lines.
- b) By roll-coater, in separate coilcoating lines, or in EC or HDG lines themselves, if sufficient room for equipment is allowed for.

Only requiring 140^o C, PMT for curing, this permits the use of low-bake hardenable steel, a quality of steel required for automobil makers for easy forming and tools maintenance.

To complete the process, the application of a second coating is required, being the objective to provide the system with extra corrosion resistance, to avoid any chromium leaching out from the coating under any conditions, whilst keeping or improving the resistance to chemical attack by acids and alkalies.

The last mentioned point is of great importance, if one thinks of the use to be given to the Zinc plated steel during body-work assembly and pre-treatment before painting.

Since, other parts of body-work, made of other materials like steel, HDG, etc., will require a pre-treatment with cleaners and phosphate solutions, it is necessary that material prepared with new process will not be affected negatively by the action of these strong chemical processes.

The second coating proposed for finishing the complete process, consist of an organic polymer film, which is deposited from a water based solution. This is also a characteristic which differs from others patents, which require the use of a solvent-based composition, in order to maintain a good degree of water resistance of the complete coating system.

Amongst the different type of organic polymers that were experimented for the purpose, those having a highly crosslinked structure and certain

functionality, able to be blocked, were preferred. After testing, those containing a polyurethane back-bone, or its mixtures with other polymers, was selected.

The use of polyurethane resins in a water based composition together with cross-linking agents, such as amine-group containing compounds and/or functional resins, can be considered as a novelty for the purpose.

The major advantage of this new type of coating is to render the final pre-coated steel surface completely resistant to chemical attack and physical degradation when in contact with alkaline cleaners and acidic phosphate solutions, as they are likely to be, when the new pre-coated steel is used, in car manufacturing, during the painting process.

This is most important point, since any deterioration of the coating by chemical attack, would lead to leaching of chromates totally or partially, with negative effects as loss in corrosion resistance and contamination of cleaning solution are concerned.

Any damage of the pre-coated steel sheet would negatively affect also to electrocoating deposition.

The polymer is applied, as a second coating of the new process, from a colloidal aqueous dispersion, laying down a very thin film (in the order of 1 μ) onto the already deposited chromate containing polymer of the first coating.

Through this technique, absolute sealing is accomplished, providing a strong barrier to permeation of oxygen and water vapours to the interface of metal and coating. Then preventing from coating disbonding, generation of rust on metal surface is avoided and a high degree of corrosion resistance is achieved.

In addition, some mineral compounds are included in the disclosed process. The mission of such compounds are to act, either as potential inhibitors and/or performing as an aid for the barrier effect. Mineral compounds were selected from a silicate group, including aluminium, calcium, magnesium silicates, and those presenting a laminar structure were preferred.

Application of this second coating onto the continuous Zinc coated strip, will be done after application and drying of the formerly described first coating, by means of roll-coating method, adjusting working conditions in order to deposit a dry film of 1μ thickness; equivalent to 1 gr./sq. mt.

The control of thickness of this coating is most important, since lower thickness would not provide sufficient organic polymer to produce a porous-free coating, and excessive thickness would sensibly modify standard welding characteristics for Zinc coated steel.

Drying of this second coating, is done also at 140° C PMT, for same reason as previous layer, to avoid hardening of the steel base metal.

In brief, the new proposed chromate-organic coating for Zinc pre-coated steel, consist of :

	COMPOSITION	THICKNESS	CURING
FIRST LAYER	WATER BASED Chromate-organic coating	$\sim 0,5\mu$	140° C
SECOND LAYER	WATER BASED Organic coating + silicates	$\sim 1\mu$	140° C

The system proposed in this patent has substantial differences with previous patents. However the composition of the applied solution is specifically if a very low pH, strongly acidic and oxidant because the addition on chromic acid, phosphoric acid, where then zinc oxide is also soluble and finally a special acrylic resin compound is dispersed.

According to our results those products can hardly be defined as chromate film system but as passivating film forming pretreatment. Anyhow those resin containing, first layers may belong to prior art as for example US 4.006.041. Along time however, have been improved systematically for optimal water and corrosion protection. However, those coatings alone can not be made to fulfill all the requirements of chemical stability to get through a phosphate and cathodic primer bath.

It is the object of this new patent our finding that, if optimal film forming passivation first layers is used, the desired full set of properties is reached with a thin coat of water based polyurethane resin emulsion single component.

The system gives a different chemical solution in the search of the pre-coated steel sheet that the industry is looking for, with the added positive features over prior art that modifications to present installations are simpler, the product has a longer pot life than the two component solvent based epoxy or epoxy-polyurethane resin based systems. Pollution to environment is very much reduced avoiding the use of solvents.

In the so called chromate passivation system practically no reaction takes place in the bath between liquid and base metal. But on drying the resin, a series of reactions mainly between resin reducing compounds and polar groups and the acidic and oxidant acids, those reactions lead to a substantial destruction of chromic acid and chromates produced to metal-organic compounds on basis of chrome, mostly present as cation, valence 3, instead of chromic or chromate anion, valence 6..

The result is very peculiar, is a continuous and amorphous layer of inorganic metals - organic resin complexes, with residual amounts of unreacted inorganic compounds, few of them chromates dissolved in the resin matrix. Special reference made in the patents to insoluble chromates, and chroma-

te layers on the metal will not apply here. Because the initial chemistry is different, by stereoscan microscopoc inspection only a continuous organic and amorphous chromate complex phase can be detected on the metal, and most essentially the reaction of the film on temperature and water is fully different, even at very moderated drying temperatures below 170° C the product properties and adhesion are excellent even if a watery emulsion is used as a second coat.

4 - CHARACTERISTICS

As mentioned, at the beginning of the present invention, the new chromate-organic precoating process is a great improvement on the protection of steel against corrosion, through the mechanism of passivation of the Zinc on precoated steel and then enlarging to outstanding limits the life of Zinc on its sacrificial action on steel.

The process of this invention has been designed to perform its benefits on almost any type of Zinc coated steel, including Electrogalvanized, Hot Dip Galvanized, and Zinc alloys coatings such as Zinc-Nickel and Zinc-Iron.

For quite evident reasons, the final performance of the new chromate-organic coating is very much influenced by the nature of the base material itself, as concerns corrosion resistance and paint adhesion, but meaning an important improvement as compared the same base material treated with conventional anti-corrosion pretreatments.

As far as corrosion resistance of the new chromate-organic coating, without further painting, is concerned, the following datae may be given, and referring them to different metal base material :

SALT SPRAY TEST (ASTM B-117)

METAL SUBSTRATE		RESISTANCE TO WHITE RUST	INITIAL RED RUST
ELECTROGALVANIZED, as Example 1	CHROMATE-ORGANIC COATING +	600 - 800 h.	1.500 - 2.000 h.
ZINC-NICKEL ELECTRODEPOSITION, as Example 4		1.200 - 1.500 h.	> 3.000 h.
HOT DIP GALVANIZED, as Example 2		600 - 800 h.	2.000 - 2.500 h.
GALVANNEALED, as Example 3		1.000 - 1.500 h.	> 2.000 h.

Improving adhesion to paints in another quality checked on Zinc coated steel treated with the process of the invention. The strong links generated between paints and the organic like pre-coated materials seem to be responsible for the high corrosion resistance showed by the complete system, (pre-coated + paint). Corrosion resistance being enhanced by the fact that interphase adhesion between metal and treatment and interlayer adhesion, prevent from water permeation and keep low electrochemical activity, and consequently physical disbonding is avoided. Disbonding of the protective coating it is believed to be the cause of actual rust initiation.

Because it is necessary than such a material be completely non-reactive and chemically estable against alkaline degreasers and phosphate solutions, for the reasons explained before, several tests were carried out :

Resistance to chemicals :

Alkaline cleaners - pH :10,5 Temperature :55°C Contact time:2-6' UNAFFECTED

Acid solutions - pH :10,5 Temperature :70°C Contact time:2' UNAFFECTED
(Phosphate)

Tests for adhesion and corrosion resistance have been carried out on Zinc coated steel plates which have been coated with a complete automotive painting system, according to the following process :

- a) ZINC COATED STEEL PLATE + 2 LAYER CHROMATE-ORGANIC
+
- b) CATHODIC ELECTROCOATING
ALKYD - EPOXY PRIMER
ALKYD - AMINE TOPCOAT

Paintability Test : Above described pannels were painted with following process :

Cataphoretic electrocoating
Epoxi primer
Alkyd top coat

Salt Spray Test results are summarized below :

<p>ELECTROGALVANIZED (50 gr./m²) as Example 1</p> <p>HOT DIP GALVANIZED (20 μ) as Example 2</p> <p>GALVANNEALED, as Example 3</p> <p>Zn - Ni ALLOY, as Example 4</p>	<p>2.000 hours, without corrosion nor disbonding at cross-hatch</p> <p>> 1.000 hours, without corrosion nor disbonding at cross-hatch</p> <p>2.500 hours, without corrosion nor disbonding at cross-hatch</p> <p>3.500 hours, without corrosion nor disbonding at cross-hatch</p>
<p>Comparative material :</p> <p>ELECTROGALVANIZED, with phosphate</p> <p>GALVANNEALED, with phosphate</p>	<p>800 hours, 2 - 3 m/m wide disbonding at cross-hatch</p> <p>600 hours, 3 - 4 m/m wide disbonding at cross-hatch</p>

Other accelerated weathering tests showed very good behaviour also. Alternative cycles of Salt Spray and Humidity Cabinet under changing conditions like 40° C / 98 % RH., 20° C / 73 % RH., and 20° C / 65 % RH., had no detrimental effect on painted pannels after 15 weeks of continuous and cycling test.

As respects formability of specimens prepared according to the invention, adhesion of the chromate-organic film showed to be excellent in bending, deep drawing and impact. Adhesion of paints is also promoted by the product of the invention.

At this respect it is necessary to mention that deformation qualities are very much dependant on specific characteristics of metal substracts, in this sense, behaviour of hot dip galvanized plates are very different from electrogalvanized, and Zinc-Nickel and galvannealed have also different degrees of formability.

Except for electrogalvanized substrate, application of the coating of the invention onto Zinc coated steel has showed always a general improvement on formability and paintability as compared to other metal pre-treatments. In the case of electrogalvanized, application of the described chromate-organic film onto phosphate layer is recommended for best formability and impact resistance, like stone chipping.

The invention is illustrated by the following examples.

EXAMPLE 1

Electrogalvanized steel pannels coated with 10 microns, were treated according to the invention in the following way, (after proper cleaning of the metal surface) :

1 st. coating - A pretreatment product in accordance with U.S. Patent 4006041 and others was prepared, in two different and separate solutions

A) Organic polymer emulsion, as described previously	40 - 70 %
Cation complex (Cr. Zn)	7 - 15 %
Deionized water	Balance

B) Chromic acid (as Cr. O ₃)	5 - 25 %
Inorganic acids	3 - 20 %
Deionized water	Balance

Both solutions were mixed together at a ratio of 2/1 and properly diluted with deionized water, so that when applied by dip onto above mentioned pannels and conveniently dried, would provide a protective film of 0,8 +/- 0,1 gr./sq. mt., equivalent to approximately 0,5 microns. Drying was done by heatching in a hot air stream at 170⁰ C during 1 minute so that metal temperature reached 140⁰ C.

After cooling, a second coating, as proposed in general description, was applied by dip also, from a diluted solution containing :

Organic polymer	20 - 35 %
Crosslinking agent	1 - 3 %
Mineral pigments	8 - 20 %
Deionized water	Balance

The product being finally diluted to 10-12 % solids content, so that after application by dip, would provide a film of 1 gr./sq. mt. equivalent to 1 micron.

Deposited coating was dried at 140⁰ C, Peak Metal Temperature, also.

A maximum curing temperature of 140⁰ C was selected in order to be a suitable process to allow the use of bake hardenable steels. Which are of very common use in automotive industrie.

EXAMPLE 2

Clean HDG steel pannels were treated with following solutions, prepared according to previous description of the invention.

Solution A) Acqueous mixture of organic polymers and a cation complex as described in Example 1	100 %
Solution B) Chromic acid (as Cr. O ₃)	6 - 14 %
Inorganic acids	< 3 %
Metallic ions	< 6 %
Deionized water	Balance

After mixing both solutions, A and B, at a ratio of 1/1, HDG pannels were treated in the same way as Example 1.

Later on, a second coating prepared according to the already described polyurethane water based lacquer was applied, and dried under the same conditions of Example 1.

EXAMPLE 3

The same product and application process as described in Example 1 was used to treat sample pannels of Zn - Fe alloy such as galvanized steel.

EXAMPLE 4

Zinc - Nickel electrodeposited steel pannels were given a similar treatment also, with products according to the composition of the invention.

Solutions were prepared as follows :

A) Acrylic polymer emulsion, having a solids content of 16 - 32 %, and according to general description.	100 %
B) Chromic acid (as Cr. O ₃)	8 - 16 %
Inorganic acids	5 - 20 %
Trivalent Chromium and other cations	< 4 %
Deionized water	Balance

After mixing both solutions, pannels were treated and dried in the same conditions as Example 1.

Finally a second coating as described in composition in Example 1 was applied also.

EXAMPLE 5

Same compositions as described on Example 1 were applied on Electro-galvanized steel pannels, to which a previous phosphate pretreatment was given, using a tricationic phosphate solution.

The use of a phosphate coating on Electrogalvanized steel before application of the product of the invention, was found to be favourable to improve some of the mechanical properties of the metal substrate. The physical modification on the surface structure will furtherly improve adhesion of coatings to the steel substrate.

The improvement found out in some specific adhesion tests, such as resistance to stone chipping, supports the strategy of using the new developed 2 coating system on phosphate EC steel rather than on bare EC steel.

As can be seen from Examples, some differences in composition of treating solution (B) have been necessarilly made in order to obtain maximum reactivity and consequently good adhesion to different metal substrates.

Various features, including optional or preferred features, of the invention may be summarized as follows:

- 1) A double layer chromate-organic coating process to improve corrosion resistance and other characteristics, such as paintability of Zinc and Zinc alloy coated steel. The double layer process consisting of a first coating containing a

special chromate acidic solution mixed and applied together with an organic polymer in emulsion state, totally or partially of acrylic nature.

The second coating applied afterwards, consisting of an organic resin from a water based composition also, which nature is essentially polyurethane polymer with added crosslinking agents and silicates.

- 2) A double coating chromate-organic process where the first layer contains chromium ions in its hexavalent state, together or not with trivalent chromium.
- 3) The said 1 st. coating, deposited from a highly acidic solution, where besides the chromic acid content, other inorganic acids are added, being phosphoric acid one of preferred.
- 4) The said 1 st. layer, containing chemical reducers also, will produce a film after drying that will contain hexavalent and trivalent chromium at the ratio of 30/70 to 5/95.
- 5) The said 1 st. layer, being able to be applied industrially by roll squeezing or roll coating, either in the galvanizing line itself or in a separate coil coating line. Drying of the coating will be made at a peak metal temperature between 130⁰ to 160⁰ C.
- 6) The nature of the organic emulsion forming part of the 1 st. layer and being mostly of acrylic nature, is chemically and physically stable at the pH of the solution, which is in the order of < 2.
- 7) A double coating chromate-organic process, where the 2 nd. layer is an organic polymer coating without the presence of any chromium metal ions.

- 8) The said 2 nd. layer is based on a polyurethane water based resin, together with crosslinking agents, such as amine function containing compounds or the like.
- 9) The said 2 nd. layer containing also mineral extenders and corrosion inhibitors such as silicates.
- 10) The said 2 nd. layer being applied industrially by roll route to provide a dry film of about 1 micron thick. The film being dried at peak metal temperature of 130° to 160° C.
- 11) A double coating process as described in summaries 1 to 10, which coating is resistant to chemical attack by cleaners and phosphate solutions and consequently there is not leaching of chromium when steel plates treated according to the invention are processed in ordinary cleaning and pretreatment lines like those used in automotive industry.
- 12) A double coating process as described in summaries 1 to 11, which is entirely water based without the presence of organic solvents.
- 13) A double coating process as described in summaries 1 to 12, suitable for application and treatment of hot dip galvanized steel.
- 14) A double coating process as described summarizes 1 to 12, suitable for application and treatment of hot dip electrogalvanized steel.
- 15) A double coating process as described in summaries 1 to 12, suitable for application and treatment of hot dip Zinc-Iron coated steel.
- 16) A double coating process as described in summaries 1 to 12, suitable for application and treatment of hot dip Zinc-Aluminium coated steel.
- 17) A double coating process as described in summaries 1 to 12, suitable for application and treatment of hot dip Zinc-Nickel coated steel.
- 18) A double coating process described in summaries 1 to 12, suitable for

application and treatment of hot dip Zinc electrocoated steel with a phosphate pretreatment.

- 19) A double coating process as application and treatment of hot dip of any type of Zinc coated steel.

CLAIMS

1. A process of applying additional coatings to zinc coated steel or zinc alloy coated steel to improve at least the corrosion resistance and paintability of zinc or zinc alloys coated steel, comprising:

applying to the zinc or zinc alloy coated steel a first composition comprising an aqueous emulsion of an organic acrylic polymer in a chromic acid solution to form a first additional coating; and

subsequently applying to the steel a second composition, being an aqueous composition comprising a polyurethane polymer, one or more crosslinking agents and one or more silicates, to form a second additional coating.

2. A process according to claim 1, wherein the first additional coating comprises hexavalent chromium and optionally trivalent chromium.

3. A process according to claim 1 or 2, wherein the first composition comprises, in addition to chromic acid, one or more other inorganic acids.

4. A process according to any preceding claim, wherein the first composition comprises one or more reducing agents and the first additional coating comprises hexavalent and trivalent chromium at a ratio in the range of 30:70 to 5:95 after curing is completed.

5. A process according to any preceding claim, wherein the first composition is applied by means of one or more rolls or the thickness of application of the first composition is controlled by one or more rolls and the first composition is dried at a temperature of 130° and 160°C to form the first additional coating.

6. A process according to any preceding claim, wherein the first

composition has a pH of less than 2 and is physically and chemically stable if kept below 50°C.

7. A process according to any preceding claim, wherein the second composition is free of chromium ions.

8. A process according to any preceding claim, wherein the second composition comprises one or more crosslinking agents.

9. A process according to any preceding claim, wherein the second composition comprises one or more mineral extenders and one or more corrosion inhibitors.

10. A process according to any preceding claim, wherein the second composition, after application to the steel, is dried at a temperature of 130° to 160°C to form the second additional coating, the second additional coating being about 1 micron thick.

11. A process according to any preceding claim, wherein the combination of the two additional coatings is resistant to chemical attack by cleaners and phosphate solutions, whereby chromium is not leached when the steel is processed in a conventional cleaning and pretreatment line such as used in the automotive industry.

12. A process according to any preceding claim, wherein both the first and second compositions are free of organic solvents.

13. A process according to any of claims 1 to 12, wherein the coated steel is hot dip galvanized steel, or zinc coated steel.

14. A process according to any of claims 1 to 12, wherein the coated steel is electrogalvanized steel.

15. A process according to any of claims 1 to 12, wherein the coated steel is hot dip zinc-iron coated steel or galvanized steel.

16. A process according to any of claims 1 to 12, wherein the coated steel is hot dip zinc-aluminium coated steel.

17. A process according to any of claims 1 to 12, wherein the coated steel is electrolytically zinc-nickel coated steel.

18. A process according to any of claims 1 to 12, wherein the coated steel is zinc electrocoated steel with a phosphate pretreatment.

19. A process according to any of claims 1 to 12, wherein the coated steel is any type of zinc coated steel.