



HU000028450T2

(19) **HU****MAGYARORSZÁG**
Szellemi Tulajdon Nemzeti Hivatala(11) Lajstromszám: **E 028 450**(13) **T2****EURÓPAI SZABADALOM**
SZÖVEGÉNEK FORDÍTÁSA(21) Magyar ügyszám: **E 08 749904**
(22) A bejelentés napja: **2008. 04. 30.**(51) Int. Cl.: **C23C 18/54** (2006.01)
C23C 28/00 (2006.01)(96) Az európai bejelentés bejelentési száma:
EP 20080749904
(97) Az európai bejelentés közzétételi adatai:
EP 2145031 A2 **2008. 11. 13.**
(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 2145031 B1 **2016. 03. 16.**(86) A nemzetközi (PCT) bejelentési szám:
PCT/EP 08/055308
(87) A nemzetközi közzétételi szám:
WO 08135478(30) Elsőbbségi adatok:
102007021364 **2007. 05. 04.** **DE**
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SBGK Szabadalmi Ügyvivői Iroda, Budapest(54) **Cink felületek metallizálószerrel történő előkezelése**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

"Metallizing pretreatment of zinc surfaces"

[2] The present invention relates to a method for metallizing pretreatment of galvanized and/or alloy-galvanized steel surfaces or joined metal components, which have at least partially surfaces made of zinc, in a surface treatment comprising multiple process steps. In the method according to the invention, a metallic layer overlay of in particular no more than 100 mg/m² iron is produced on the treated zinc surfaces. Such metallized zinc surfaces have excellent suitability as a starting material for subsequent passivation and coating steps (Fig. 1, methods II-V) and give rise to a much higher efficiency of the anticorrosion coating, in particular after the pretreatment according to the invention of galvanized metal surfaces. Application of the method to galvanized steel strip suppresses the corrosive delamination of the paint coating, especially at the cut edges. In a further aspect, therefore, the invention comprises an uncoated or subsequently coated metal component to which a metallizing pretreatment according to the invention has been applied, as well as the use of such a component in vehicle body construction in automobile manufacturing, in shipbuilding, in the construction industry and for the production of white goods.

[3] A large number of surface-finished steel materials are currently being produced in the steel industry, and today almost 80% of the fine sheet metal products in Germany are supplied in surface-finished form. In order to produce finished products, these fine sheet metal products are processed further so that many different metallic materials or many different combinations of metallic base materials and surface materials may be present in one component and must be present in order to meet certain product requirements. During the further processing, especially of surface-finished steel strips, the material is cut to size, shaped and joined by welding or adhesive bonding methods. These processing operations are highly typical of vehicle body construction in the automobile industry, where mainly galvanized steel strip from the coil coating industry is processed further and joined for example to ungalvanized steel strip and/or aluminum strip. Vehicle bodies thus consist of a multitude of sheet metal parts which are connected to one another by spot welding.

[4] From this variety of combinations of metallic strip materials in one component and the primary use of surface-finished steel strips, special requirements are derived for corrosion protection, which must be capable of reducing both the consequences of bimetal corrosion as well as corrosion at cut edges. Although metallic zinc coatings applied to steel strip electrolytically or in a melt-dip process impart a cathodic protective effect, which prevents active dissolution of the more noble core material at cut edges and mechanically induced damage to the zinc coating, it is equally important to reduce the corrosion rate per se to ensure the material properties of the core material. The requirements placed on the anticorrosion coating, usually consisting of an inorganic conversion layer and an organic barrier layer, are accordingly high.

[5] At cut edges and at any damage to the zinc overlay caused by processing or other influences, the galvanic coupling between the core material and the metallic coating gives rise to an active, unhindered local dissolution of the coating material, which in turn represents an activation site for corrosive delamination of the organic barrier layer. The phenomenon of paint debonding or of "blistering" is observed especially at the cut edges, where unhindered corrosion of the less noble coating material takes place. The same applies in principle to the sites on a component at which different metallic materials are joined to one another directly by joining techniques. The local activation of such a "defect" (cut edge, damage to the metallic coating, spot welds) and thus the corrosive debonding of paint starting from these "defects" are all the more pronounced, the greater the electric potential difference between the metals in direct contact. Good results with regard to paint adhesion at cut edges are therefore offered by steel strip having zinc coatings alloyed with more noble metals, for example iron-alloyed zinc coatings (galvannealed steel).

[6] Since steel strip producers are increasingly making the transition to integrating further corrosion coatings, in particular paint coatings, into the strip processing system, in addition to surface finishing with metallic coatings, there is an increased demand both there and in the processing industry, particularly in automobile manufacture, for anticorrosion treatments which effectively prevent the paint adhesion problems associated with cut edge corrosion and contact corrosion.

[7] Various pretreatments which address the problem of edge protection are described in the prior art. The main strategy is that of improving the paint adhesion of the organic barrier layer to the surface-finished steel strip.

[8] The closest prior art is considered to be the German laid-open specification DE19733972, which contains a method for the alkaline passivating pretreatment of galvanized and alloy-galvanized steel surfaces in strip processing systems. Therein, the surface-finished steel strip is brought into contact with an alkaline treatment agent containing magnesium ions, iron(III) ions and a complexing agent. At the predefined pH of above 9.5, the zinc surface is passivated so as to form the anticorrosion layer. According to the teaching of DE19733972, a surface passivated in this way already offers paint adhesion comparable to that of methods using nickel and cobalt. This pretreatment to improve the corrosion protection may optionally be followed by further treatment steps, such as a chromium-free post-passivation, before the paint system is applied. However, it has been found that this pretreatment system is unable to suppress in a satisfactory manner the debonding of paint caused by corrosion at the cut edges.

[9] The object of the present invention is therefore to provide a method for pretreatment of galvanized and alloy-galvanized steel surfaces which considerably improves, in comparison to the

prior art, the debonding of paint proceeding from defects in the zinc overlay on the steel strip, particularly at the cut edges.

[10] This problem has been solved by a method for metallizing pretreatment of galvanized or alloy-galvanized steel surfaces, whereby the galvanized or alloy-galvanized steel surface is brought into contact with an aqueous agent (1) whose pH is not less than 2 and not greater than 6, characterized in that agent (1) contains

- (a) cations and/or compounds of a metal (A), which are selected from cations and/or compounds of iron in a concentration of at least 0.001 M,
- (b) accelerators selected from oxoacids of phosphorus and the salts thereof, whereby at least one phosphorus atom is present in a medium oxidation state,

whereby iron(II) ions and/or iron(II) compounds are used as cations and/or compounds of metal (A), and the molar ratio of accelerators to the concentration of the cations and/or compounds of metal (A) does not fall below the value of 1:5 and the redox potential E_{Redox} of the cations and/or compounds of metal (A), measured on a metal electrode of metal (A) at a predetermined process temperature and concentration of cations and/or compounds of metal (A) in the aqueous agent (1), is more anodic than the electrode potential E_{Zn} of the galvanized or alloy-galvanized steel surface in contact with an aqueous agent (2), differing from agent (1) only in that it does not contain any cations and/or compounds of metal (A).

[11] The method according to the invention is suitable for all metal surfaces, for example steel strip, and/or joined metal components which consist at least partially also of zinc surfaces, for example automobile bodies. Preference is given to the material combination of iron-containing surfaces and zinc surfaces.

[12] In the context of this invention, pretreatment refers to passivation by means of inorganic barrier layers (for example phosphating, chromating) or to a process step preceding the paint coating for the purpose of conditioning the cleaned metal surface. Such a conditioning of the surface gives rise to an improvement in corrosion prevention and paint adhesion for the entire layer system resulting at the end of a process chain for corrosion-preventing surface treatment. Fig. 1 summarizes typical process chains in the context of the present invention which draw particular benefit from the pretreatment according to the invention.

[13] The specifying designation of the pretreatment as "metallizing" is to be understood to mean a pretreatment process which directly brings about a metallic deposition of metal cations (A) on the zinc surface, whereby, after the metallizing pretreatment has taken place, at least 50 at% of the element (A) is present on the zinc surface in the metallic state according to the analysis method defined in the example portion of this application.

[14] According to the invention, the redox potential E_{Redox} is measured directly in the agent (1) on a metal electrode of the metal (A) with respect to a commercial standard reference electrode, for example a silver/silver chloride electrode. For example, in an electrochemical measuring chain of the following type:

E_{Redox} in Volt: $\text{Ag} / \text{AgCl} / 1\text{M KCl} // \text{metal(A)} / \text{M(1)}$

where $\text{Ag} / \text{AgCl} / 1\text{M KCl} = 0.2368\text{ V}$ with respect to a standard hydrogen electrode (SHE)

where M(1) denotes the agent (1) according to the invention containing cations and/or compounds of the metal (A).

[15] The same applies to the electrode potential E_{Zn} which is determined on a zinc electrode in the agent (2), the latter differing from the agent (1) only by the absence of the cations and/or compounds of the metal (A), with respect to a commercial standard reference electrode:

E_{Zn} in Volt: $\text{Ag} / \text{AgCl} / 1\text{M KCl} // \text{Zn} / \text{M(2)}$

[16] The method according to the invention is now characterized in that a metallizing pretreatment of the zinc surface is performed when the redox potential E_{Redox} is more anodic than the electrode potential E_{Zn} . This is the case when $E_{\text{Redox}} - E_{\text{Zn}} > 0$.

[17] The potential difference of redox potential E_{Redox} and electrode potential E_{Zn} according to the above definitions is to be regarded as the electromotive force (EMF), that is to say as the thermodynamic driving force for the currentless metallizing pretreatment. The electromotive force (EMF) corresponds here to an electrochemical measuring chain of the following type:

$\text{Zn} / \text{M(2)} // \text{metal(A)} / \text{M(1)}$

where M(1) denotes the agent (1) containing cations and/or compounds of the metal (A) and

where M(2) denotes the agent (2) which differs from M(1) only in that it does not contain any cations and/or compounds of the metal (A).

[18] For the method according to the invention, it is advantageous if the redox potential E_{Redox} of the cations and/or compounds of the metal (A) in the aqueous agent (1) is more anodic than the electric potential E_{Zn} of the zinc surface in contact with the aqueous agent (2) by at least +50 mV, preferably at least +100 mV and particularly preferably at least +300 mV, but at most +800 mV. If the EMF is less than +50 mV, sufficient metallization of the galvanized surface may not be achieved within technically relevant contact times, so that in a subsequent passivating conversion treatment the metal overlay of the metal (A) is completely removed from the galvanized surface and the effect of the pretreatment is thus canceled. Conversely, an excessively high EMF of more than +800 mV may lead within short periods of time to complete and massive coverage of the

galvanized surface with the metal (A), so that in a subsequent conversion treatment the desired formation of an inorganic corrosion-preventing and adhesion-promoting layer is prevented or at least hindered.

[19] It has been found that the metallization is particularly effective when the concentration of cations and/or compounds of the metal (A) is at least 0.01 M but does not exceed 0.2 M, preferably 0.1 M.

[20] Further cations and/or compounds of a metal which according to the pretreatment are deposited in the metallic state onto the galvanized surface may be contained and are selected from cations and/or compounds of molybdenum, tungsten, cobalt, nickel, lead, and/or tin. As iron(II) ions and/or iron(II) compounds, use may be made for example of iron(II) sulfate. Compared to the sulfate, the organic salts iron(II) lactate and/or iron(II) gluconate are particularly preferred due to the lower corrosiveness of the anions as a source for iron(II) cations.

[21] If additionally metals according to the aforementioned selection are present in the agent (1), then the redox potential E_{redox} of the metal (A) must be determined individually and in the absence of the respective other metals in the aqueous agent.

[22] However, particular preference is given to those agents (1) which contain only cations and/or compounds of the metal (A) and thus no cations and/or compounds of the aforementioned selection of metals.

[23] According to the invention, those cations and/or compounds of the metal (A) are present which in the agent (1) both satisfy the condition for the electromotive force (EMF) as described above and also have a standard potential E_{Me}^0 of the metal (A) which is more cathodic than the normal potential $E_{\text{H}_2}^0$ of the standard hydrogen electrode (SHE), whereby the standard potential E_{Me}^0 of the metal (A) is based on the reversible redox reaction $\text{Me}^0 \rightarrow \text{Me}^{n+} + n e^-$ in an aqueous solution of the metal cation Me^{n+} with the activity 1 at 25°C.

[24] If this second condition is not satisfied, then passivation layers which are less homogeneous and have more defects are formed in a conversion treatment following the method according to the invention due to reduced pickling rates of the substrate surface. In the extreme case, the passivating conversion of the substrate surface pretreated in the method according to the invention is not carried out in the subsequent method step. The same applies to an organic coating which directly follows the pretreatment according to the invention and which is based on a self-deposition process initiated by the pickling attack of the substrate (autophoretic dip coating, abbreviated: AC for "Autodepositable Coating").

[25] In the pretreatment method according to the invention, accelerators having a reducing effect are added to the aqueous agent (1) in order to increase the rate of deposition of the cations and/or compounds of the metal (A), that is to say the metallization of the galvanized or alloy-galvanized surface. As possible accelerators, mention may be made of oxoacids of phosphorus and the salts thereof, whereby at least one phosphorus atom must be present in a medium oxidation state. Such accelerators are for example hypophosphoric acid, hypodiphosphonic acid, diphosphoric(III, V) acid, phosphonic acid, diposphonic acid and particularly preferably phosphinic acid, and the salts thereof.

[26] Use may also be made of accelerators which are known to the person skilled in the art from the prior art in phosphating. Besides their reducing properties, these also have depolarizing properties, that is to say they act as hydrogen scavengers and thus additionally promote the metallization of the galvanized steel surface. These include hydrazine, hydroxylamine, nitroguanidine, N-methylmorpholine N-oxide, glucoheptonate, ascorbic acid and reducing sugars.

[27] The molar ratio of accelerators to the concentration of the cations and/or compounds of the metal (A) in the aqueous agent (1) is preferably no greater than 2:1, particularly preferably no greater than 1:1.

[28] The aqueous agent (1) in the method according to the invention may optionally additionally contain small amounts of copper(II) cations, which can likewise be deposited as metals on the galvanized surface simultaneously with the cations and/or compounds of the metal (A). However, it should be noted here that no massive, almost complete surface-covering cementation of copper occurs since otherwise a subsequent conversion treatment is completely suppressed and/or the paint adhesion is considerably impaired. The aqueous agent (1) should therefore additionally contain no more than 50 ppm, preferably no more than 10 ppm, but at least 0.1 ppm copper(II) cations.

[29] In addition, the aqueous agent (1) for the metallizing pretreatment may additionally contain surfactants which are able to remove impurities from the metallic surface without themselves inhibiting the surface due to the formation of compact adsorbate layers for the metallization. For this purpose, use may preferably be made of non-ionic surfactants having average HLB values of at least 8 and at most 14.

[30] Since cations and/or compounds of iron(II) can be used for the pretreatment method according to the invention, the pH of the aqueous agent is no less than 2 and no greater than 6, preferably no greater than 4, in order on the one hand to prevent overpickling of the galvanized steel surface at low pH values, since this inhibits the metallization of the surface, and on the other hand to ensure the stability of the iron(II) ions in the treatment solution.

[31] For stabilization purposes, the treatment solution containing iron(II) may also contain chelating complexing agents having oxygen and/or nitrogen ligands. Such a treatment solution is additionally suitable for increasing the EMF for the metallization since iron(II) ions are less strongly complexed by such ligands than zinc(II) ions. Increasing the EMF by adding complexing agents is important for establishing a shorter duration of treatment and an optimal iron coverage of the galvanized surface.

[32] As chelating complexing agents, mention may be made especially of those selected from triethanolamine, diethanolamine, monoethanolamine, monoisopropanolamine, aminoethylethanolamine, 1-amino-2,3,4,5,6-pentahydroxyhexane, N-(hydroxyethyl)ethylene-diaminetriacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminopentaacetic acid, 1,2-diaminopropanetetraacetic acid, 1,3-diaminopropanetetraacetic acid, tartaric acid, lactic acid, mucic acid, gallic acid, gluconic acid, and/or glucoheptonic acid, and salts and stereoisomers thereof, as well as sorbitol, glucose, and glucamine, and stereoisomers thereof.

[33] One particularly effective formulation of the aqueous agent (1) containing the aforementioned complexing agents is obtained with a molar ratio of chelating complexing agents to the concentration of cations and/or compounds of divalent iron of no greater than 5:1, preferably no greater than 2:1, but of at least 1:5. Molar ratios lower than 1:5 result in only insignificant changes in the EMF for the metallization. The same applies to molar ratios higher than 5:1, at which a high proportion of free complexing agent is present, so that the EMF for the metallization remains almost unaffected and the result is an uneconomical procedure.

[34] Use is also made of water-soluble and/or water-dispersible polymeric complexing agents having oxygen and/or nitrogen ligands based on Mannich addition products of polyvinyl phenols with formaldehyde and aliphatic amino alcohols. Such polymers are described in detail in the patent US 5,298,289 and are hereby included as complexing polymer compounds according to the invention. Particularly suitable are water-soluble and/or water-dispersible polymeric complexing agents which are composed of x-(N-R¹-N-R²-aminomethyl)-4-hydroxystyrene monomer units, where the substitution site x on the aromatic ring is x = 2, 3, 5 or 6, R¹ is an alkyl group having no more than 4 carbon atoms, and R² is a substituent of general sum formula H(CHOH)_mCH₂- having a number m of hydroxymethylene groups of no more than 5 and no less than 3. Poly(5-vinyl-2-hydroxy-N-benzyl-N-glucamine) is used with particular preference due to its excellent complexing effect.

[35] In a manner analogous to the complexing of iron(II) ions with low-molecular complexing agents, for the polymeric compounds a molar ratio of chelating complexing agents, defined as the concentration of monomer units of the water-soluble and/or water-dispersible polymeric compound

to the concentration of cations and/or compounds of the metal (A), of no greater than 5:1, preferably no greater than 2:1, but of at least 1:5 is particularly effective.

[36] For the pretreatment method according to the invention which is part of the process chain of surface treatment of galvanized and/or alloy-galvanized steel surfaces, the application methods customary in strip steel production and strip steel finishing are practical. These include in particular dipping and spraying methods. However, the contact time or pretreatment time with the aqueous agent (1) should be at least 1 second but no longer than 30 seconds, preferably no longer than 10 seconds. Within this contact time, when the method is carried out according to the invention, this results in metallic coatings of the metal (A) with a layer overlay of preferably at least 1 mg/m^2 but preferably no more than 100 mg/m^2 and particularly preferably no more than 50 mg/m^2 . In the context of the present invention, the metallic layer overlay is defined as the amount of the element (A) by weight relative to area on the galvanized or alloy-galvanized steel surface immediately after the pretreatment according to the invention.

[37] Both the preferred contact times and layer overlays and also the preferred application methods likewise apply to the pretreatment according to the invention of components assembled from multiple metallic materials, in so far as they have at least partially zinc surfaces.

[38] The subject matter of the present invention also includes those combinations of alloy-galvanized steel surfaces and aqueous agents (1) in which an alloy component of the galvanized steel surface is the same element (A) as the metal (A) in the form of its cations and/or compounds in the aqueous agent (1). For example, flame-galvanized Galvannealed® fine metal sheet may also be pretreated according to the invention with an agent (1) containing iron ions, with the consequence that slightly improved corrosion properties and delamination properties are obtained in a subsequent application of anticorrosion layers.

[39] The pretreatment method according to the invention is tailored to the downstream process steps of surface treatment of galvanized and/or alloy-galvanized steel surfaces with regard to optimized corrosion protection and excellent paint adhesion, particularly at cut edges, surface defects and bimetal contacts. Consequently, the present invention encompasses various aftertreatment processes, that is to say conversion coatings and paint coatings, which in conjunction with the pretreatment described above deliver the desired results in terms of corrosion protection. Fig. 1 illustrates various process chains, to which preference is given in the context of the present invention, for the anticorrosion coating of metallic surfaces in automobile production, which processes are started as early as at the steel production plant ("coil industry") and are continued in the paint shop of the automobile manufacturer.

[40] In a further aspect, therefore, the invention relates to the production of a passivating conversion coating on the metallized pretreated galvanized and/or alloy-galvanized steel surface with or without an intermediate rinsing and/or drying step (Fig. 1, method IIa).

[41] To this end, use may be made of a conversion solution which contains chromium or which is preferably free of chromium. Preferred conversion solutions with which the metal surfaces pretreated according to the present invention can be treated prior to the application of a permanent organic anticorrosion coating can be found in DE 199 23 084 and in the literature cited therein. According to this teaching, apart from hexafluoro anions of Ti, Si and/or Zr, a chromium-free aqueous conversion agent may contain the following as further active ingredients: phosphoric acid, one or more compounds of Co, Ni, V, Fe, Mn, Mo or W, a water-soluble or water-dispersible film-forming organic polymer or copolymer, and organophosphonic acids which have complexing properties. A detailed list of organic film-forming polymers which may be contained in the aforementioned conversion solutions is given on page 4, lines 17 to 39 of said document.

[42] Thereafter, said document discloses a very extensive list of complexing organophosphonic acids as further possible components of the conversion solutions. Specific examples of these components can be found in said document DE 199 23 084.

[43] Water-soluble and/or water-dispersible polymeric complexing agents having oxygen and/or nitrogen ligands based on Mannich addition products of polyvinyl phenols with formaldehyde and aliphatic amino alcohols may also be present. Such polymers are disclosed in the patent US 5,298,289.

[44] The process parameters for a conversion treatment in the context of this invention, such as for example treatment temperature, treatment duration and contact time, are to be selected in such a way that a conversion layer is produced which has, per m^2 of surface, at least 0.05, preferably at least 0.2, but no more than 3.5, preferably no more than 2.0 and particularly preferably no more than 1.0 mmol of the metal M, which is the essential component of the conversion solution. Examples of metals M are Cr(III), B, Si, Ti, Zr, Hf. The density of coverage of the zinc surface with the metal M may be determined for example by an X-ray fluorescence method.

[45] In one particular aspect of a method (IIa) according to the invention, which comprises a conversion treatment following the metallizing pretreatment, the chromium-free conversion agent additionally contains copper ions. The molar ratio of metal atoms M selected from zirconium and/or titanium to copper atoms in such a conversion agent is preferably selected in such a way that it produces a conversion layer containing at least 0.1, preferably at least 0.3, but no more than 2 mmol of copper.

[46] The present invention thus also relates to a method (IIa) which comprises the following process steps including the metallizing pretreatment and a conversion treatment of the galvanized and/or alloy-galvanized steel surface:

- i) optional cleaning/degreasing of the surface of the material
- ii) metallizing pretreatment with an aqueous agent (1) according to the present invention
- iii) optional rinsing and/or drying step
- iv) chromium(VI)-free conversion treatment, in which a conversion layer is produced which contains, per m^2 of surface, 0.05 to 3.5 mmol of the metal M which is the essential component of the conversion solution, the metals M being selected from Cr(III), B, Si, Ti, Zr, Hf.

[47] As an alternative to a method (IIa), in which the metallizing pretreatment is followed by a conversion treatment to form a thin amorphous inorganic coating, it is also possible to use a method (Fig. 1, IIb) in which the metallization according to the invention is followed by a zinc phosphating to form a crystalline phosphate layer with a preferred layer weight of no less than 3 g/m^2 . According to the present invention, however, preference is given to a method (IIa) on account of the much lower process complexity and the considerable improvement in corrosion protection of conversion layers on galvanized surfaces which have been previously treated by metallization.

[48] Furthermore, the metallizing pretreatment and the subsequent conversion treatment are usually followed by further method steps for applying additional layers, in particular organic paints or paint systems (Fig. 1, methods III-V).

[49] In a further aspect, therefore, the present invention relates to a method (III) which extends the process chain (i-iv) of the method (II), whereby an organic coating agent (1) is applied which contains organic resin components dissolved or dispersed in an organic solvent or solvent mixture, characterized in that the coating agent (1) contains at least the following organic resin components:

- a) epoxy resin, in the form of a hydroxyl group-containing polyether, based on a bisphenol-epichlorohydrin polycondensation product,
- b) blocked aliphatic polyisocyanate,
- c) unblocked aliphatic polyisocyanate,
- d) at least one reaction component selected from hydroxyl group-containing polyesters and hydroxyl group-containing poly(meth)acrylates.

[50] Component a) is a fully reacted polycondensation product of epichlorohydrin and a bisphenol. It essentially has no more epoxy groups as reactive groups. The polymer is then in the form of a hydroxyl group-containing polyether which, via these hydroxyl groups, can enter into crosslinking reactions with polyisocyanates for example.

[51] The bisphenol component of this polymer may for example be selected from bisphenol A and bisphenol F. The average molecular weight (according to the manufacturer's data, able to be determined for example by gel permeation chromatography) is preferably in the range from 20,000 to 60,000, in particular in the range from 30,000 to 50,000. The OH number is preferably in the range from 170 to 210 and in particular in the range from 180 to 200. Particular preference is given to polymers having a hydroxyl content, based on the ester resin, in the range from 5 to 7% by weight.

[52] The aliphatic polyisocyanates b) and c) are based preferably on HDI, in particular on HDI trimer. As the blocking agent in the blocked aliphatic polyisocyanate b), use may be made of the usual polyisocyanate blocking agents. The following may be mentioned by way of example: butanone oxime, dimethylpyrazole, malonic ester, diisopropylamine/malonic ester, diisopropylamine/triazole and ϵ -caprolactam. Preferably, a combination of malonic ester and diisopropylamine is used as the blocking agent.

[53] The content of blocked NCO groups in component b) is preferably in the range from 8 to 10% by weight, in particular in the range from 8.5 to 9.5% by weight. The equivalent weight is preferably in the range from 350 to 600, in particular in the range from 450 to 500 g/mol.

[54] The unblocked aliphatic polyisocyanate c) preferably has an equivalent weight in the range from 200 to 250 g/mol and an NCO content in the range from 15 to 23% by weight. By way of example, an aliphatic polyisocyanate may be selected which has an equivalent weight in the range from 200 to 230 g/mol, in particular in the range from 210 to 220 g/mol, and an NCO content in the range from 18 to 22% by weight, preferably in the range from 19 to 21% by weight. Another suitable aliphatic polyisocyanate has for example an equivalent weight in the range from 220 to 250 g/mol, in particular in the range from 230 to 240 g/mol, and an NCO content in the range from 15 to 20% by weight, preferably in the range from 16.5 to 19% by weight. Each of these aforementioned aliphatic polyisocyanates may constitute component c). However, a mixture of these two polyisocyanates may also be present as component c). If a mixture of the two aforementioned polyisocyanates is used, then the quantity ratio of the first-mentioned polyisocyanate to the last-mentioned polyisocyanate for component c) is preferably in the range from 1:1 to 1:3.

[55] Component d) is selected from hydroxyl group-containing polyesters and hydroxyl group-containing poly(meth)acrylates. By way of example, use may be made of a hydroxyl group-containing poly(meth)acrylate having an acid number in the range from 3 to 12, in particular in the range from 4 to 9 mg KOH/g. The hydroxyl group content is preferably in the range from 1 to 5 and

in particular in the range from 2 to 4% by weight. The equivalent weight is preferably in the range from 500 to 700, in particular in the range from 550 to 600 g/mol.

[56] If a hydroxyl group-containing polyester is used as component d), then a branched polyester having an equivalent weight in the range from 200 to 300, in particular in the range from 240 to 280 g/mol may be selected for this. Also suitable, for example, is a weakly branched polyester having an equivalent weight in the range from 300 to 500, in particular in the range from 350 to 450 g/mol. These different types of polyester may each per se or as a mixture form component d). Of course, component d) could also be a mixture of hydroxyl group-containing polyesters and hydroxyl group-containing poly(meth)acrylates.

[57] The coating agent (1) in the method (III) according to the invention thus contains both a blocked aliphatic polyisocyanate b) and also an unblocked aliphatic polyisocyanate c). The hydroxyl group-containing components a) and d) are available as potential reaction components for these two types of polyisocyanate. By possible reaction of each of components a) and d) with each of components b) and c), a complex polymer network of polyurethanes is formed during the curing of the agent (2). In addition, if hydroxyl group-containing poly(meth)acrylates are used as component d), further crosslinkages may occur via the double bonds of these components. If not all the double bonds of the poly(meth)acrylates crosslink during the curing, then double bonds present at the surface in particular may bring about improved adhesion to a subsequently applied paint if the latter also contains components having polymerizable double bonds. From this point of view, it is preferred that component d) consists at least partially of hydroxyl group-containing poly(meth)acrylates.

[58] During the curing of the coating agent (1) in the method (III) according to the invention, it is to be expected that first the unblocked aliphatic polyisocyanate c) reacts with one or both of components a) and d). If the hydroxyl groups of component d) are more reactive than those of component a), then a reaction of component c) with component d) preferably takes place first during the curing.

[59] In contrast, the blocked aliphatic polyisocyanate b) reacts with one or both of components a) and d) only once the deblocking temperature is reached. Then only those of the reaction partners a) and d) which have fewer reactive OH groups are available for polyurethane formation. For the polyurethane network being formed, this means for example that, when the OH groups of component a) are less reactive than those of component d), two polyurethane networks are created from the reaction of components c) and d) on the one hand and of components a) and b) on the other hand.

[60] The coating agent (1) in the method (III) according to the invention contains components a) and b) on the one hand and c) and d) on the other hand preferably in the following relative weight ratios:

a):b) = 1:0.8 to 1:1.3

c):d) = 1:1.4 to 1:2.3

[61] Components a) and d) on the one hand and b) and c) on the other hand are preferably present in the following relative weight ratio.

a):d) = 1:2 to 1:6 and (preferably 1:3 to 1:5)

b):c) = 1:0.5 to 1:5 (preferably 1:1 to 1:3).

[62] Preferred absolute quantity ranges of the aforementioned four components a) to d) are specified further below since these depend on the density of conductive pigments which are optionally present (Fig. 1, method IIIb). The coating agent (1) preferably contains, in addition to components a) to d), a conductive pigment or a mixture of conductive pigments. These may have a relatively low density, such as carbon black and graphite for example, or a relatively high density, such as metallic iron for example. The absolute content of conductive pigments in the coating agent (1) depends on the density of said pigments since the effect as conductive pigment depends less on the proportion by weight than on the proportion by volume of the conductive pigment in the cured coating.

[63] In general, the coating agent (1) contains, based on the total weight of the agent, (0.8 to 8)·p% by weight of conductive pigment, where p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm³. The coating agent (1) preferably contains, based on its total weight, (2 to 6) p% by weight of conductive pigment.

[64] By way of example, this means: if the coating agent (1) contains as the conductive pigment only graphite having a density of 2.2 g/cm³, then it preferably contains at least 1.76, in particular at least 4.4% by weight and preferably no more than 17.6, in particular no more than 13.2% by weight of graphite. If iron powder having a density of 7.9 g/cm³ is used as the sole conductive pigment, then the coating agent (1) contains, based on its total weight, preferably at least 6.32, in particular at least 15.8% by weight and no more than 63.2, in particular no more than 47.4% by weight. The proportions by weight are calculated in a corresponding manner when the conductive pigment used is for example solely MoS₂ having a density of 4.8 g/cm³, aluminum having a density of 2.7 g/cm³ or zinc having a density of 7.1 g/cm³.

[65] However, a favorable combination of properties may be obtained if the coating agent (1) contains not just one single conductive pigment but rather a mixture of at least two conductive pigments, which then preferably differ greatly in terms of their density. By way of example, use may

be made of a mixture in which the first mixture partner is a light conductive pigment, such as for example carbon black, graphite or aluminum, and the second partner of the mixture is a heavy conductive pigment, such as for example zinc or iron. In these cases, the average density of the mixture, which can be calculated from the proportions by weight of the components in the mixture and from their respective density, is used for the density p in the formula mentioned above.

[66] Accordingly, one special embodiment of a coating agent (1) in the method (IIIb) is characterized in that it contains both a conductive pigment having a density of less than 3 g/cm^3 and also a conductive pigment having a density of greater than 4 g/cm^3 , wherein the total amount of conductive pigment, based on the total weight of the agent (2), is (0.8 to 8) p% by weight, where p is the average density of the mixture of the conductive pigments in g/cm^3 .

[67] By way of example, the coating agent (1) may contain as the conductive pigment a mixture of carbon black or graphite on the one hand and iron powder on the other hand. In this case, the weight ratios of carbon black and/or graphite on the one hand and iron on the other hand may be in the range from 1:0.1 to 1:10, in particular in the range from 1:0.5 to 1:2.

[68] The coating agent (1) may also contain aluminum flakes, graphite and/or carbon black as the light electrically conductive pigment. Preference is given to the use of graphite and/or carbon black. Carbon black and particularly graphite not only give rise to an electric conductivity of the coating obtained but also contribute toward this layer having a desired low Mohs hardness of no more than 4 and being readily able to be shaped. In particular, the lubricant effect of graphite contributes toward reduced wear on the shaping tools. This effect can be further promoted by additionally using pigments which have a lubricating effect, such as molybdenum sulfide for example. As further lubricants or shaping aids, the coating agent (1) may contain waxes and/or Teflon.

[69] The electrically conductive pigment having a specific weight of at most 3 g/cm^3 may be in the form of small beads or aggregates of such beads. In this case, it is preferred that the beads or the aggregates of these beads have a diameter of less than $2 \mu\text{m}$. Preferably, however, these electrically conductive pigments are in the form of flakes having a thickness of preferably less than $2 \mu\text{m}$.

[70] The coating agent (1) in the method (III) according to the invention contains at least the resin components and solvents described above. The resin components a) to d) are usually in the form of solutions or dispersions in organic solvents in their commercial form. The coating agent (1) prepared therefrom then likewise contains these solvents.

[71] These are desirable in order to establish a viscosity that makes it possible to apply the coating agent (1) to the substrate by the coil coating method, despite the additional presence of the electrically conductive pigment such as graphite for example and optionally further pigments such as, in particular, anticorrosion pigments. If necessary, solvent may additionally be added. The chemical nature of the solvents is usually determined by the choice of raw materials contained in the solvent in question. By way of example, the following may be present as solvent(s): cyclohexanone, diacetone alcohol, diethylene glycol monobutyl ether acetate, diethylene glycol, propylene glycol methyl ether, propylene glycol n-butyl ether, methoxypropyl acetate, n-butyl acetate, xylene, glutaric acid dimethyl ester, adipic acid dimethyl ester and/or succinic acid dimethyl ester.

[72] The preferred proportion of solvent(s) on the one hand and of organic resin components on the other hand in the coating agent (1) depends, when expressed in % by weight, on the proportion of conductive pigment in % by weight in the coating agent (1). The higher the density of the conductive pigment, the higher the preferred proportion by weight thereof in the total coating agent (1) and the lower the proportions by weight of solvent(s) and resin components. The preferred proportions by weight of solvent(s) and resin components therefore depend on the density p of the conductive pigment used and/or on the average density p of a mixture of conductive pigments.

[73] In general, the coating agent (1) in the method (III) according to the invention preferably contains, based on the total weight of the coating agent (1), [(25 to 60) fitting factor]% by weight, preferably [(35 to 55) fitting factor]% by weight organic solvent and [(20 to 45) fitting factor]% by weight, preferably [(25 to 40) fitting factor]% by weight organic resin components, where the sum of the percentages by weight of organic resin component and solvent is no greater than [93 fitting factor]% by weight, preferably no greater than [87 fitting factor]% by weight, and the fitting factor is $[100 - 2.8p] : 93.85$ and p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm^3 .

[74] With regard to the individual resin component a), preferably the coating agent (1) contains, based on the total weight of the coating agent (1), [(2 to 8) fitting factor]% by weight, preferably [(3 to 5) fitting factor]% by weight of the resin component a), where the fitting factor is $[100 - 2.8p] : 93.85$ and p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm^3 . The preferred quantities of the resin components b) to d) in the coating agent (1) can be calculated from the quantity of resin component a) using the preferred quantity ratios of the individual resin components specified above. By way of example, the proportion of component b) in the total weight of the coating agent may be [(2 to 9) · fitting factor]% by weight, preferably [(3 to 6) fitting factor]% by weight, the proportion of resin components c) may be [(4 to 18) fitting factor]% by weight, preferably [(6 to 12) fitting factor]% by weight, and the proportion of resin

components d) may be [(7 to 30) fitting factor]% by weight, preferably [(10 to 20) fitting factor]% by weight. The "fitting factor" has the meaning given above.

[75] It is also preferred that the layer b) additionally contains corrosion inhibitors and/or anticorrosion pigments. Use may be made here of corrosion inhibitors or anticorrosion pigments which are known for this purpose in the prior art. The following may be mentioned by way of example: magnesium oxide pigments, in particular in nanoscale form, finely divided and very finely divided barium sulfate or anticorrosion pigments based on calcium silicate. The preferred proportion by weight of the anticorrosion pigments in the total weight of the coating agent (1) once again depends on the density of the anticorrosion pigments used. The coating agent (1) in the method (III) according to the invention preferably contains, based on the total weight of the coating agent, [(5 to 25) fitting factor]% by weight, in particular [(10 to 20) fitting factor]% by weight anticorrosion pigment, where the fitting factor is $[100-2.8p]:93.85$ and p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm^3 .

[76] The mechanical and chemical properties of the coating obtained after baking the coating agent (1) in the method (III) according to the invention may be further improved if said coating additionally contains fillers. By way of example, these may be selected from silicic acids or silicon oxides (optionally hydrophobicized), aluminum oxides (including basic aluminum oxide), titanium dioxide and barium sulfate. With regard to the preferred amounts thereof, the coating agent (1) contains [(0.1 to 3) fitting factor]% by weight, preferably [(0.4 to 2) fitting factor]% by weight filler, selected from silicic acids and/or silicon oxides, aluminum oxides, titanium dioxide and barium sulfate, where the fitting factor is $[100-2.8p]:93.85$ and p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm^3 .

[77] If lubricants or shaping aids are additionally also used, then the coating agent (1) contains, based on its total weight, lubricants or shaping aids, preferably selected from waxes, molybdenum sulfide and Teflon, preferably in an amount of [(0.5 to 20) fitting factor], in particular in an amount of [(1 to 10) fitting factor]% by weight, where the fitting factor is $[100-2.8p]:93.85$ and p is the density of the conductive pigment or the average density of the mixture of conductive pigments in g/cm^3 .

[78] The method (III) according to the invention, which also comprises the application of organic paints, thus consists of the following process chain:

- i) optional cleaning/degreasing of the surface of the material
- ii) metallizing pretreatment with an aqueous agent (1) according to the present invention
- iii) optional rinsing and/or drying step
- iv) chromium(VI)-free conversion treatment, in which a conversion layer is produced which contains, per m^2 of surface, 0.01 to 0.7 mmol of the metal M which is the essential

component of the conversion solution, the metals M being selected from Cr(III), B, Si, Ti, Zr, Hf

- v) optional rinsing and/or drying step
- vi) coating with a coating agent (1) according to the above description and curing at a substrate temperature in the range from 120 to 260°C, preferably in the range from 150 to 170°C.

[79] All steps (i-vi) are preferably carried out as strip treatment methods, whereby in step (vi) the liquid coating agent (1) is applied in such an amount that, after curing, the desired layer thickness in the range from 0.5 to 10 µm is obtained. Preferably, therefore, the coating agent (1) is applied in the so-called coil coating method, in which moving metal strips are coated continuously. The coating agent (1) may be applied by different methods, which are common in the prior art. By way of example, applicator rollers may be used, with which the desired wet film thickness can be set directly. Alternatively, the metal strip may be dipped into the coating agent (1) or sprayed with the coating agent (1), after which the desired wet film thickness is established with the aid of squeeze rollers.

[80] When coating metal strips which have been electrolytically coated or melt-dip-coated immediately beforehand with a metal overlay, for example with zinc or zinc alloys, then it is not necessary to clean the metal surfaces prior to carrying out the metallizing pretreatment (ii). However, if the metal strips have already been stored and in particular treated with anticorrosion oils, then a cleaning step (i) is necessary before carrying out step (ii).

[81] After applying the liquid coating agent (1) in step (vi), the coated sheet is heated to the required drying and/or crosslinking temperature for the organic coating. The heating of the coated substrate to the required substrate temperature ("peak metal temperature" = TMP) in the range from 120 to 260°C, preferably in the range from 150 to 170°C, may take place in a heated continuous furnace. However, the treatment agent may also be brought to the appropriate drying and/or crosslinking temperature by infrared radiation, in particular by near-infrared radiation.

[82] In automobile manufacturing, metal sheets precoated in this way are suitably cut to size and shaped in order to produce vehicle bodies. The assembled component or the assembled rough body consequently has unprotected cut edges which must additionally be treated to protect against corrosion. In the so-called "paint shop", therefore, a further anticorrosion treatment takes place and ultimately the paint structure typical of an automobile is implemented.

[83] In a further aspect, therefore, the present invention relates to a method (IV) which extends the process chain (i-vi) of the method (III), whereby first a crystalline phosphate layer is deposited on the exposed metal surfaces, in particular on the cut edges, in order then to implement a final

corrosion protection, in particular protection against delamination of the paint system at the cut edges, by means of dip coating. If the first coating in the method (III) with an organic coating agent (1) leads to a conductive coating, the entire metallic component including the phosphated cut edges and the surfaces first coated in the method (III) may be electro-dip-coated (Fig. 1, method IVb). If the conductivity of the first coating is insufficient, then only the phosphated cut edges are electro-dip-coated, without any further paint structure being implemented on the first-coated surfaces. The same applies when the cut edges are not phosphated but are coated with a self-depositing dip coating (AC) (Fig. 1, method IVc). However, the present invention is characterized in that the zinc surfaces pretreated by metallizing according to the invention are excellent at suppressing edge corrosion in particular. Therefore, in a process chain according to the invention which comprises the electro-dip-coating (KTL, ATL) in the method (IV) and the application of further paint layers in a method (V), the amount of dip coating deposited per m^2 of the component consisting of zinc surfaces pretreated according to the invention (Fig. 1, method I) and/or the amount of filler to be applied, which above all has the task of protecting the sheet metal of the body against stone impact and of compensating any irregularities in the metal surface, can be considerably reduced in the second coating (Fig. 1, method V), without this leading to a loss of performance in terms of corrosion prevention and paint adhesion.

[84] In a further aspect, the present invention relates to the galvanized and/or alloy-galvanized steel surface and to the metallic component, which consists at least partially of a zinc surface pretreated by metallizing according to the method according to the invention with the aqueous agent (1) or coated after this pretreatment with further passivating conversion layers and/or paints, for example in accordance with methods (II-IV) according to the invention.

[85] A steel surface or component treated in this way is used in vehicle body construction in automobile manufacturing, in shipbuilding, in the construction industry and for the production of white goods.

[86] Exemplary embodiments:

[87] An electrochemical measuring chain for determining the electromotive force (EMF) for the metallizing pretreatment according to the invention is shown in Fig. 2. The measuring chain consists of two galvanic half-cells, whereby one half-cell contains the agent (1) containing cations and/or compounds of a metal (A) while the other half-cell contains the agent (2) which differs from the agent (1) in that it does not contain any cations and/or compounds of a metal (A). Both half-cells are connected to a salt bridge, and the voltage difference between a metal electrode of the metal (A) in the agent (1) and a zinc electrode in the agent (2) is measured in a currentless manner. A positive EMF means that the redox potential E_{redox} of the cations and/or compounds of the metal (A) in the agent (1) is more anodic than the electrode potential E_{Zn} . Table 1 below shows the EMF, measured according to a measuring chain analogous to Fig. 2, for an agent (1) containing iron(II) cations, which is suitable for the metallizing pretreatment according to the invention.

Table 1

EMF of various agents (1) composed of iron sulfate, hypophosphoric acid and lactic acid, measured using a measuring chain according to Fig. 2

Cations of metal (A) in the agent (1)*	T in °C	EMF in V
0.01 mol/l Fe(II)#	20	0.445
0.1 mol/l Fe(II)#	20	0.462
0.2 mol/l Fe(II)#	20	0.468

* Composition of the agent (1):

0.15 mol/l H_3PO_2

0.033 mol/l lactic acid

Fe(II) as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

[88] In order to demonstrate, by way of example, the improvement in the protection of cut edges after the metallizing pretreatment ("ironizing") according to the invention of galvanized strip steel has taken place, the process chain of the method (III) according to the invention is carried out below on electrolytically galvanized steel sheets (DC04, ZE 75/75, automotive grade). The galvanized steel sheets treated and coated in this way were clamped at the cut edges in a beechwood block and stored for 10 weeks in a constantly moist environment in the VDA alternating climate test (621-415).

[89] Examples B1-B3 according to the invention:

[90] The method (III) according to the invention is broken down in detail below, including the formulations used:

- (i) the electrolytically galvanized steel sheet (ZE) is degreased with alkaline cleaning agents (for example Ridoline® C 72, Ridoline® 1340, dip and spray cleaning products of the applicant);
- (ii) the metallizing pretreatment ("ironizing") takes place at a temperature of the aqueous agent (1) of 50°C at a pH of 2.5 in the dip-coating method with a contact time of $t = 2$ sec (B1) or $t = 5$ sec (B2), the agent (1) being composed of:

B1: 27.8 g/l $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

B2: 13.9 g/l $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

9.9 g/l H_3PO_2

3.0 g/l lactic acid

- (iii) rinsing step by immersing the pretreated sheet in tap water;
- (iv) a commercial pretreatment solution based on phosphoric acid, manganese phosphate, H_2TiF_6 and aminomethyl-substituted polyvinyl phenol (Granodine® 1455T from the applicant) is applied to the metal surface using the Chemcoater (roller application method). Drying takes place at 80°C and the resulting layer overlay of titanium is between 10-15 mg/m^2 , determined by X-ray fluorescence analysis;
- (v) rinsing step by immersing the pretreated sheet in tap water;
- (vi) a commercial coating agent (1) containing graphite as the conductive pigment, based on the composition specified in the example portion of the German application (DE 102007001654.0) (see Example 1 therein) is applied to the pretreated sheets using a Chemcoater and cured by heating in a drying cabinet at a substrate temperature of 160°C. The application of the coating agent yields dry film layer thicknesses of 1.8 μm .

[91] The layer overlay of iron on the electrolytically galvanized steel surface can be dissolved in a wet chemical process in 10% by weight hydrochloric acid immediately after process step (ii) and then determined by means of atomic absorption spectroscopy (AAS) or, as an alternative, in comparative experiments on pure zinc substrates (99.9% Zn) by means of X-ray fluorescence analysis (XFA). In the metallizing pretreatment according to B1 in process step (ii), it amounts to approximately 20 mg/m^2 Fe.

[92] Comparative Example V1:

[93] Method (III) according to the invention is modified in that process step (ii), that is to say the metallizing pretreatment, is omitted.

[94] Comparative Example V2:

[95] Method (III) according to the invention is modified in that, instead of process step (ii), an alkaline passivating pretreatment with the commercial product from the applicant (Granodine® 1303) is carried out according to the formulation based on iron(III) nitrate indicated in German laid-open specification DE19733972 (see Table 1, Example 1 therein).

[96] Comparative Example V3:

[97] After degreasing with an alkaline cleaning agent system from the applicant (Ridoline® 1565 / Ridolol® 1237), the sheet is activated in a commercial activating solution (Fixodine® 9112) and passivated in a three-cation phosphating bath from the applicant (Granodine® 958A) before being coated with the paint system in a manner analogous to process step (vi).

[98] After the process chain according to method (III), all the sheets are cut to create the cut edge and again are subjected to a phosphating as specified in Comparative Example V3.

[99] A cathodic dip coat (EV 2005, PPG Industries) having a layer thickness of 18-20 µm is subsequently deposited on all the sheets thus treated and coated, and then baked in a circulating oven for 20 minutes at 175°C. Overall, therefore, a process chain beginning with the anticorrosion pretreatment of the zinc substrate at the steel manufacturer (Fig. 1, methods II and IIb) and ending with the deposition of the dip coat in the "paint shop" of the vehicle body manufacturing plant (Fig. 1, method IVb) is reconstructed experimentally.

[100] Table 2 shows the results with regard to the corrosive delamination of the paint at the cut edge after 10 weeks of the alternating climate test. Since the delamination of the paint advances to varying extents at different locations on the cut edge, Table 2 shows in each case the maximum delamination in mm for the coating system in question.

Table 2

Delamination at the cut edge after VDA alternating climate test (621-415)

Examples	Delamination at the cut edge / mm
V1	7.9
V2	6.5
V3	9.4
B1	1.5

[101] Based on the results in the VDA alternating climate test, the superior corrosion protection of the metallizing pretreatment ("ironizing") according to the invention at the cut edge in comparison to the conventional treatment methods is obvious. The alkaline passivation by means of iron(III)-containing solutions, as described in the prior art, offers improved protection of cut edges in comparison to phosphated sheets (V3) and sheets without any passivating pretreatment (V1), but said method is far less effective than the metallic pretreatment (B1) according to the invention.

[102] The excellent result in terms of minimizing edge corrosion and delamination of the paint system at the cut edge with the pretreatment (B1, B2) according to the invention in comparison to an alkaline-pretreated zinc surface (V2) for a coating system according to a process chain

IIa→IIIa→IVb (see Fig. 1) is illustrated in Fig. 3. It is also found that, even if the iron(II) concentration (B2) in the pretreatment according to the invention is reduced, continued suppression of paint delamination at the cut edge can be achieved if the contact time with the agent (1) is increased from 2 sec (B1) to 5 sec (B2) as in the examples according to the invention. With reference to Fig. 3, the negative effect of omitting the pretreatment (V1) according to the invention within the same process chain as for the examples (B1, B2) according to the invention is also clear. Even conventionally treated galvanized surfaces, which were phosphated without the pretreatment according to the invention and then electro-dip-coated (V3), exhibit clear bubble formation and corrosive delamination at the cut edge.

[103] An improvement in the results in the stone impact test by means of the metallizing pretreatment ("ironizing") is also evident. The photographs in Fig. 4 show that on the one hand the paint adhesion appears to be increased by the pretreatment according to the invention, and on the other hand there is hardly any discernible corrosive delamination.

[104] The corrosive delamination at the scratch also proves the advantages of the pretreatment ("ironizing" of the zinc surface) according to the invention, as can be seen from Fig. 5. The reduced corrosive delamination in comparison to galvanized steel surfaces which have only been phosphated and dip-coated (V3) is thus achieved on the zinc surfaces (B1) pretreated according to the invention and conversion-treated and coated according to a process chain IIa→IIIa→IVb (see Fig. 1). The omission of the pretreatment according to the invention as per process step I (see Fig. 1) in a treatment method according to Example V2 leads to particularly negative delamination properties of the entire coating at the scratch.

[105] In an alternative process chain, in which the pretreatment according to the invention (Fig. 1, method I) is followed by a zirconium-based conversion treatment (Fig. 1, method IIa) and directly thereafter, that is to say without any application and curing of an organic coating agent (Fig. 1, method IIIa or IIIb) by the deposition of an electro-dip coating (Fig. 1, method IVa), it can likewise be shown that the corrosive delamination at the scratch is significantly minimized.

[106] To this end, the galvanized steel sheets (ZE, Z) were first cleaned and degreased in accordance with the procedure described above, in order then, after intermediate rinsing with deionized water ($\kappa < 1 \mu\text{Scm}^{-1}$) has taken place, to be pretreated according to the invention (Fig. 1, method I) by metallizing with an agent having the composition according to Example B1 for 2 sec at a particular pH and at a temperature of 50°C. The conversion treatment carried out after an intermediate rinsing with deionized water took place in an acidic aqueous composition of

750 ppm Zr as H_2ZrF_6
 20 ppm Cu as $\text{Cu}(\text{NO}_3)_2$
 10 ppm Si as SiO_2

200 ppm Zn as $\text{Zn}(\text{NO}_3)_2$

at a pH of 4 and a contact time of 90 sec at a temperature of 20°C (Fig. 1, method IIa). After a further rinsing step with deionized water, a cathodic dip coating (CathoGuard 500) was applied in a layer thickness of 20 µm, and the sheets thus coated were cured for 30 min at 180°C in a circulating air oven before scratching the surface along several centimeters in the middle of the sheet down to the steel substrate using a scratch testing tool according to Clemen. Table 3 shows the delamination values resulting from this experiment at the scratch after the VDA alternating climate test.

Table 3

Delamination at the scratch of steel sheets (Gardobond® test sheets, from the company Chemetall), coated according to a process chain I → IIa → IVa (see Fig. 1), after 10 cycles of a VDA alternating climate test (821-415)

Example	pH of the agent (1)	Substrate	U/2 in mm
V4*	-	Z	4.1
		ZE	3.5
B1	2.7	Z	1.6
		ZE	1.1
	3.5	Z	1.8
		ZE	1.8

* No pretreatment

pH adjusted using ammonia solution or sulfuric acid

Z Melt dip galvanized steel

ZE Electrolytically galvanized steel

[107] Figs. 6 and 7 again prove, based on the X-ray photoelectronic (XPS) detail spectra of $\text{Fe}(2p^{3/2})$, that the thin iron overlay applied in the method according to the invention has a metallic character and considerably more than 50 at% of the iron atoms are in metallic form. This is qualitatively discernible by the clear shift in the total peak intensity in favor of peak 1 (Fig. 7) at lower bonding energies in comparison to the intensity of this individual peak in alkaline passivation (V2). Quantification takes place as standard via a numerical fitting process of the XP detail spectrum by means of Gaussian individual peaks, via which it is possible to determine the individual peak area. Table 4 shows quantitatively the chemical bond state of the iron overlay immediately after the respective exemplary pretreatments (V2) or inventive pretreatments (B1).

Table 4

Percentages of different bond states of iron on the galvanized steel surfaces, determined by X-ray photoelectron spectroscopy (XPS)

H07552

Example	Fe, metallic / at%	Fe, oxidic / at%
V2	28	72
B1	63	37

Cink felületek metallizálószerrel történő előkezelése

SZABADALMI IGÉNYPONTOK

1. Eljárás galvanizált vagy ötvözettel galvanizált acél felületek metallizálószerrel történő előkezelésére, ahol a galvanizált vagy ötvözettel galvanizált acél felületet érintkezésbe hozzuk egy vizes szerrel (1), amelynek a pH-ja 2-nél nem kisebb, és 6-nál nem nagyobb, azzal jellemezve, hogy az (1) szer a következőket tartalmazza:

(a) egy (A) fém kationjai és/vagy vegyületei, amelyeket a vas kationjai és/vagy vegyületei közül választunk ki, legalább 0,001 M koncentrációban,

(b) akcelerátorok, amelyeket a foszfor oxosavai, valamint azok sói közül választunk ki, ahol legalább egy foszforatom közepes oxidációs állapotban van,

ahol a vas(II) ionokat és/vagy a vas(III) ion vegyületeket használjuk az (A) fém kationjaiként és/vagy vegyületeiként, és az akcelerátoroknak az A vegyület kationjaihoz és/vagy vegyületei koncentrációjához viszonyított molaránya nem csökken az 1:5 érték alá, és az (A) vegyület kationjainak és/vagy vegyületeinek az E_{Redox} redoxpotenciálja, amit az (A) fém egy fémelektrodján mérünk, előre meghatározott eljárási hőmérsékleten és az (A) vegyület kationjainak és/vagy vegyületeinek koncentrációjánál az (1) vizes szerben, sokkal anódosabb, mint a galvanizált vagy ötvözettel galvanizált acélfelület E_{Zn} elektródpotenciálja egy vizes szerrel (2) érintkezve, amely az (1) szertől csak annyiban tér el, hogy nem tartalmazza az (A) fém semmilyen kationját és/vagy vegyületét.

2. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy az (A) fém kationjainak és/vagy vegyületeinek az E_{Redox} redoxpotenciálja az (1) vizes szerben legalább +50 mV-tal, de legfeljebb +800 mV-tal anódosabb, mint a galvanizált vagy ötvözettel galvanizált acélfelület E_{Zn} elektródpotenciálja a (2) vizes szerrel érintkezve.

3. Az 1. vagy 2. igénypont, vagy mindkettő szerinti eljárás, azzal jellemezve, hogy a az (A) fém kationjainak és/vagy vegyületeinek a koncentrációja legalább 0,01 M, de nem haladja meg a 0,2 M értéket.

4. A 3. igénypont szerinti eljárás, azzal jellemezve, hogy a vizes szer pH-ja 4-nél nem nagyobb.

5. Az előző igénypontok közül az egyik vagy több szerinti eljárás, azzal jellemezve, hogy a vizes szer emellett oxigén és/vagy nitrogén ligandumokkal rendelkező, komplex kelátképző szereket tartalmaz.

6. Az 5. igénypont szerinti eljárás, azzal jellemezve, hogy a komplex kelátképző szereket a következők közül választjuk ki: trietanolamin, dietanolamin, monoetanolamin, monoizopropanolamin, aminoetiletanolamin, 1-amino-2,3,4,5,6-pentahidroxihexán, N-(hidroxietil)etiléndiamintriécetsav, etiléndiamintetraecetsav, dietiléntriaminpentaecetsav, 1,2-diaminopropántetraecetsav, 1,3-diaminopropántetraecetsav, borkősav, tejsav, mucinsav, glükonsav, és/vagy glükoeptonsav, valamint ezek sói és sztereoizomerjei valamint szorbit, glükóz, és glükamin, és ezek sztereoizomerjei.

7. A 6. igénypont szerinti eljárás, azzal jellemezve, hogy a komplex kelátképző szereknek az (A) vegyület kationjaihoz és/vagy vegyületeihez viszonyított molaránya 5:1-nél nem nagyobb, de legalább 1:5.

8. Az 1-7. igénypontok közül az egyik vagy több szerinti eljárás, azzal jellemezve, hogy a vizes szer tartalmaz még a következők közül választott akcelerátorokat is: hidrazin, hidroxilamin, nitroguanidin, N-metilmorfolin-N-oxid, glükoeptonát, aszkorbinsav és redukáló cukrok.

9. Az 1-8. igénypontok közül az egyik vagy több szerinti eljárás, azzal jellemezve, hogy a vizes szer tartalmaz még maximum 50 ppm, de legalább 0,1 ppm réz(II) kationt is.

10. Az 1-9. igénypontok közül az egyik vagy több szerinti eljárás, azzal jellemezve, hogy van még egy fémbevonás az (A) fémmel, egy legalább 1 mg/m^2 , de maximum 100 mg/m^2 felülréteggel, a galvanizált vagy ötvözettel galvanizált acélfelületet érintkezésbe hozva a vizes szerrel.

11. Az 1-10. igénypontok közül az egyik vagy több szerinti eljárás, azzal jellemezve, hogy elvégezzük a fémesen előkezelt, galvanizált vagy ötvözettel galvanizált acélfelület passzíváló konverziós kezelését, a galvanizált vagy ötvözettel galvanizált acélfelület és a vizes szer érintkezésbe hozása után, közbenső öblítési és/vagy szárítási lépés nélkül.

12. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy további eljárási lépések követik, további rétegek, például festékek vagy festékrendszer alkalmazása.

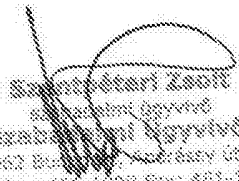

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Figure 1

Overview diagram of preferred anticorrosion coating methods based on the metallizing pretreatment according to the invention.

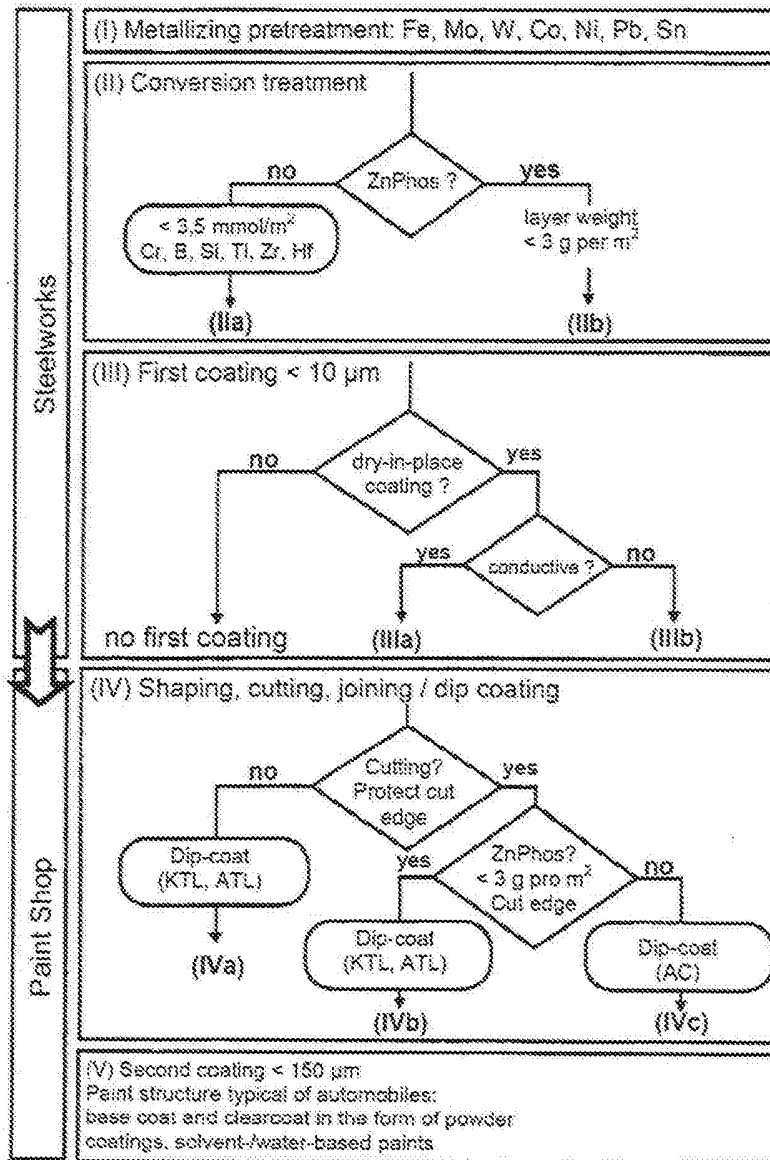


Figure 2

Schematic diagram of an electrochemical measuring chain for determining the electromotive force for the metallizing according to the invention of a zinc surface with iron by measuring, without using external current, the potential difference (V) of galvanic half-cells (HZ1, HZ2) connected to a salt bridge (S).

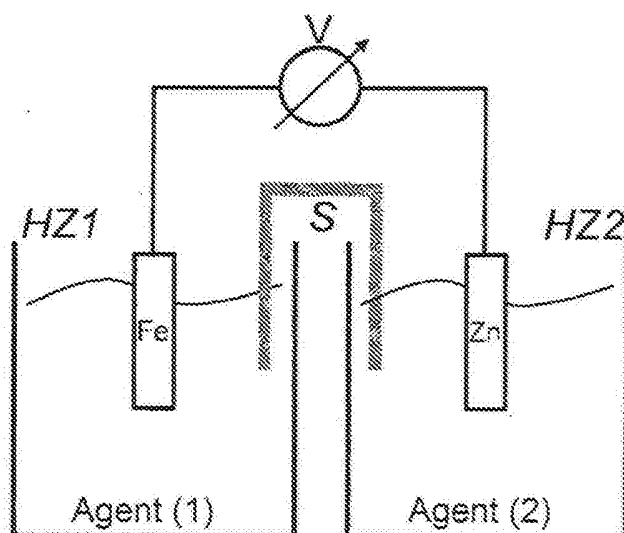
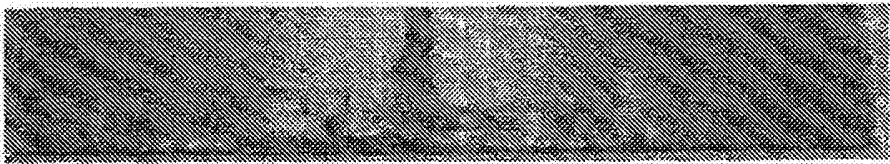
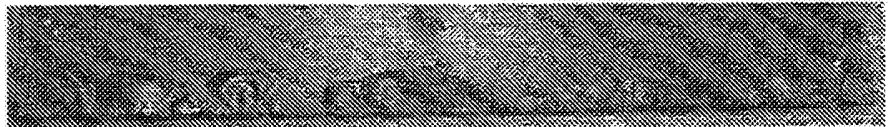
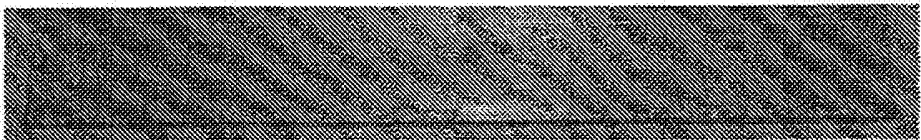
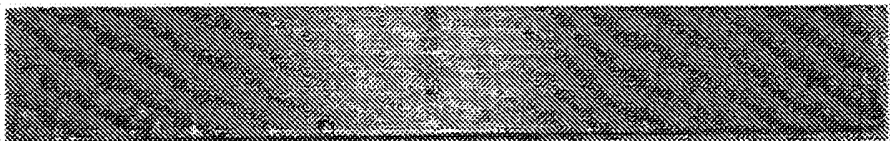
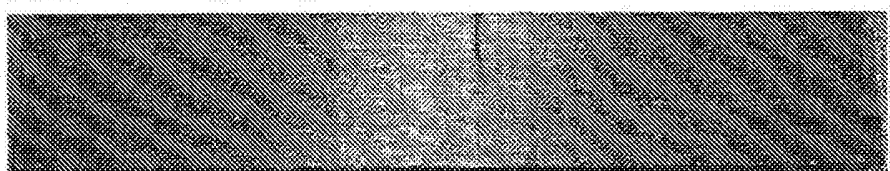


Figure 3

Delamination at the cut edge after constantly moist storage of the galvanized steel sheets (ZE 75/75) treated according to a typical process chain IIa→IIIa→IVb (see Fig. 1) and stored in a beechwood block according to the VDA alternating climate test (621-415) for 20 cycles.

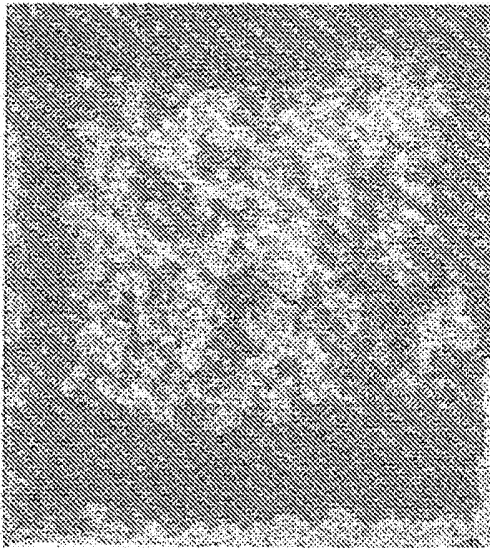
Example	Photograph
V1	
V2	
V3*	
B1	
B2	

* Comparative test without metallizing pretreatment according to the invention but with phosphating (Granodine® 958) and electro-dip-coating (EV 2005®) according to a conventional process chain IIb → Iva (see Fig. 1)

Figure 4

Stone impact according to DIN 55996-1 after 11 cycles of corrosion storage according to VDA 621-415 of the galvanized steel sheets (ZE 75/75) treated according to a typical process chain (see Fig. 1, method IVb). For better distinction between free metal surface and coated substrate, the sheets are immersed in an aqueous solution of copper sulfate and the free metal surface is thereby copper-plated.

V2



B1

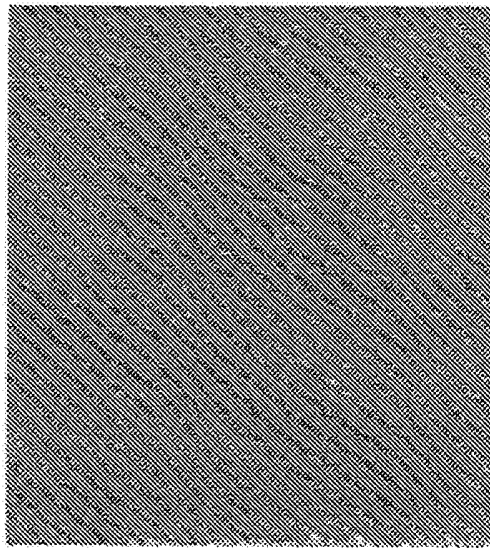


Figure 5

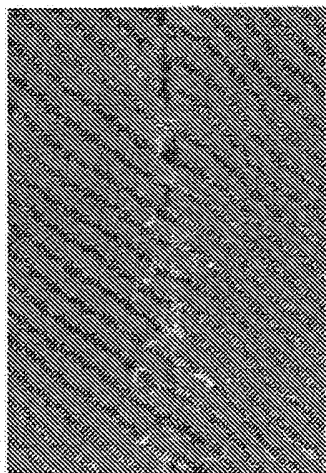
Delamination at the scratch after storage according to VDA alternating climate test (621-415) for 11 cycles on differently coated galvanized steel sheets (DC04, ZE 75/75) as shown in Fig. 1.

V1: IIb → IVa

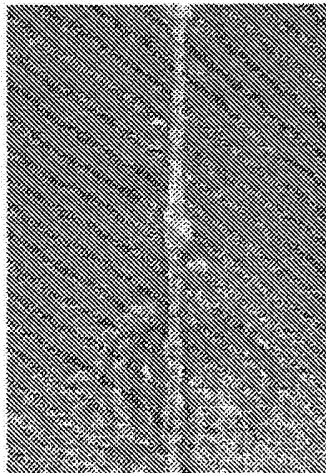
V3: IIa → IIIa → IVb

B1: I → IIa → IIIa → IVb

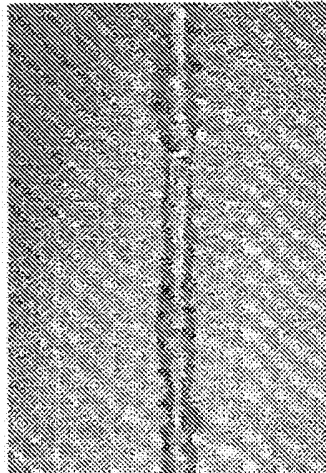
V1



V3



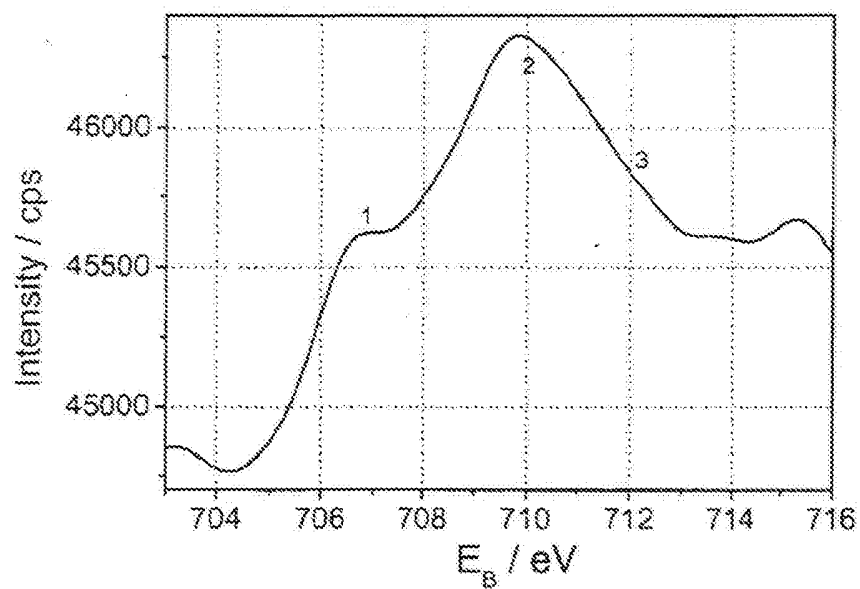
B1



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Figure 6

Fe ($2p^{3/2}$) XP detail spectrum according to Comparative Example V2, immediately after process step (ii)



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Figure 7

Fe ($2p^{3/2}$) XP detail spectrum according to Example B1 according to the invention, immediately after process step (ii)

