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APPLICATION THEREOF

(57) **Abrégé/Abstract:**

The invention relates to an aqueous coating agent for metal substrates, containing a water-dispersible and/or water-soluble polymer (P) with covalent bonded ligands (A), forming chelates with the metal ions released on corrosion of the substrate and/or the substrate surface and with cross-linking functional groups (B) which can form covalent bonds with themselves, with further complementary functional groups (B') of the polymer (P) and/or with further functional groups (B) and/or (B') on cross-linkers (V).



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STROMFREIER APPLIKATION(57) Abstract: The invention relates to an aqueous coating agent for metal substrates, containing a water-dispersible and/or water-
soluble polymer (P) with covalent bonded ligands (A), forming chelates with the metal ions released on corrosion of the substrate
and/or the substrate surface and with cross-linking functional groups (B) which can form covalent bonds with themselves, with
further complementary functional groups (B') of the polymer (P) and/or with further functional groups (B) and/or (B') on cross-linkers
(V).(57) Zusammenfassung: Die Erfindung betrifft ein wäßriges Beschichtungsmittel für metallische Substrate enthaltend ein was-
serdispergierbares und/oder wasserlösliches Polymerisat P mit kovalent gebundenen Liganden A, welche mit den bei der Korro-
sion des Substrats freigesetzten Metallionen und/oder der Substratoberfläche Chelate bilden, sowie mit vernetzenden funktionellen
Gruppen B, die mit sich selbst, mit weiteren komplementären funktionellen Gruppen B' des Polymerisats P und/oder mit weiteren
funktionellen Gruppen B und/oder B' an Vernetzern V kovalente Bindungen ausbilden können.

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CORROSION-PROTECTION AGENT FORMING A LAYER OF PAINT AND
METHOD FOR CURRENT-FREE APPLICATION THEREOF

Processes and coating materials for the electroless corrosion-control
5 coating of a variety of metal substrates are known. In comparison to
anodic or cathodic electrodeposition (AED or CED, respectively), where
the application of electrical voltages is a requirement, they offer the
advantage, in particular, of a simpler and less expensive operation and
of a shorter operating time. The electroless processes make it possible,
10 in particular, to coat cavities in or edges on the target substrates more
effectively than using processes requiring the application of electrical
voltages.

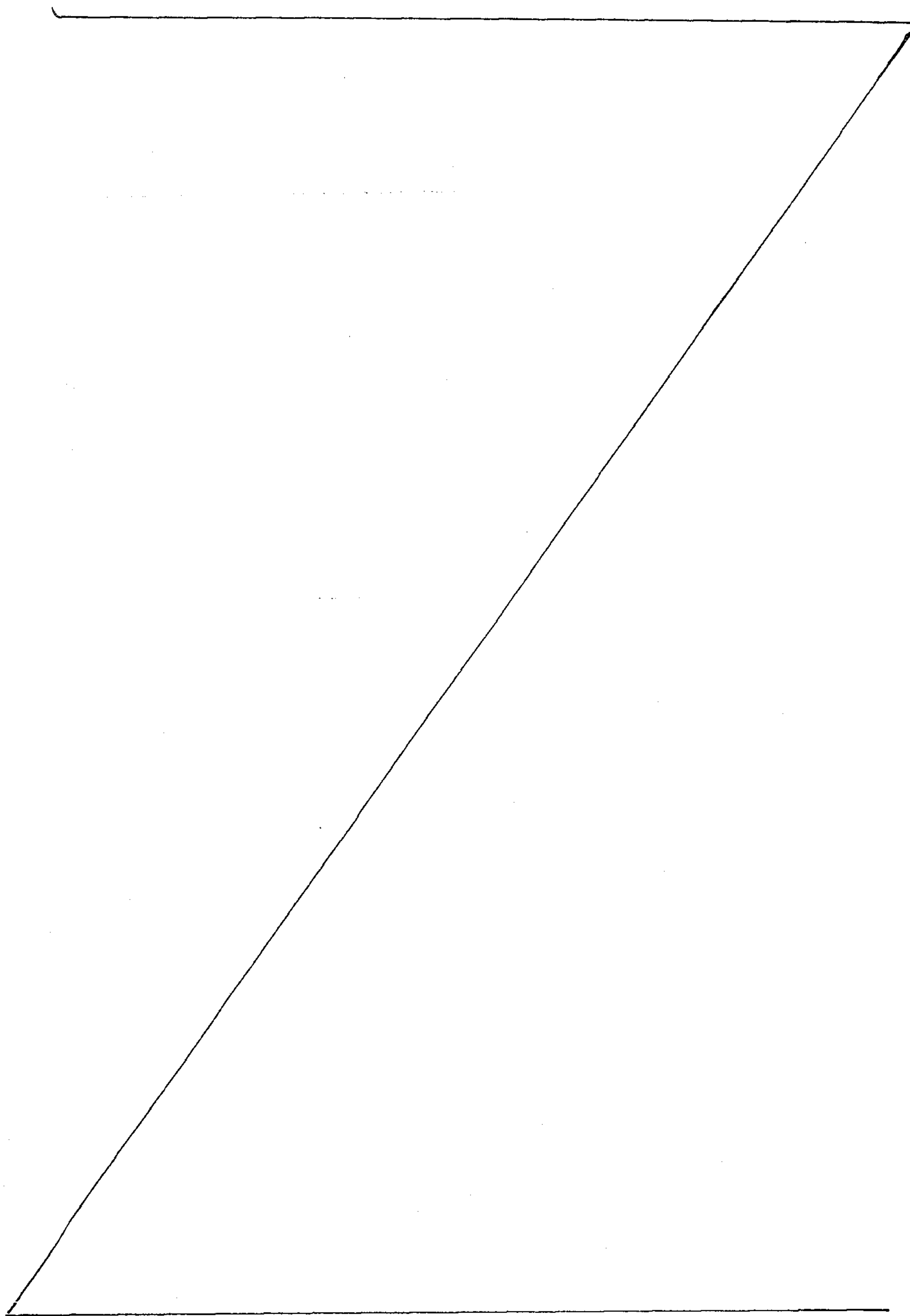
In the case of electroless corrosion-control coating, also called ACC
15 (autophoretic chemical coating) process, polymers are generally used,
examples being emulsion polymers containing acrylates or
styrene/butadiene, which are anionically stabilized. As compared with
the aforementioned AED and CED processes, however, the ACC
processes have the drawback that the deposited coats exhibit defects
20 which render the substrate significantly more susceptible to corrosion.
Consequently, coats of this kind deposited by means of ACC processes
are generally treated by rinsing with aqueous coating materials
containing chromium, in order to improve corrosion control at the
defects. Recently, however, it has turned out that chromium coating
25 materials have great problems in terms of environmental compatibility,
and are to be classified as highly hazardous to health. The aim is
therefore completely to replace chromium in corrosion-control coatings.

In the train of the development of chromium-free coating materials it has
30 been found, furthermore, that ACC coating materials comprising salts of
the lanthanide elements and of the d elements and also an organic, film-

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forming component likewise ensure very good corrosion control, comparable with that of the chromium coating materials.

WO-A-01/86016 describes a corrosion preventative comprising a



vanadium component and a further component which comprises at least one metal selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and cerium. In order to ensure effective stability and corrosion control on the part of the conversion coating material it is necessary to set a defined ratio of trivalent and tetravalent vanadium to total vanadium and, optionally, to add an organic compound. The primary purpose of the organic compound is to reduce the pentavalent vanadium compounds; it may comprise polymers, such as polyvinyl alcohol, polyethylene glycol, polyacrylic acid, polyacrylamide, and polyethyleneimine, for example. The activity of the corrosion preventative described in WO-A-01/86016 is based essentially on a defined ratio of trivalent and tetravalent vanadium to total vanadium, but the setting of this mandatory ratio is comparatively inconvenient. It is achieved, for example, by means of a mixture of vanadium compounds with the vanadium in different oxidation states. A drawback of corrosion preventatives of WO-A-01/86016 type is the tendency of the metal ions formed from the substrate to migrate through the deposited corrosion-control coat, since the polymers result in deficient film formation.

20

WO-A-99/29927 describes a chromium-free, aqueous corrosion preventative whose components comprise hexafluoro anions of titanium(IV) and/or zirconium(IV), vanadium ions, transition-metal ions, and phosphoric and/or phosphonic acid. In one preferred embodiment the corrosion preventative described in WO-A-99/29927 further comprises an organic film-former, in particular a polyacrylate-based film-former, which is preferably crosslinkable. Crosslinking may be accomplished by means of different reactive groups in the film-former itself or by addition of curing agents tailored to the film-former. The application of an inorganic passivating coat and an organic polymer coat in the same treatment step is described as advantageous, and sufficient corrosion control is achieved. Disadvantages associated with corrosion

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preventatives of the WO-A-99/29927 type is the tendency of the metal ions formed from the substrate to migrate through the deposited corrosion-control coat, since the polymers result in deficient film formation, and the use of environmentally critical substances, such as
5 fluorides in particular.

WO-A-96/10461 describes an aqueous corrosion preventative whose components comprise anions with a central atom selected from the group consisting of titanium, zirconium, hafnium, and silicon, and at
10 least 4 fluorine-atom ligands, and an organic polymer dispersion. Inventive advantages described include in particular the absence of chromium and the one-stage coating operation.

A drawback of the invention according to WO-A-96/10461 is that deposition of the corrosion preventative on the substrate surface is
15 accompanied by flocculation of the polymer-dispersion particles, which makes their surface contact area small. Moreover, the latex particles have the drawback of a relatively low migration rate in the context of diffusion into cavities or onto edges of three-dimensional substrates, in comparison to polymers whose distribution is molecularly disperse.
20 Moreover, coats with a thickness of between 1 micrometer and 1 mm are formed, entailing a corresponding consumption of material per unit area of the substrate to be coated. Further drawbacks include the tendency of the metal ions formed from the substrate to migrate through the deposited corrosion-control coat, and the use of environmentally
25 critical substances, such as fluorides in particular.

DE-A-37 27 382 embraces chromium-free, aqueous dispersions of adducts of carboxylic acids and isocyanates with epoxides, which are suitable for autophoretic coating of metallic surfaces. In dispersed form
30 such dispersions have a particle diameter of less than 300 nm, preferably between 100 and 250 nm, and after deposition on the metal surface can be crosslinked at temperatures between 60 and 200°C.

Crosslinking is carried out using the usual initiators known from autophoretic deposition, such as, in particular, the HF/FeF₃ system. The coatings described in DE-A-37 27 382 exhibit good corrosion control and, furthermore, are also solvent-resistant.

- 5 Latex particles of this kind, too, have the drawback of having a relatively low migration rate in the context of diffusion into cavities or onto edges of three-dimensional substrates, in comparison to polymers whose distribution is molecularly disperse. Moreover, coats with a thickness of between 1 micrometer and 1 mm are formed, entailing a corresponding
10 consumption of material per unit area of the substrate to be coated. Further drawbacks include the tendency of the metal ions formed from the substrate to migrate through the deposited corrosion-control coat, and the use of environmentally critical substances, such as fluorides in particular.

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Problem and Solution

- In the light of the aforementioned prior art the problem addressed by the
20 invention was that of finding a corrosion preventative which is largely unobjectionable from an environmental standpoint and which can be applied by a readily technically accomplishable operation to the substrate that is to be protected. In particular the corrosion preventative ought substantially to prevent the migration of the metal ions formed
25 from the substrate and ought to be deposited effectively on edges and in cavities of the substrate. Moreover, the effect of extraneous metal ions ought to be kept very low, and effective corrosion control ought to be obtained with a comparatively low level of material employed. Furthermore, the conversion coating material ought to develop effective
30 protection for as many different metal substrates as possible and ought to be substantially independent of the redox potential of the substrate to be coated.

In the light of the aforementioned problems, surprisingly, an aqueous corrosion preventative for metallic substrates, offering effective corrosion control, has been found which comprises a water-dispersible and/or water-soluble polymer P with covalently bonded ligands A, which form chelates with the metal ions released during the corrosion of the substrate and/or with the substrate surface, and having crosslinking functional groups B, which with themselves, with further functional groups B' of the polymer P and/or with further functional groups B and/or
10 B' are able to form covalent bonds to crosslinkers V.

A process has also been found for the corrosion-control treatment of metallic substrates, which comprises immersing the substrate in a bath of the aforementioned corrosion preventative, the corrosion preventative being deposited electrolessly. In a further preferred embodiment of the process of the invention, prior to the deposition of the corrosion preventative of the invention, in a further upstream process step, the substrate is pretreated with a corrosion inhibitor K.

The invention a claimed is however more specifically directed to a two-stage process for the corrosion-control treatment of a metallic substrate, characterized in that:

- (a) in a first stage, the substrate is immersed in a bath of a corrosion preventative K, which results in conversion at the substrate surface, the corrosion preventative K comprising at least one compound having as its cation a lanthanide metal and/or as its cation a d-element metal with the exception of chromium, and/or having as its anion ad-element metallate, with the exception of metallates containing chromium, and also at least one acid capable of oxidation, with the exception of acids containing phosphorus and/or containing chromium, and
- (b) in a second stage, the substrate treated as per stage (a) is immersed in an aqueous coating material EK for metallic substrates, comprising a water-dispersible

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and/or watersoluble polymer P having covalently bonded ligands A, which form chelates with the metal ions released during the corrosion of the substrate and/or with the substrate surface, and having crosslinking functional groups B, which are able to form covalent bonds with themselves, with further, complementary functional groups B' of the polymer P and/or with further functional groups B and/or B' on crosslinkers V,

the ligands A being selected from the group consisting of ureas, amines, amides, imines, imides, pyridines, organosulphur compounds, organophosphorus compounds, organoboron compounds, oximes, acetylacetonates, acids, phytic acids, acetylenes, carbenes and mixtures thereof, and

the substrate being immersed in the baths of the coating materials K and EK in stages (a) and (b) for a time of 1 second to 15 minutes and at a temperature between 20 and 90°C.

Description of the Invention

The Coating Material of the Invention

The water-dispersible and/or water-soluble polymers P of the coating material of the invention carry ligands A, which form chelates with the metal ions released during the corrosion of the substrate, and crosslinking functional groups B, which are able with themselves and/or with further functional groups C to form covalent bonds to crosslinkers V.

For the purposes of the invention, water-dispersible or water-soluble means that the polymers P in the aqueous phase form aggregates

having an average particle diameter of < 50 nm, preferably < 35 nm, and more preferably < 20 nanometers, or else are in molecularly disperse solution. Such aggregates differ critically in their average particle diameter from dispersion particles, as are described, for example, in
5 DE-A-37 27 382 or WO-A-96/10461. Polymers P in molecularly disperse solution generally have molecular weights of $< 100\,000$, preferably $< 50\,000$, and more preferably $< 20\,000$ daltons.

The size of the aggregates composed of polymer P comes about, in conventional manner, through the introduction of hydrophilic groups HG
10 on the polymer P. The number of hydrophilic groups HG on the polymer P depends on the solvation capacity and the steric accessibility of the groups HG and can be adjusted by the skilled worker likewise conventionally. Preferred hydrophilic groups HG on the polymer P are sulfate, phosphate, phosphonate, amine, amide and/or carboxylate
15 groups, especially amine and/or phosphonate groups.

Polymers which can be used as the backbone of the polymers P are arbitrary per se, preference being given to polymers having molecular weights of 1000 to $50\,000$ daltons and more preference to those having
20 molecular weights of 2000 to $20\,000$ daltons. Preferred backbone polymers used are polyolefins or poly(meth)acrylates, polyurethanes, polyalkyleneamines, polyvinylamines, polyalkyleneimines, polyethers, polyesters, and polyalcohols, which in particular are partially acetalized and/or partially esterified. The polymers P may be linear, branched
25 and/or dendritic in construction. Especially preferred polymer backbones are polyalkyleneimines, polyvinylamines, polyalcohols, poly(meth)acrylates, and hyperbranched polymers, as are described, for example, in WO-A-01/46296.

30 The polymers P are preferably stable to hydrolysis in the acidic pH range, in particular at pH values < 5 , more preferably at pH values < 3 .

Suitable ligands A are all groups or compounds which are able to form chelates with the metal ions released during the corrosion of the substrate. Preference is given to monodentate and/or polydentate, potentially anionic ligands. Particularly preferred ligands are

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- unfunctionalized or functionalized ureas and/or thioureas, especially acylthioureas such as benzoylthiourea, for example;
- unfunctionalized or functionalized amines and/or polyamines, such as EDTA in particular;
- 10 - unfunctionalized or functionalized amides, especially carboxamides;
- imines and imides, such as imine-functionalized pyridines in particular;
- oximes, preferably 1,2-dioximes such as functionalized
- 15 diacetyldioxime;
- organosulfur compounds, such as, in particular, unfunctionalized or functionalized thiols such as thioethanol, thiocarboxylic acids, thioaldehydes, thioketones, dithiocarbamates, sulfonamides, thioamides, and, with particular preference, sulfonates;
- 20 - organophosphorus compounds, such as, in particular, phosphates, more preferably phosphoric esters of (meth)acrylates, and also phosphonates, more preferably vinylphosphonic acid and hydroxy-, amino- and amido-functionalized phosphonates;
- 25 - unfunctionalized or functionalized organoboron compounds, such as boric esters in particular;
- unfunctionalized or functionalized polyalcohols, such as, in particular, carbohydrates and their derivatives and also chitosans;
- unfunctionalized or functionalized acids, such as, in particular,
- 30 difunctional and/or oligofunctional acids, or unfunctionalized or functionalized (poly)carboxylic acids, such as, in particular, carboxylic acids, which may be attached ionically and/or

coordinatively to metal centers, preferably (poly)methacrylates containing acid groups, or difunctional or oligofunctional acids;

- unfunctionalized or functionalized carbenes;
- acetylacetonates;
- 5 - unfunctionalized or functionalized acetylenes; and
- phytic acid and its derivatives.

Suitable crosslinking functional groups B on the polymer P are those which with themselves and/or with complementary functional groups B' 10 are able to form covalent bonds. Preferably the covalent bonds are formed thermally and/or by exposure to radiation. With particular preference the covalent bonds are formed thermally. The crosslinking functional groups B and B' result in the formation of an intermolecular network between the molecules of the polymer P.

15 Functional groups B and/or B' which crosslink on exposure to radiation contain activable bonds, such as carbon-hydrogen, carbon-carbon, carbon-oxygen, carbon-nitrogen, carbon-phosphorus or carbon-silicon bonds, which may be single or double bonds. Carbon-carbon double bonds are particularly advantageous in this context. Especially suitable 20 carbon-carbon double bonds as groups B are

- with particular preference (meth)acrylate groups
- ethyl acrylate groups
- vinyl ether groups and vinyl ester groups
- 25 - crotonate groups and cinnamate groups
- allyl groups
- dicyclopentadienyl groups
- norbornyl groups and isoprenyl groups
- isopropenyl groups or butenyl groups.

Thermally crosslinking functional groups B are able with themselves or, preferably, with complementary crosslinking functional groups B' to form covalent bonds on exposure to thermal energy.

Especially suitable thermally crosslinking functional groups B and B' are

5

- with particular preference hydroxyl groups
- mercapto groups and amino groups
- aldehyde groups
- azide groups
- 10 - acid groups, especially carboxylic acid groups
- acid anhydride groups, especially carboxylic anhydride groups
- acid ester groups, especially carboxylic ester groups
- ether groups
- with particular preference carbamate groups
- 15 - urea groups
- epoxide groups
- with particular preference isocyanate groups, which with very particular preference have been reacted with blocking agents which unblock at the baking temperatures of the coating materials
- 20 of the invention and/or without unblocking are incorporated into the network that forms.

Particularly preferred combinations of thermally crosslinking groups B and complementary groups B' are:

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- hydroxyl groups with isocyanate and/or carbamate groups,
 - amino groups with isocyanate and/or carbamate groups, and
 - carboxylic acid groups with epoxide groups.
- 30 Suitable crosslinkers V containing groups B and/or B' which crosslink thermally and/or by exposure to radiation are, in principle, all crosslinkers known to the skilled worker. Preference is given to low

molecular weight or oligomeric crosslinkers V, having a molecular weight of < 20 000 daltons, more preferably < 10 000 daltons. The backbone of the crosslinkers V that carries the crosslinking groups B and/or B' may be linear, branched and/or hyperbranched in construction. Preference is
5 given to branched and/or hyperbranched structures, particularly those as described in, for example, WO-A-01/46296.

The crosslinkers V are preferably stable to hydrolysis in the acidic pH range, in particular at pH values < 5, more preferably at pH values < 3.
10 Particularly preferred crosslinkers V carry the above-described crosslinking groups B and/or B' which react with the crosslinking groups of the polymer P to form covalent bonds. Especially preferred crosslinkers V are those having groups B and/or B' which crosslink thermally and, if desired, additionally by exposure to radiation.
15 In one further particularly preferred embodiment of the invention the crosslinkers V, as well as the crosslinking groups B and/or B', carry ligands L, which may be identical with and/or different from the ligands L of the polymer P. Particularly suitable crosslinking functional groups B and B' for the crosslinkers V are:

20

- especially hydroxyl groups
- especially aldehyde groups
- azide groups
- acid anhydride groups, especially carboxylic anhydride groups
- 25 - carbamate groups
- urea groups
- especially isocyanate groups, which with very particular preference are reacted with blocking agents which unblock at the baking temperatures of the coating materials of the invention
30 and/or without deblocking are incorporated into the network which forms
- (meth)acrylate groups

- vinyl groups

or combinations thereof.

- 5 Especially preferred crosslinkers V are branched and/or hyperbranched polyisocyanates which are at least partly blocked and which additionally carry ligands L.

In one further embodiment of the invention the crosslinkers V carry groups B and/or B' which are capable of forming covalent bonds with the
10 ligands L of the polymer P.

The continuous phase used for the coating material of the invention is water, preferably deionized and/or distilled water. A further preferred component used is at least one acid capable of oxidation, which is used
15 such that the pH of the coating material of the invention is preferably between 1 and 5, more preferably between 2 and 4. Particularly preferred acids are selected from the group consisting of oxidizing mineral acids, such as, in particular, nitric acid, nitrous acid, sulfuric acid and/or sulfurous acid. To adjust the pH it is possible, where necessary,
20 to use a buffer medium, such as, for example, salts of strong bases and weak acids, such as ammonium acetate in particular.

In one particularly preferred embodiment of the invention the coating material of the invention further comprises a salt having as its cationic constituent lanthanide-metal cations and/or d-metal cations.

- 25 Preferred lanthanide metal cations are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium and/or dysprosium cations. Lanthanum, cerium, and praseodymium cations are especially preferred. The lanthanide-metal cations can be in monovalent, divalent and/or trivalent oxidation state, preference being
30 given to the trivalent oxidation state.

Preferred d-metal cations are titanium, vanadium, manganese, yttrium, zirconium, niobium, molybdenum, tungsten, cobalt, ruthenium, rhodium,

palladium, osmium and/or iridium cations. Barred from consideration as a d-element cation is the chromium cation in any oxidation state.

Vanadium, manganese, tungsten, molybdenum and/or yttrium cations are especially preferred. The d-element cations can be present in

- 5 monovalent to hexavalent oxidation state, preference being given to a trivalent to hexavalent oxidation state.

The Process for Applying the Coating Material of the Invention

- 10 Before the coating material of the invention is applied, in one preferred embodiment of the invention the substrate is clean, in particular of oily and fatty residues, employing preferably detergents and/or alkaline cleaning materials. In a further preferred version of the invention the cleaning with detergents and/or alkaline cleaning materials is followed,
- 15 and the application of the coating material of the invention preceded, by rinsing with water. In order to remove deposits and/or chemically modified films, especially oxidized films, from the surface of the substrate, in a further preferred embodiment of the invention the rinse step is preceded by mechanical cleaning of the surface, using abrasive
- 20 media for example, and/or by chemical removal of the surface films, using deoxidizing cleaning materials for example.

- The substrate thus pretreated is contacted with the coating material of the invention. This is preferably accomplished by immersing the
- 25 substrate in or drawing it through a bath comprising the coating material of the invention. The residence times of the substrate in the coating material of the invention amount to preferably 1 second to 15 minutes, more preferably 10 seconds to 10 minutes, and very preferably 30 seconds to 8 minutes. The temperature of the bath comprising the
- 30 coating material of the invention is preferably between 20 and 90°C, more preferably between 25 and 80°C, and very preferably between 30 and 70°C.

Treatment of the substrate with the coating material of the invention is followed preferably by drying of the system comprising substrate and coating material at temperatures between about 30 and 200°C, in particular between 100 and 180°C; the drying apparatus can be regarded as largely uncritical to the advantageous effect of the coating material of the invention. Where the crosslinking groups B and/or B' are at least partly radiation-curing, the coat of the coating material of the invention is irradiated, preferably in a manner known to the skilled worker by actinic radiation and/or by electron beams, this irradiation taking place, where appropriate, in addition to the thermal treatment.

The coating material of the invention can, surprisingly, be employed on a wide spectrum of substrates and is largely independent of the substrate's redox potential.

Preferred substrate materials are zinc, iron, magnesium, and aluminum, and also alloys thereof, said alloys preferably containing at least 20% by weight of the aforementioned metals. The substrates are preferably formed as metal sheets, as are employed, for example, in the automotive, construction, and mechanical engineering industries. The sheets coated with the coating material of the invention are employed in connection in particular with profiled sheets and with the coil-coating of sheets.

In one especially preferred embodiment of the invention the coating materials of the invention are used for sealing cut edges of the above-described sheets, especially for sealing the cut edges of sheets which have already been coated.

In a further embodiment of the invention the above-described substrates, before the coating material of the invention is deposited, are coated with a further corrosion inhibitor which can likewise be deposited electrolessly. Preference is given to corrosion inhibitors having inorganic

constituents which exhibit effective adhesion both to the coat of the coating material of the invention and to the uncoated substrate.

Inorganic corrosion inhibitors of this kind are described in, for example, EP-A-1 217 094, EP-A-0 534 120, US-A-5,221,371, and

5 WO-A-01/86016.

In one particularly preferred embodiment of the invention the application of the coating material of the invention is preceded, in a separate step, by application of an aqueous corrosion preventative K having a pH of
10 between 1 and 5 and comprising at least one compound AA having as its cation a lanthanide metal and/or a d-element metal bar chromium and/or as its anion a d-element metallate, bar chromium-containing metallates, and also BB at least one acid capable of oxidation, with the exception of phosphorous and/or chromium acids.

15

The salt forming component AA has as its cationic constituent lanthanide-metal cations and/or d-metal cations. Preferred lanthanide-metal cations are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium and/or dysprosium cations.

20 Lanthanum, cerium, and praseodymium cations are especially preferred.

The lanthanide-metal cations can be in monovalent, divalent and/or trivalent oxidation state, the trivalent oxidation state being preferred.

Preferred d-metal cations are titanium, vanadium, manganese, yttrium, zirconium, niobium, molybdenum, tungsten, cobalt, ruthenium, rhodium,
25 palladium, osmium and/or iridium cations. Barred from consideration as a d-element cation is the chromium cation in any oxidation state.

Vanadium, manganese, tungsten, molybdenum and/or yttrium cations are especially preferred. The d-element cations can be in a monovalent to hexavalent oxidation state, preference being given to a trivalent to
30 hexavalent oxidation state.

The salts of the aforementioned cations of component AA are preferably of very good solubility in water. Particular preference is given to

[cation]_n[anion]_m salts (with n and m each >= 1) having a solubility product SP, i.e., [cation]ⁿ * [anion]^m, > 10⁻⁸ * mol^(n+m)/l^(n+m), with very particular preference salts having a solubility product SP > 10⁻⁶ * mol^(n+m)/l^(n+m). In one especially preferred embodiment of the

5 invention the concentration of the salt or salts (A) in the corrosion preventative is 10⁻¹ to 10⁻⁴ mol/l, in particular 5*10⁻¹ to 10⁻³ mol/l.

The anions which together with the d-element cations form the salts AA are preferably selected such that the aforementioned conditions for the solubility product SP are met. Preference is given to using anions of
10 oxidizing acids of the elements of transition groups VI, VII and VIII of the Periodic Table of the Elements and also to anions of oxidizing acids of the elements of main groups V and VI of the Periodic Table of the Elements, with the exception of anions of oxidizing acids of phosphorus and chromium, particular preference being given to the use of nitrates,
15 nitrites, sulfites and/or sulfates. Further preferred anions are halides, such as chlorides and bromides in particular.

In a further preferred embodiment of the invention the d-element cations can also be present in the form of complexes with monodentate and/or
20 polydentate, potentially anionic ligands. Preferred ligands are unfunctionalized or functionalized terpyridines, unfunctionalized or functionalized ureas and/or thioureas, unfunctionalized or functionalized amines and/or polyamines, such as EDTA in particular, imines, such as imine-functionalized pyridines in particular, organosulfur compounds,
25 such as, in particular unfunctionalized or functionalized thiols, thiocarboxylic acids, thioaldehydes, thioketones, dithiocarbamates, sulfonamides, thioamides, and, with particular preference, sulfonates, unfunctionalized or functionalized organoboron compounds, such as boric esters in particular, unfunctionalized or functionalized polyalcohols,
30 such as, in particular, carbohydrates and their derivatives and also chitosans, unfunctionalized or functionalized acids, such as difunctional and/or oligofunctional acids in particular, unfunctionalized or

functionalized carbenes, acetylacetonates, unfunctionalized or functionalized acetylenes, unfunctionalized or functionalized carboxylic acids, such as, in particular, carboxylic acids which can be attached ionically and/or coordinatively to metal centers, and also phytic acid and
5 its derivatives.

Especially preferred ligands are phytic acids, derivatives thereof, and sulfonates, which may have been functionalized.

In a further embodiment of the invention the salts AA contain as their anions d-element metallates which together with the d-element cations
10 or else on their own are able to form the salt AA. Preferred d elements for the metallates are vanadium, manganese, zirconium, niobium, molybdenum and/or tungsten. Vanadium, manganese, tungsten and/or molybdenum are especially preferred. Barred from consideration as a d-element metallate are chromates in any oxidation states. Particularly
15 preferred d-element metallates are oxo anions, such as tungstates, permanganates, vanadates and/or molybdates in particular.

Where the d-element metallates form the salt AA on their own, in other words without lanthanide-metal cations and/or d-metal cations, the abovementioned comments regarding the preferred solubility product
20 SP of such salts apply here as well. Preferred cations of such salts are ammonium ions, phosphonium ions and/or sulfonium ions, with or without substitution by organic radicals; alkali metal cations, such as lithium, sodium and/or potassium in particular; and alkaline earth metal cations, such as magnesium and/or calcium in particular. Particularly
25 preferred ions are the ammonium ions, unsubstituted or substituted by organic radicals, and the alkali metal cations, which ensure a particularly high solubility product SP on the part of the salt AA.

As component BB of the corrosion preventative K use is made of at
30 least one acid which is capable of oxidation, it being used such that the pH of the corrosion preventative is between 1 and 5, preferably between 2 and 4. Preferred acids BB are selected from the group consisting of

oxidizing mineral acids, such as, in particular, nitric acid, nitrous acid, sulfuric acid and/or sulfurous acid.

In order to set the pH it is possible where necessary to employ a buffer medium, such as, for example, salts of strong bases and weak acids,
5 such as ammonium acetate in particular.

The continuous phase used for the corrosion preventative K of the invention is water, preferably deionized and/or distilled water.

10 In one preferred embodiment of the invention, prior to application of the corrosion preventive K, the substrate is cleaned, especially of oily and fatty residues, employing preferably detergents and/or alkaline cleaning materials. In another preferred version of the invention the cleaning with
15 detergents and/or alkaline cleaning products is followed, and the application of the corrosion preventative K preceded, by a rinse with water. In a further preferred embodiment of the invention, for the purpose of removing deposits and/or chemically modified films, especially oxidized films, from the surface of the substrate, the rinse step is preceded by mechanical cleaning of the surface, using abrasive
20 media for example, and/or by chemical removal of the surface films, using deoxidizing cleaning materials, for example.

The substrate thus pretreated is contacted with the corrosion preventative K. This is preferably accomplished by immersing the
25 substrate in or drawing it through a bath comprising the corrosion preventative K. The residence times of the substrate in the corrosion preventative K amount to preferably 1 second to 10 minutes, preferably 10 seconds to 8 minutes, and more preferably 30 seconds to 6 minutes. The temperature of the bath comprising the corrosion preventative K is
30 preferably between 25 and 90°C, more preferably between 30 and 80°C, and very preferably between 35 and 70°C.

After the substrate has been treated with the corrosion preventative of the invention it is preferred to carry out drying of the system comprising substrate and corrosion preventative, by means of blow drying or by means of drying at temperatures between about 30 and 200°C; the
5 drying temperature and also the type of drying or drying apparatus can be regarded as being largely uncritical to the advantageous effect of the corrosion preventative K.

In the second step of the preferred process the substrates coated with
10 the corrosion preventative K are coated with the coating material of the invention. This is accomplished preferably by immersing or drawing the coated substrate in or through a bath comprising the coating material of the invention. The residence times of the substrate in the coating material of the invention amount to preferably 1 second to 15 minutes,
15 more preferably 10 seconds to 10 minutes, and very preferably 30 seconds to 8 minutes. The temperature of bath comprising the coating material of the invention is preferably between 20 and 90°C, more preferably between 25 and 80°C, and very preferably between 30 and 70°C.

20

After the substrate has been treated with the coating material of the invention it is preferred to carry out drying of the system comprising the substrate and the coats of the corrosion preventative K and also the coating material of the invention, at temperatures between 30 and
25 200°C, in particular between 100 and 180°C; the drying apparatus can be regarded as being largely uncritical to the advantageous effect of the coating material of the invention. Where the crosslinking groups B and/or B' are at least partly radiation-curing, irradiation of the coat of the coating material of the invention, preferably in a manner known to the
30 skilled person, using actinic radiation and/or electron beams, is carried out, where appropriate in addition to the thermal treatment.

The examples given below are intended to provide further illustration of the invention.

Examples

Example 1: Preparation of the first tank with the corrosion preventative K

- 5 In one liter of water 1.77 g (0.01 mol) of ammonium molybdate tetrahydrate are dissolved. The solution is adjusted using nitric acid to a pH = 2.5. Counter-buffering with aqueous ammonia solution is used if desired in order to set the aforementioned pH.

10 Example 2a: Synthesis of the polymer component P for the coating material of the invention

- 5 g ($6.25 \cdot 10^{-3}$ mol) of a polyethyleneimine having an average molecular weight $M_w = 800$ g/mol (Lupasol FG from BASF AG, ratio of primary to secondary to tertiary amino groups (p-s-t): 1:0.9:0.5) in 100 g of ethanol
15 are introduced as an initial charge under a nitrogen atmosphere and at 75°C a solution of 10.7 g (0.066 mol) of benzoyl isothiocyanate in 86 g of ethanol is added over the course of 45 minutes. Stirring is continued at this temperature for 4 h and the product is employed without further purification.

20

Example 2b: Synthesis of the crosslinker V for the coating material of the invention

- 3.1 g (0.008 mol) of cerium(III) chloride heptahydrate in 50 ml of water are introduced as an initial charge. A solution is prepared from 4.1 g
25 (0.025 mol) of 4-hydroxycinnamic acid and 1 g (0.025 mol) of sodium hydroxide in 50 ml of water and adjusted using hydrochloric acid to a pH = 7.9. This solution is slowly added to the cerium solution, so that the pH of the cerium solution does not rise above 6. The precipitate is washed with ethanol and water.

- 30 1.7 g (0.003 mol) of this cerium complex is reacted at 40°C for five hours with 9.1 g (2.5% NCO content) of a branched polyisocyanate with 75% dimethylpyrazole blocking (Bayhydur VP LS 2319 from Bayer AG) in

80.1 g of ethyl acetate and 0.7 g of an OH-functional dipropylenetriamine (Jeffcat-ZR 50 from Huntsmann). The product is employed without further purification.

5 **Example 2: Preparation of the second tank with the coating material of the invention**

In one liter of water 3 g of the polymer component P from Example 2a, and 2 g of the crosslinker V from Example 2b are dissolved. The solution is adjusted using nitric acid to a pH = 2.5. Counter-buffering with
10 aqueous ammonia solution is used if desired in order to set the aforementioned pH.

Example 3: Coating of the substrate with the corrosion preventative K and the coating material of the invention

15 The substrate (sheet of galvanized steel) is cleaned in a cleaning solution (Ridoline C72 from Henkel) at 55°C for 5 minutes and thereafter rinsed with distilled water.

Subsequently the sheet rinsed with distilled water is immediately immersed in the first tank of the corrosion preventative K from
20 Example 1 at 45°C for 4 minutes. Thereafter the coated sheet is rinsed with distilled water and blown dry with nitrogen.

Directly after that the sheets are immersed in the second tank of the corrosion preventative of the invention from Example 2 at 35°C for 5 minutes. Thereafter the coated sheet is rinsed with distilled water and
25 blown dry with nitrogen.

The sheet is subsequently dried at 150°C for 30 minutes.

The sheet thus coated, and the reference samples below, are cut with sheet shears in order to obtain free edges on all the sheets.

30 The reference used for the coating material of the invention is Gardobond 958 54 (Chemetall GmbH: galvanized steel sheet with phosphating and a zirconium hexafluoride solution afterrinse).

Example 4: Accelerated corrosion test with 3% strength aqueous sodium chloride solution on the substrates coated as per Example 3

- 5 A solution of 3% sodium chloride in free deionized water is used. Substrates which can be utilized here are steel, galvanized steel or zinc alloys. For aluminum and its alloys the sodium chloride solution is additionally adjusted using acetic acid to a pH = 3. The samples (3*3 cm) are immersed in 170 ml of this solution and are stored in a
- 10 desiccators at a humidity of almost 100%. The humid atmosphere is produced by fat-free compressed air which is passed through two wash bottles containing fully deionized water and then flows through the desiccators. This setup ensures a constant atmospheric humidity and a constant carbon dioxide content, the temperature being held at 25°C.
- 15 Prior to immersion, the samples are weighed on an analytical balance. Untreated reference sheets (steel, galvanized steel) are cleaned in ethanol in an ultrasound bath for 5 minutes. After storage for 24 hours the sheets are removed from the solution and rinsed with the exposed 3% strength sodium chloride solution (about 10 ml of sodium chloride
- 20 solution per sample side) over a glass beaker, using a disposable pipette. The sheet is subsequently blown dry with nitrogen, then dried at 50°C for 15 minutes and weighed. Subsequently the sheet is suspended again in a fresh sodium chloride solution of the same concentration. 1 ml of 32% strength hydrochloric acid is added to the used sodium chloride
- 25 solution in order to dissolve any precipitates. The clear solution obtained is assayed for substrate metal (Zn, Fe, Al, Mg) by means of ICP-OES (inductively coupled plasma – optical emission spectrometry).
- The procedure described above is repeated after 24 h, 72 h, 96 h, and 168 h. The measurement is verified by means of a duplicate
- 30 determination.

Evaluation of the corrosion test:**a) ICP-OES data of the immersion solution**

The ICP-OES data are standardized for the area of the samples. These data produce a linear plot. Because of the linearity of the corrosion kinetics it is possible to compare the different coatings through the slopes of the graph. The ICP-OES data reproduce the dissolution of the substrate per unit area and unit time and are therefore a direct measure of the corrosion rate which is possible for any particular coating.

10 b) Weighing of the samples

The weighings provide information, furthermore, on the possibility to what extent the coating allows or does not allow the surface to be passivated. For this purpose the weight loss is converted into molarities and standardized for the area of the samples. The respective substrate given only an alkaline clean is used for comparison of the corrosion kinetics. Then the slopes from the ICP-OES data are shown, in comparison to the blank reference (untreated substrate) and other references.

Table 1: Results of the corrosion test

Substrate	ICP-OES data (10^{-4} *mol/l *h*cm ²)
Galvanized steel sheet (uncoated)	8.136
Galvanized steel sheet coated as per Example 3	4.580
Gardobond* 958 54 (reference)	6.171

The results of the corrosion tests clearly show the superiority of the coating material of the invention over a conventional corrosion control (reference).

* trademark

WHAT IS CLAIMED IS:

1. A two-stage process for the corrosion-control treatment of a metallic substrate, characterized in that:

(a) in a first stage, the substrate is immersed in a bath of a corrosion preventative K, which results in conversion at the substrate surface, the corrosion preventative K comprising at least one compound having as its cation a lanthanide metal and/or as its cation a d-element metal with the exception of chromium, and/or having as its anion a d-element metallate, with the exception of metallates containing chromium, and also at least one acid capable of oxidation, with the exception of
10 acids containing phosphorus and/or containing chromium, and

(b) in a second stage, the substrate treated as per stage (a) is immersed in an aqueous coating material EK for metallic substrates, comprising a water-dispersible and/or watersoluble polymer P having covalently bonded ligands A, which form chelates with the metal ions released during the corrosion of the substrate and/or with the substrate surface, and having crosslinking functional groups B, which are able to form covalent bonds with themselves, with further, complementary functional groups B' of the polymer P and/or with further functional groups B and/or B' on crosslinkers V,

the ligands A being selected from the group consisting of ureas, amines,
20 amides, imines, imides, pyridines, organosulphur compounds, organophosphorus compounds, organoboron compounds, oximes, acetylacetonates, acids, phytic acids, acetylenes, carbenes and mixtures thereof, and

the substrate being immersed in the baths of the coating materials K and EK in stages (a) and (b) for a time of 1 second to 15 minutes and at a temperature between 20 and 90°C.

2. The two-stage process for the corrosion-control treatment of metallic substrates according to claim 1, characterized in that the crosslinkers V comprise covalently bonded ligands A.

3. The two-stage process for the corrosion-control treatment of metallic substrates according to claim 1 or 2, characterized in that the polymer P and the crosslinker V comprise crosslinking groups B and/or B' which are crosslinkable thermally and/or by means of radiation.
4. The two-stage process for the corrosion-control treatment of metallic substrates according to any one of claims 1 to 3, characterized in that the polymer P comprises as its backbone one or more building blocks selected from the group consisting of polyesters, polyacrylates, polyurethanes, polyolefins, polyalcohols, polyvinyl ethers, polyvinylamines and polyalkyleneimine.
- 10 5. The two-stage process for the corrosion-control treatment of metallic substrates according to any one of claims 1 to 4, characterized in that, following the deposition of the coating materials K and EK, the substrate is aftertreated thermally at temperatures between 50 and 200°C and/or by irradiation.
6. The two-stage process for the corrosion-control treatment of metallic substrates according to any one of claims 1 to 5, characterized in that the substrate comprises at least 20% by weight of a metal selected from the group consisting of Fe, Al, Zn and mixtures thereof.