Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2440151 A1 2002/09/12

(21) 2 440 151

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) **Date de dépôt PCT/PCT Filing Date**: 2002/03/01
(87) **Date publication PCT/PCT Publication Date**: 2002/09/12
(85) **Entrée phase nationale/National Entry**: 2003/09/05
(86) **N° demande PCT/PCT Application No.**: EP 2002/002290
(87) **N° publication PCT/PCT Publication No.**: 2002/070782
(30) **Priorité/Priority**: 2001/03/06 (101 10 834.6) DE

(51) **Cl.Int.^{7}/Int.Cl.^{7}** C23C 22/18, C23C 22/36
(71) **Demandeur/Applicant**:
CHEMETALL GMBH, DE
(72) **Inventeurs/Inventors**:
KOLBERG, THOMAS, DE;
BITTNER, KLAUS, DE;
WENDEL, THOMAS, DE;
WIETZORECK, HARDY, DE;
SCHUELLERMANN, GERRIT, DE;
SPECHT, JUERGEN, DE;
RENGNET-FERRIER, SEVERINE, CA
(74) **Agent**: ROBIC

(54) **Titre** : PROCEDE DE REVETEMENT DE SURFACES METALLIQUES ET UTILISATION DES SUBSTRATS AINSI REVETUS
(54) **Title**: METHOD FOR COATING METALLIC SURFACES AND USE OF THE SUBSTRATES COATED IN THIS MANNER

(57) **Abrégé/Abstract**:

The invention relates to a method for coating metallic surfaces by a manganese-zinc phosphatizing process, using an aqueous phosphatizing solution, in which nickel is deliberately not added. Said method is characterized in that the zinc: manganese weight ratio of the phosphatizing solution is maintained in the region of between 0.05: 1 and 0.99: 1 and that the phosphatizing solution has the following contents: between 0.05 and 5 g/l zinc, between 0.075 and 5.2 g/l manganese and between 0.008 and 0.050 g/l copper and/or hexafluoride complexes of titanium, hafnium and/or zirconium totalling between 0.002 and 0.5 g/l, calculated as F_6. The invention also relates to the use of the metal parts coated in this manner.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
12. September 2002 (12.09.2002)

PCT

(10) Internationale Veröffentlichungsnummer
WO 02/070782 A2

(51) Internationale Patentklassifikation^7: **C23C 22/18**, 22/36

(21) Internationales Aktenzeichen: PCT/EP02/02290

(22) Internationales Anmeldedatum: 1. März 2002 (01.03.2002)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
101 10 834.6 6. März 2001 (06.03.2001) DE

(71) Anmelder *(für alle Bestimmungsstaaten mit Ausnahme von US)*: **CHEMETALL GMBH** [DE/DE]; Trakehner Strasse 3, 60487 Frankfurt (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder *(nur für US)*: **KOLBERG, Thomas** [DE/DE]; Veilchenweg 7, 64646 Heppenheim (DE). **RENGNET-FERRIER, Séverine** [FR/CA]; 3994 rue Saint Andre, Montreal, Québec H2L 3W1 (CA). **BITTNER, Klaus** [DE/DE]; Berger Strasse 329, 60385 Frankfurt (DE). **WENDEL, Thomas** [DE/DE]; Avrille Strasse 11, 65824 Schwalbach (DE). **WIETZORECK, Hardy** [DE/DE]; Werner-Bockelmann-Strasse 86, 65934 Frankfurt (DE). **SCHÜLLERMANN, Gerrit** [DE/DE]; Adalbert-Stifter-Strasse 25, 63477 Maintal (DE). **SPECHT, Jürgen** [DE/DE]; Albert-Schweitzer-Strasse 11, 63110 Rodgau (DE).

(74) Anwälte: UPPENA, Franz usw.; Dynamit Nobel Aktiengesellschaft, Patente Marken & Lizenzen, 53839 Troisdorf (DE).

(81) Bestimmungsstaaten *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Bestimmungsstaaten *(regional)*: ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:
— *ohne internationalen Recherchenbericht und erneut zu veröffentlichen nach Erhalt des Berichts*

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR COATING METALLIC SURFACES AND USE OF THE SUBSTRATES COATED IN THIS MANNER

(54) Bezeichnung: VERFAHREN ZUR BESCHICHTUNG VON METALLISCHEN OBERFLÄCHEN UND VERWENDUNG DER DERART BESCHICHTETEN SUBSTRATE

(57) Abstract: The invention relates to a method for coating metallic surfaces by a manganese-zinc phosphatizing process, using an aqueous phosphatizing solution, in which nickel is deliberately not added. Said method is characterized in that the zinc: manganese weight ratio of the phosphatizing solution is maintained in the region of between 0.05: 1 and 0.99: 1 and that the phosphatizing solution has the following contents: between 0.05 and 5 g/l zinc, between 0.075 and 5.2 g/l manganese and between 0.008 and 0.050 g/l copper and/or hexafluoride complexes of titanium, hafnium and/or zirconium totalling between 0.002 and 0.5 g/l, calculated as F_6. The invention also relates to the use of the metal parts coated in this manner.

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur Beschichtung von metallischen Oberflächen durch Mangan-Zink-Phosphatieren mit einer wässerigen Phosphatierungslösung, bei dem der Phosphatierungslösung kein Nickel absichtlich zugesetzt wird, das dadurch gekennzeichnet ist, daß das Zink : Mangan - Gewichtsverhältnis der Phosphatierungslö- sung im Bereich von 0,05 : 1 bis 0,99 : 1 gehalten wird und daß die Phosphatierungslösung folgende Gehalte aufweist: Zink im Bereich von 0,05 bis 5 g/L, Mangan im Bereich von 0,075 bis 5,2 g/L sowie Kupfer im Bereich von 0,008 bis 0,050 g/L oder/und insgesamt 0,002 bis 0,5 g/L an Hexafluoridkomplexen von Titan, Hafnium oder/und Zirkonium, berechnet als F6.Außerdem betrifft die Erfindung die Verwendung der derart beschichteten Metallteile.

WO 02/070782 A2

METHOD FOR COATING METALLIC SURFACES AND USE OF THE SUBSTRATES COATED IN THIS MANNER

The present invention relates to a process for coating metallic surfaces as well as the use of the substrates with metallic surfaces coated by the process according to the invention. This process is intended to serve as a pretreatment before a further coating, in particular paint application, or as a treatment without subsequent coating.

In zinc phosphating on galvanised substrates and in the subsequent painting, in particular with cathodic dipping paint, paint adhesion problems always arise, in which small or even relatively large parts of the overall paint structure may become detached and the paint can be removed without any difficulty. In a cross-hatch adhesion test total detachment can be detected in a part of the test body. In this connection the detachment normally occurs between the galvanised surface and the phosphate layer with the paint structure.

In the past these problems were circumvented on an industrial scale by adding nickel to the phosphating solution in an amount such that this generally had nickel contents in the range from 0.5 to 1.5 g/l. In zinc-manganese-nickel phosphating generally zinc contents were chosen in the range from 0.6 to 2 g/l and manganese contents were chosen in the range from 0.4 to 1 g/l, the zinc content normally being higher than the manganese content.

On account of the toxicity and environmental incompatibility, increased nickel contents in the phosphating solution, which lead to unavoidable high heavy metal contents in the waste water, in the phosphate slurry and in the grinding dust, are becoming increasingly less acceptable. Some attempts have therefore been made to operate with nickel-free or at least low nickel content phosphating solutions. These phosphating solutions have up to now still not been widely adopted however, and in addition have hitherto also continued to exhibit significant disadvantages compared to the high nickel content phosphating processes. When hitherto phosphating was carried out with low nickel contents in the automobile industry, problems arose on account of variable paint adhesion, with the result that these trials were not continued further.

Prephosphating has hitherto been used for galvanised steel strip material. Prephosphating is nowadays normally understood to denote a phosphating process in which metallic substrates are phosphated either without prior cleaning directly after the galvanising or are phosphated following a prior cleaning if no galvanising or a storage of optionally oiled substrates is chosen, and are then phosphated once more. Cutting and/or working of the substrates, forming, bonding to other parts that have optionally also been prephosphated, and/or welding of the substrates may take place between the prephosphating and the second phosphating (= post-phosphating). However, according to the applicant's knowledge up to now no prephosphating processes are known that can be carried out largely or completely free of nickel without significant loss of quality.

DE-A1-40 13 483 describes a process for the phosphating of metal surfaces with aqueous, acidic phosphating solutions that contain zinc, manganese, copper, phosphate and oxidising agents as well as only traces of nickel, in which the concentration of Fe^{2+} ions should be kept below 0.1 g/l. Copper contents in the range from 3 to 5 mg/l are mentioned in the examples. Serious problems may however arise with the phosphating solutions mentioned there on galvanised surfaces, while the quality of the tri-cation processes based on high nickel content Zn-Mn-Ni phosphating is achieved.

DE-A1-42 10 513 relates to a process for producing copper-containing, nickel-free phosphate layers by spraying and/or dipping with a phosphating solution that contains 0.2 to 2 g/l of zinc, 5 to 30 g/l of P_2O_5, 0.005 to 0.025 g/l of copper and 0.5 to 5 g/l of a compound based on hydroxylamine, calculated as HA, by means of which phosphate crystals are produced having an edge length in the range from 0.5 to 10 µm. Low pore content, compact phosphate layers with a low surface density, excellent corrosion resistance and very good paint adhesion are said to be produced in this way. All copper-containing embodiments either have a Zn:Mn ratio of > 1 or a high nickel content.

EP-A-0 675 972 describes a process for the production of copper-containing, largely nickel-free zinc phosphate layers with an aqueous composition, as well as the aqueous composition itself, which contains 0.026 to 0.074 g/l of copper, 0.45 to 2 g/l of zinc, 0.1 to 10 g/l of compounds based on hydroxylamine, calculated as HA, total acid values in the range from 5 to 40 points as well as free acid in the range from -0.5 to +0.8 point, and which may preferably contain total contents of up to 2 g/l of manganese and cobalt. This process is said to be more environmentally friendly and cheaper than the conventional nickel-containing phosphating processes, and coatings of the same quality as those produced by conventional ZnMnNi phosphating are said to be obtained. All copper-containing embodiments either have a Zn:Mn ratio of > 1 or even no manganese at all..

DE-A1-196 06 017 describes a process for the phosphating of metal surfaces with aqueous, acid phosphating solutions that contain specific contents of zinc but only traces of manganese and copper in addition to phosphate and at least one accelerator and also, as far as possible, only traces of nickel. No aqueous compositions with a Zn:Mn ratio of < 1 can be employed in this process.

DE-A1-196 34 685 discloses an aqueous solution for producing phosphate layers as well as the associated phosphating process, in which the phosphating solution is adjusted with zinc, phosphate, nitroguanidine as accelerator and with further additives so that phosphate crystals with a maximum edge length of < 15 µm are produced at comparatively low temperatures, and a low layer weight and a good paint adhesion are achieved. All copper-containing embodiments have a Zn:Mn ratio of > 1, or with a Zn:Mn ratio of < 1 have copper contents of only up to 0.005 g/l. The use of nitroguanidine as accelerator is however often disadvantageous, since with prolonged use of the phosphating bath - in some cases even after a day - in the presence of copper a bath poison is formed that seriously affects the layer formation on steel surfaces. If necessary the bath then has to be discarded and reconstituted.

In the manganese-zinc phosphating processes commonly used at the present time contents of zinc to manganese in the ratio of about 1.3:1 to 3:1 are normally used. It has now surprisingly been found that the paint adhesion was significantly improved if the weight ratio of zinc to manganese is less than 1:1.

The object of the invention is therefore to obviate the disadvantages of the prior art in a phosphating system free of added nickel and also to eliminate the serious paint adhesion problems, in particular on galvanised or zinc surfaces. In particular a process should be provided for coating galvanised surfaces that is as far as possible industrially suitable for coating individual parts as well as for coating strip material at high speeds. The phosphating process should be at least equivalent as regards corrosion resistance to the phosphating systems that are currently used for pretreatment or treatment, but should also be inexpensive and should be able to be used in an environmentally friendly manner, in particular largely free of nickel. The object consisted in particular of providing an industrially usable, largely nickel-free phosphating process for prephosphating.

This object is achieved by a process for the coating of metallic surfaces by manganese-zinc phosphating with an aqueous phosphating solution, in which no nickel is intentionally added to the phosphating solution, which process is characterised in that

the zinc:manganese weight ratio of the phosphating solution is maintained in the range from 0.05:1 to 0.99:1,

and that the phosphating solution has the following contents:

zinc in the range from 0.05 to 5 g/l,
manganese in the range from 0.075 to 5.2 g/l,
as well as
copper in the range from 0.008 to 0.050 g/l
and/or
a total amount of 0.002 to 0.5 g/l of hexafluoride complexes of boron, aluminium,

titanium, hafnium and/or zirconium, calculated as F_6.

It was surprisingly found that with phosphating solutions free of added nickel significantly better coating results can be achieved with a Zn:Mn ratio of less than 1:1 without the occurrence of the otherwise described problems of defective paint adhesion. The zinc:manganese weight ratio of the phosphating solution is preferably in the range from 0.5:1 to 0.9:1, in particular in the range from 0.65:1 to 0.8:1. Surprisingly the coating is of high quality over a very wide range of the zinc:manganese weight ratios of the phosphating solution. If however in very acidic solutions the zinc content drops below 0.2 g/l, the coating quality on high iron content surfaces may also fall.

The phosphating solution preferably has zinc contents in the range from 0.5 to 3.8 g/l, for strip material especially in the range from 1.6 to 3.5 g/l and for parts especially in the range from 0.6 to 2 g/l and particularly preferably in the range from 0.8 to 1.1 g/l. In the case of phosphating by spraying of parts a zinc content in the range from 0.3 to 1.3 g/l is often sufficient, whereas with dipping, zinc contents in the range from 0.7 to 1.9 g/l are necessary. For the prephosphating the zinc content is preferably in the range from 1.1 to 3.5 g/l. If the zinc content of the phosphating solution is too low, then the layer formation is incomplete, in particular on high iron content surfaces. With zinc contents of less than 0.4 g/l, in certain circumstances good coating results can no longer be expected in the case of parts, in particular on high iron content surfaces. With zinc contents greater than 2.5 g/l the paint adhesion may already deteriorate slightly, even if the manganese contents are only in the range from about 2.55 to 2.8 g/l. The smaller the zinc:manganese weight ratio, the more efficiently is this effect controlled, so that with zinc contents of greater than 3.5 g/l the paint adhesion may deteriorate slightly only with manganese contents in the range from about 3.55 to 3.8 g/l.

The term "zinc surfaces" within the context of the present invention includes not only the surfaces of zinc alloys, but also galvanised surfaces, in particular those of iron alloys and steel. Similarly, the terms "aluminium surfaces" include surfaces of aluminium and aluminium alloys, and "iron surfaces" include surfaces of high iron content alloys.

The manganese content of the phosphating solution is preferably in the range from 0.2 to 4 g/l, for strip material especially in the range from 1.7 to 3.0 g/l, and for parts in particular in the range from 0.5 to 3.8 g/l and particularly preferably in the range from 1 to 3 g/l. A significant improvement in the paint adhesion on the phosphated surfaces is achieved by an increased manganese content. For the prephosphating the manganese content is preferably in the range from 1.9 to 2.4 g/l.

The copper content is preferably in the range from 0.009 to 0.045 g/l, particularly preferably in the range from 0.010 to 0.040 g/l, and for strip material especially in the range from 0.012 to 0.25 g/l and for parts especially in the range from 0.012 to 0.030 g/l. For the prephosphating the copper content is preferably in the range from 0.008 to 0.048 g/l, particularly preferably in the range from 0.017 to 0.043 g/l. In the prephosphating experiments it was found that the results as regards corrosion protection and paint adhesion in the BMW paint structure improved continuously, starting from the poor results with copper-free phosphating solutions to the good results starting from 0.017 g/l of copper; it was also found however that these results may become worse again above about 0.040 to 0.043 g/l of copper.

In the resultant phosphate coating the copper content was generally found to be in the range from 5 to 35 mg/m^2. By adding minor amounts of copper better coating results and paint adhesion values can be obtained than without adding copper and also with very small additions of copper. In particular the corrosion resistance of an iron surface is improved by adding copper. Copper contents in the range from 0.020 to 0.050 g/l do not lead to poorer quality layers; however, higher copper contents in combination with too long a residence time of the substrates in the baths can result in a non-uniform deposition of copper on the surfaces to be phosphated.

The paint adhesion can be significantly improved by the addition of small amounts of titanium, hafnium and/or zirconium hexafluoride. These amounts are preferably in the range from 0.003 to 0.3 g/l, particularly preferably in the range from 0.004 to 0.1 g/l. However, in the case of aluminium surfaces these hexafluorides should generally be limited to values of up to 0.05 g/l - calculated as F_6 - since otherwise there may be a marked interference in the layer formation. In addition a content of silicon hexafluoride, in particular in the range from 0.5 to 4 g/l SiF_6 and preferably in the range from 1 to 3 g/l, may be advantageous in order to improve the homogeneity of the phosphate layer, in particular with zinc surfaces, and to stabilise the bath as regards zinc precipitation in the presence of free fluoride and thereby to ensure that the zinc contents remain dissolved in the bath.

Preferably the phosphating solution is free of additions of oxo anions of halogens, in particular of nickel, and of aluminium contents greater than 0.05 g/l. Even if no nickel is intentionally added to the phosphating solution, on account of the nickel content of the metallic surface of the substrate to be coated, on account of the possibly nickel-containing vessel materials and to a minor extent on account of trace impurities in the additives, the bath may have a nickel content of up to 0.1 g/l and in extreme cases, on account of very high nickel content metallic surfaces, even up to 0.25 g/l.

Whereas in the frequently employed nickel-containing phosphating in many cases 1 to 2 g/l of nickel are used in the phosphating, in the case of the copper-containing and largely or wholly nickel-free phosphating according to the invention it is possible to manage with only 0.008 to 0.050 g/l of copper. Whereas with the aforementioned nickel contents in the bath about 10 to 20 mg/m^2 of nickel and 0.7 to 1.3 wt.% of nickel are contained in the phosphate coating, despite the much lower copper contents in the phosphating solution about 5 to 35 mg/m^2 of copper and 0.3 to 2 wt.% of copper are found in the phosphate coating according to the invention.

The coating process according to the invention may be distinguished by the fact that the phosphating solution has a content of silver in the range from 0.0001 to 0.05 g/l, preferably in the range from 0.001 to 0.03 g/l.

In addition the phosphating solution may also contain contents of Fe^{2+} ions in the range of up to about 1 g/l, especially in the case of iron surfaces. Neither minor nor larger Fe^{2+} contents in the phosphating bath normally interfere in widely different metal surfaces.

In the coating process according to the invention the phosphating solution may have a content of sodium in the range from 0.01 to 10 g/l and/or a content of potassium in the range from 0.01 to 10 g/l, preferably a content of sodium in the range from 1 to 5 g/l, most particularly preferably in the range from 3 to 4 g/l. The addition of sodium is usually advantageous in order to reduce the levels of free acid. Furthermore the addition of sodium may help to precipitate, for example as cryolite, a part of the aluminium content in the phosphating solution, which depending on the circumstances can adversely affect the layer formation on steel and in some cases also the paint adhesion. Potassium is less recommended than sodium, not only on account of the somewhat higher costs but also, in certain circumstances, on account of the poorer coat properties.

In the coating process according to the invention the zinc:phosphate weight ratio of the phosphating solution may be maintained in the range from 0.016:1 to 1.33:1, phosphate being calculated as PO_4. Preferably this ratio is maintained in the range from 0.02:1 to 0.8:1, particularly preferably in the range from 0.025:1 to 0.25:1.

In the coating process according to the invention the phosphating solution may have a content of phosphate in the range from 3 to 75 g/l, phosphate being calculated as PO_4, preferably in the range from 7.5 to 37 g/l, particularly preferably in the range from 10 to 30 g/l, most particularly preferably in the range from 12 to 26 g/l, and in the case of strip material especially in the range from 17 to 21 g/l. For the prephosphating the phosphate content is preferably in the range from 12 to 18 g/l. If the weight ratio (zinc+manganese):phosphate is too high, then the bath may tend to become unstable unless the content of free acid is increased, failing which there may be a fairly marked precipitation of phosphate. If this weight ratio is too low, then the corrosion resistance and the paint adhesion may be impaired.

In the coating process according to the invention the phosphating solution may have a chloride content in the range from 0.01 to 10 g/l and/or a chlorate content in the range from 0.01 to 5 g/l, preferably a chloride content in the range from 0.1 to 6 g/l and preferably a chlorate content in the range from 0.1 to 3 g/l. An addition of chloride and possibly also chlorate or chlorate alone in specific amounts should be avoided in the phosphating of zinc surfaces on account of the danger of the formation of white spots (specks), if nitrate and/or nitrite are present.

Since aluminium contents from aluminium or aluminium-zinc surfaces may be a problem without the presence of fluoride, it is accordingly advantageous to add free fluoride, for example as HF or as sodium bifluoride, and/or silicon hexafluoride. Silicon hexafluoride can stabilise the phosphating solution, i.e. reduce the precipitation of phosphates, and can also reduce the formation of specks in zinc surfaces.

In the coating process according to the invention the phosphating solution may have a content of free fluoride in the range from 0.001 to 0.8 g/l, preferably in the range from 0.01 to 0.5 g/l, particularly preferably in the range from 0.03 to 0.2 g/l, calculated as F. A content of free fluoride may be beneficial for the phosphating of aluminium surfaces and for the precipitation of aluminium. Typically about 1 to 60% of the total fluorine content is present in the form of free fluoride and the remainder is present as complex fluoride and as unassociated hydrofluoric acid.

In the coating process according to the invention the phosphating solution may have a content of total fluoride in the range from 0.01 to 5 g/l, preferably in the range from 0.1 to 1 g/l, calculated as F.

In the coating process according to the invention the phosphating solution may have a content of at least one accelerator in the range from 0 to 40 g/l, preferably in the range from 0.02 to 30 g/l, particularly preferably in the range from 0.1 to 20 g/l. The accelerator may help to suppress the formation of hydrogen bubbles on the surfaces. Due to the better contact with the surface to be coated - since this is not partially covered by hydrogen bubbles - more crystal nuclei can be formed there. The presence of an accelerator is not absolutely essential, especially in the case of zinc surfaces. An accelerator is however of considerable advantage, generally in the case of aluminium, iron and steel surfaces, since in this way the phosphate layer can be produced in a finely crystalline form because the phosphate layer can thereby be sealed more quickly and easily and because the corrosion protection and the paint adhesion can be improved in this way.

In the coating process according to the invention the phosphating solution may have a nitrite content in the range from 0.01 to 0.3 g/l, a nitrate content in the range from 1 to 30 g/l, a content of compounds based on peroxide in the range from 0.001 to 3 g/l, preferably in the range from 0.01 to 0.15 g/l, calculated as H_2O_2, a content of nitrobenzenesulfonate (NBS), nitropropane, nitroethane and/or other nitro-organic compounds with oxidising properties - with the exception of compounds based on nitroguanidine - with a total content in the range from 0.1 to 3 g/l calculated as NO_2, a content of compounds based on nitroguanidine in the range from 0.1 to 5 g/l, a chlorate content preferably in the range from 0.05 to 4 g/l, a content of reducing sugar compounds in the range from 0.1 to 10 g/l and/or a content of compounds based on hydroxylamine (HA) in the range from 0.1 to 6 g/l, calculated as HA. Chlorate additions are normally used in nitrite-free and nitrate-free baths if zinc surfaces are to be coated. For the prephosphating the nitrate content is preferably in the range from 12 to 19 g/l. If low nitrate contents or even nitrate-free solutions are used in the prephosphating, then an addition of 0.5 to 3 g/l of peroxide, calculated as H_2O_2, is preferred.

Preferably the phosphating solution has a content of nitrite in the range from 0.05 to 0.2 g/l. Although nitrite, like the nitrogen-containing gases that may possibly be formed therefrom, has the disadvantage that it is extremely toxic, nitrite has the advantage that it is inexpensive and its action is very well known and can be effectively controlled. Preferably the phosphating solution has a content of nitrate in the range from 5 to 25 g/l. On account of the weak action of this accelerator higher contents of nitrate are often employed. Preferably the phosphating solution has a content of compounds based on peroxide in the range from 0.01 to 0.1 g/l. Preferably the phosphating solution has a total content of nitrobenzenesulfonate and/or other nitro-organic compounds with oxidising properties in the range from 0.5 to 2 g/l. Preferably the phosphating solution has a content of compounds based on hydroxylamine in the range from 0.5 to 2 g/l. Preferably the ratio of the contents of compounds based on hydroxylamine, calculated as HA, to the sum total of zinc and manganese in the phosphating solution is in the range from 1:2 to 1:4. However, in certain circumstances hydroxylamine may be catalytically decomposed in the presence of a specific copper content.

At least one compound based on perboric acid, lactic acid, tartaric acid, citric acid and/or a chemically related hydroxycarboxylic acid may advantageously be added in order to stabilise the bath, the concentrate or the replenishment solution, in particular to prevent or reduce precipitations from one of these solutions, as well as to increase the crystallinity of the phosphate layer, whereby the water resistance of the phosphate layer is substantially improved.

Furthermore, an addition of a polymeric alcohol may also be advantageous in order to form phosphoric acid esters with this alcohol, especially during the drying, which have a beneficial effect as lubricants in forming. At the same time the addition of a polymeric alcohol may affect the reaction with the excess free phosphoric acid that is possibly present in the phosphating solution, by improving the crystallinity and the water resistance of the phosphate coating.

It was surprisingly found that the prephosphating using copper-containing phosphating solutions with a Zn:Mn weight ratio of less than 1:1 leads to extremely good paint adhesion results, in particular on galvanised surfaces, if post-phosphating was carried out wholly or largely nickel-free after the prephosphating and before the painting. It was also surprisingly found that, due to the almost complete absence of nickel, the good results of a nickel-containing prephosphating layer as regards corrosion protection, formability, bondability and weldability are retained, and in the case of formability however lead to even better results. The prephosphating is particularly suitable for the implementation of a rinse phosphating by spraying and/or dipping with spraying/dipping times approximately in the range from 3 to 15 seconds and at a temperature in the range from 45° to 65°C, particularly with galvanised surfaces.

The prephosphating is particularly suitable for the production of strip material by rinse processes, in which rinsing is performed after the application of the phosphate layer. This process is suitable in particular for automobile production.

In the coating process according to the invention the phosphating solution for the prephosphating may contain the following amounts:

zinc in the range from 0.4 to 5 g/l,
manganese in the range from 0.5 to 5.2 g/l,
copper in the range from 0.008 to 0.050 g/l.

If prephosphating, in particular prephosphating according to the invention, is carried out, then post-phosphating according to the invention may also be carried out in the following way, in which first of all prephosphated, optionally at least partially formed/shaped and optionally at least partially welded metallic substrates are phosphated by manganese/zinc phosphating with an aqueous phosphating solution in which no nickel is intentionally added to the phosphating solution or the phosphating solution only has a nickel content of up to 0.3 g/l, which is characterised in that

the phosphating solution contains the following amounts:
zinc in the range from 0.05 to 5 g/l and
manganese in the range from 0.075 to 5.2 g/l.

The coating results and corrosion protection results that were obtained are outstanding, especially with zinc-containing surfaces.

In the coating process according to the invention the phosphating solution may have the following contents, in particular for parts:

zinc in the range from 0.6 to 1.4 g/l,
manganese in the range from 0.7 to 2.0 g/l,
zinc:manganese weight ratio in the range from 0.6:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 12 to 25 g/l,
zinc:phosphate weight ratio in the range from 0.02 to 0.12,
copper in the range from 0.008 to 0.025 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex

fluoride, in the range from 0 to 6 g/l, calculated as F,
wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l calculated as SiF_6, and
nitrate in the range from 0 up to 22 g/l and/or at least one other accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

In the coating process according to the invention the phosphating solution may have the following contents, in particular for strip material, particularly preferably for galvanised strip surfaces:

zinc in the range from 0.1 to 4 g/l,
manganese in the range from 0.5 to 5 g/l,
zinc:manganese weight ratio in the range from 0.02:1 to 0.9:1,
phosphate calculated as PO_4 in the range from 10 to 40 g/l,
zinc:phosphate weight ratio in the range from 0.0025 to 0.4,
copper in the range from 0.008 to 0.032 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride in the range from 0 to 6 g/l, calculated as F,
wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 up to 22 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

In the coating process according to the invention the phosphating solution for the prephosphating may preferably have the following contents:

zinc in the range from 1.3 to 2.3 g/l,
manganese in the range from 1.7 to 2.6 g/l,
zinc:manganese weight ratio in the range from 0.5:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 10 to 20 g/l,
zinc:phosphate weight ratio in the range from 0.06 to 0.23,
copper in the range from 0.008 to 0.048 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride in the range from 0 to 6 g/l, calculated as F,
wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 up to 30 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds based on hydroxylamine and/or nitroguanidine, in each case in the range from 0.01 to 2 g/l, or peroxide in the range from 0.01 to 3 g/l.

In this connection the nitrate content, if nitrate is added as accelerator, is preferably in the range from 3 to 22 g/l, and the content of at least one compound based on peroxide is in the range from 0.5 to 2.5 g/l, especially if a nitrate-free process is used.

In the coating process according to the invention the phosphating solution may also preferably have the following contents:

zinc in the range from 0.6 to 1.4 g/l,
manganese in the range from 0.7 to 2.0 g/l,
zinc:manganese weight ratio in the range from 0.6:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 12 to 25 g/l,
zinc:phosphate weight ratio in the range from 0.02 to 0.12,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride in the range from 0.012 to 6 g/l calculated as F,
wherein the total content of complex fluorides of titanium, hafnium and/or zirconium is in the range from 0.002 to 0.5 g/l, calculated as F_6, and wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 up to 22 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

In the coating process according to the invention the metallic substrates may be coated for a time of up to 20 minutes, strip material preferably being coated for a time ranging from 0.1 to 120 seconds and particularly preferably for a time ranging from 0.3 to 60 seconds, and parts preferably being coated for a time ranging from 1 to 12 minutes and particularly preferably for a time ranging from 2 to 8 minutes.

In the coating process according to the invention the temperature of the phosphating solution for the coating may be in the range from 10° to 72°C, for strip material preferably in the range from 40° to 70°C and for parts preferably in the range from 20° to 60°C and particularly preferably in the range from 32° to 58°C.

In the coating process according to the invention the free acid level may be from 0.1 to 10 points, the total acid may be from 5 to 50 points, the total acid according to Fischer may be from 3 to 25 points, and the ratio of the free acid to total acid according to Fischer (S value) may in particular be in the range from 0.01 to 0.7, wherein the concentration of free acid is preferably 0.15 to 4 points, the concentration of total acid according to Fischer is preferably 12 to 35 points and the ratio of the free acid to total acid according to Fischer (S value) is preferably in the range from 0.03 to 0.3. For the prephosphating it is particularly preferred to have values of the free acid in the range from 3 to 4.4 points and values of the total acid according to Fischer in the range from 18.5 to 21 points and thus an S value in the range from 0.14 to 0.24.

In order to determine the free acid 1 ml of the phosphating solution, after dilution to ca. 50 ml with distilled water and optionally with the addition of $K_3(Co(CN)_6)$ or of $K_4(Fe(CN)_6)$ in order to remove interfering metal cations, is titrated with 0.1 M NaOH using dimethyl yellow as indicator until the colour turns from pink to yellow. The amount of 0.1 M NaOH used in ml represents the value of the free acid (FA) in points.

The total content of phosphate ions is determined following the measurement of the free acid, by titrating the titration solution after addition of 20 ml of 30% neutral potassium oxalate solution, with 0.1 M NaOH using phenolphthalein as indicator until the colour turns from colourless to red. The consumption of 0.1 M NaOH in ml between the colour change with dimethyl yellow and the colour change with phenolphthalein corresponds to the total acid according to Fischer (TAF). If this value is multiplied by 0.71, the total content of phosphate ions is obtained (see W. Rausch: "Die Phosphatierung von Metallen", Eugen G. Leuze-Verlag 1988, pp. 300 ff).

The so-called S value is obtained by dividing the value of the free acid by the value of the total acid according to Fischer.

The total acid (TA) is the sum total of the contained divalent cations as well as free and bound phosphoric acids (the latter being phosphates). The total acid is determined from the consumption of 0.1 M sodium hydroxide using phenolphthalein as indicator. This consumption in ml corresponds to the point value of the total acid.

In the coating process according to the invention the pH of the phosphating solution may be in the range from 1 to 4, preferably in the range from 2.2 to 3.6.

In the coating process according to the invention the phosphating solution may be applied to the surface of the substrates by knife coating, flow coating, spraying, sprinkling, brushing, dipping, nebulising or rolling, individual process steps being able to be combined with one another - in particular spraying and dipping, spraying and squeezing off as well as dipping and squeezing off, and optionally subsequent squeezing off.

In the coating process according to the invention substrates with a metallic surface predominantly containing aluminium, iron, copper, magnesium, tin or zinc, in particular surfaces of at least one of the materials based on aluminium, iron, steel, zinc and/or alloys with a content of aluminium, iron, copper, magnesium, tin or zinc, can be coated with the phosphating solution.

In the coating process according to the invention a phosphate coat can be precipitated from the phosphating solution that has a layer weight in the range from 0.2 to 6 g/m^2, preferably in the range from 1 to 4 g/m^2. Particularly in the case of aluminium surfaces it may be desirable in some cases to apply only very low layer weights. In the pretreatment or treatment of surfaces of aluminium or aluminium alloys it is not absolutely essential to achieve a high degree of covering in the phosphating process. A layer weight of the phosphate layer in the range from 0.2 g/m^2 to 1 g/m^2 is sufficient. A layer weight of up to 6 g/m^2 and thus a complete covering is however not disadvantageous, apart from an increased consumption of chemicals. With surfaces of iron, steel and zinc an almost complete or complete covering with the phosphate layer is however necessary. This is achieved with a layer weight in the range from 1 g/m^2 to 6 g/m^2. In the prephosphating a layer weight in the range from 0.8 to 2.4 g/m^2 is particularly preferred, especially 1 to 2 g/m^2, in particular if the substrates with the prephosphate coating are to be used for welding.

In the coating process according to the invention metallic surfaces may be cleaned, pickled, rinsed and/or activated before the phosphating. The cleaning is preferably carried out with an alkaline agent and takes place in particular over a time ranging from 10 seconds to 15 minutes. A weak alkaline cleaning agent may be employed for metallic surfaces, in most cases over 2 to 4 minutes. The treatment times are correspondingly shorter for strong alkaline cleaning agents. It may be advantageous to add a titanium-containing activator to the cleaning agent. An acidic cleaning may also be chosen in particular for aluminium and aluminium alloys.

In principle any water of sufficiently pure quality is suitable for the subsequent rinsing. Tap water is recommended. If the activation can take place in a separate bath or rinsing step, which is most advantageous, then fully deionised water should be used as solvent after prior rinsing. An activation is often very advantageous in order to form crystal seeds. The activation may in particular be based on titanium. An activation over 10 to 30 seconds is often sufficient, although in principle the activation time may range from 0.1 second up to at least 5 minutes. The activation may also be longer than 5 minutes, though this does not have any beneficial effect. It may be advantageous to add copper and/or one of the additives known in principle to the activation.

In the coating process according to the invention the phosphated substrates may be rinsed at least once and optionally treated after a rinse procedure or between two rinse procedures, with a post-rinse solution to confer additional passivation. In principle any water of sufficiently pure quality is suitable for the rinsing after the phosphating. Tap water or fully deionised water is recommended - for example dipping in cold tap water for 10 seconds - followed in the next rinse step by fully deionised water - for example spraying with cold, fully deionised water for 10 seconds. In the post-rinsing an addition of for example zirconium hexafluoride or of one of the organic substances known in principle may be employed, whereby a further improvement in the corrosion resistance and paint adhesion of the coating may be achieved.

In the coating process according to the invention the metallic surfaces can be prephosphated before the phosphating. The prephosphating of substrates is advantageous if for example the prephosphated strip is subsequently formed/shaped or if parts are intermediately stored, bonded and/or welded in the corrosion-protected state. The substrates pretreated in this way can thereby be much more easily formed/shaped and are protected against corrosion. In a particularly advantageous process variant the metallic surfaces are welded, bonded and/or formed/shaped after the phosphating (prephosphating) and are then optionally rephosphated.

In most cases the phosphating plants in the automobile industry use weakly alkaline cleaning agents, but in some cases also strongly alkaline cleaning agents. It was surprising that the first crystalline prephosphating layer according to the invention is substantially more resistant to the influence of strongly alkaline cleaning agents. With the short treatment times that are normally employed, the first phosphate layer according to the invention was not or was only slightly affected by a strong alkaline cleaning agent.

The first and/or second phosphate layer applied to the metal part may be wetted with an oil, a dispersion or a suspension, in particular with a forming oil or anti-corrosion oil and/or with a lubricant such as a dry lubricant, for example with a wax-containing mixture. The oil or the lubricant serves as additional temporary corrosion protection and may in addition also facilitate a forming procedure, the unformed metal part also having an increased corrosion resistance. A coating with an oil may also be of benefit for the second phosphate layer if the parts to be painted have to be transported to a distant paint shop.

Any oil layer or lubricant layer that is present can be removed from the first or second phosphate layer in order to prepare the coating for painting, forming, assembly, bonding or welding. The oil must be removed before a subsequent paint coat, though it does not necessarily have to be removed for other process procedures.

The metal parts provided with a first and/or second phosphate layer may be painted, coated with another type of organic coating and/or with an adhesive layer, and then optionally formed/shaped, wherein the metal parts coated in this way may in addition be bonded and/or welded to other parts. At the present time a very wide range of organic coatings are known that can be used on a phosphate layer. In this connection not all organic coatings are covered by the definition of paints. The metal parts provided with a first and/or second phosphate layer may be provided with a coating either before or only after the forming and/or assembly.

The phosphate-coated metal parts according to the invention may if necessary be oiled in a so-called strip plant or may if necessary be degreased and/or cleaned, before they are subsequently coated in a paint shop.

The phosphate-coated metal parts according to the invention may if necessary be oiled for the production of for example equipment linings, may if necessary be formed/shaped and may if necessary may be degreased and/or cleaned, before they are subsequently - if desired - coated in a paint shop. For economic reasons the deoiling is preferably omitted before the bonding or welding.

The phosphate-coated metal parts according to the invention may be oiled and formed/shaped for the production of for example automobiles, in which connection several metal parts are then welded together, bonded together or joined together in some other way, following which the assembled parts can be degreased and/or cleaned before they can subsequently be coated in a paint shop.

The metal parts coated by the process according to the invention may, as prephosphated metal parts, for a renewed conversion treatment or for a renewed conversion pretreatment, in particular before being painted, or, as pretreated metal parts - in particular for the automobile industry - especially before being painted or as end-phosphated metal parts that are optionally also subsequently painted, organically coated in some other way and/or coated with a film, be coated with an adhesive layer, formed/shaped, assembled and/or welded together. However, a normal precondition for welding is that the phosphate layer is not too thick and that any organic coating that optionally is applied is electrically conducting.

In the coating process according to the invention the metal parts provided with a first and/or second phosphate layer may be coated with a paint, with another type of organic coating, with a film and/or with an adhesive layer and if necessary formed/shaped, wherein the metal parts coated in this way may in addition be bonded or welded to other parts and/or may be joined to one another in a some other way.

Also a mix of various materials such as for example metal parts formed from uncoated steel and prephosphated metal parts can be coated next to one another at the same time by a process according to the invention without any problem.

In the case of pre-assembled or assembled metal parts a better corrosion protection than according to the aforementioned prior art can be achieved in hollow spaces and cavities by the prephosphating, even without application of a paint coat.

It may be advantageous to apply a passivating solution directly to the first and/or second phosphate layer, in particular by spraying, dipping or rolling. In this case a post-rinse solution is preferably used to further enhance the corrosion resistance and the paint adhesion, which solution may contain at least one substance based on Cr, Ti, Zr, Ce and/or other rare earth elements including lanthanum or yttrium, tannin, silane/siloxane, phosphorus-containing self-assembling molecules, phosphonates or polymers.

On comparing various types of metallic surfaces, such as for example those of cold-rolled steel (CRS) and galvanised steels, the same phosphating solution produces significantly different results in some cases. With hot-dip galvanised steels (HDG) and with electrolytically galvanised steels (EG) the zinc that can dissolve out from the galvanising has a marked effect on the bath composition. With HDG steels the content of aluminium in the HDG surface in certain circumstances has a negative effect: in order to optimise the phosphating in the case of HDG steels and aluminium surfaces an addition of fluorides in free and/or bound form, for example as hydrofluoric acid or silicon hexafluoride, is then favourable.

Surprisingly the coating according to the invention is equivalent as regards corrosion resistance and paint adhesion to a comparable high nickel content coating, but is significantly cheaper and significantly more environmentally friendly than the high nickel content coating. In this connection it is especially surprising that the high-grade coating quality is largely independent of the chosen accelerator or accelerator mixture. The coating process according to the invention is also unexpectedly robust. Furthermore, it was extremely surprising that the same high-grade properties could be achieved by a Zn:Mn ratio in the very wide range from 0.9:1 to 0.3:1. Moreover, the same high-grade properties could be obtained also outside this range provided the composition of the bath was suitably adapted.

The process according to the invention has the advantage compared to the aforedescribed and implemented processes that it provides excellent coatings with low consumptions of chemicals and comparatively low costs, in particular of HDG, and is in this connection particularly environmentally friendly. On account of the fact that no nickel is added in this process, fewer heavy metals are discharged into the waste water, phosphate slurry and in the grinding dust. In contrast to similar baths, it is possible to reduce the bath temperature still further during the phosphating. On account of a slightly raised copper content the paint adhesion can be improved still further.

A concentrate for making up the phosphating solution or a replenishment solution for replenishing the phosphating solution may contain in particular zinc, manganese, copper and phosphoric acid, but only in certain cases alkalis and/or accelerators.

The substrates coated by the process according to the invention may be used for strip production, for the production of components or car body parts or preassembled elements in the automobile or aerospace industry, in the building and construction industry, in the furniture industry, for the production of instruments and units, in particular domestic appliances, measuring instruments, control devices, testing devices, structural components, claddings/ linings as well as small parts; as wire, wire coiling, wire mesh, metal sheeting, cladding/lining, screening, car bodies or parts of car bodies, parts of vehicles, trailers, mobile homes or missiles, as electronic or microelectronic components, as coverings, housings, lamps, lights, hanging light units, items of furniture or furniture parts, components of domestic appliances, frames, profiled sections, moulded parts of complicated geometry, beam-barrier, radiator or sauna parts, automobile bumpers, parts of or with at least one pipe and/or a profiled section, window, door or bicycle frames, or as small parts such as for example screws, nuts, flanges, springs or spectacle frames.

Examples:

The subject matter of the invention is illustrated in more detail with the aid of embodiments:

The examples were carried out using the substrates and process steps itemised hereinafter:

The test sheets consisted of an aluminium alloy AlMgSi of thickness 1.2 mm or of uncoated, continuously annealed car body steel (CRS) or of steel galvanised on both sides with a coating of a hot-dip galvanising (HDG) or of an electrolytic galvanising (EG) with a total thickness of 0.7 mm. The surface area of the substrates was 400 cm^2 (measured over both surfaces).

a) The substrate surfaces were cleaned and thereby thoroughly degreased in a 2% solution of an alkaline cleaning agent for 5 minutes at 60°C.

b) This was followed by rinsing with tap water for 0.5 minute at room temperature.

c) The surfaces were then activated by dipping in a titanium-containing activation solution for 0.5 minute at room temperature.

d) The surfaces were then phosphated for 3 minutes at 55°C by dipping in the phosphating solution.

e) The surfaces were next rinsed, first of all with tap water and then with fully deionised water.

f) The coated substrates were then dried in a drying oven at 80°C for 10 minutes.

g) Finally the dry test sheets were provided with a coat of a cathodic dipping paint and coated with the further layers of a paint structure conventionally used in the automobile industry for car body parts (layer structure and paints corresponding to Daimler Chrysler in "Moon Silver").

The composition of the relevant phosphating solution as well as the results of the tests are shown in Tables 1 to 3.

Table 1: Composition of the phosphating solutions in g/l or points of free acid (FA) or total acid (TA)

	Zn	Mn	Ni	Cu	TiF6 + ZrF6 **	PO_4	NO_2	NO_3	HA etc.	FA	TA
B 1	1.2	1.25	-	0.008	-	16.5	0.1	-	-	1.8	32
B 2	1.2	1.5	-	0.008	-	18	0.1	3	-	1.8	32
B 3	1.2	2.5	-	0.008	-	18	0.1	3	-	1.8	32
B 4	1.4	2.5	-	0.010	-	16.5	-	3	0.04 H_2O_2	1.8	32
B 5	1.4	1.5	-	0.015	-	16.5	-	5	1.5 HA	1.8	32
B 6	1.4	2.5	-	0.015	-	16.5	-	5	1.5 HA	1.8	32
B 7	1.4	1.5	-	0.025	-	16.5	-	5	1.5 HA	1.8	32
B 8	1.4	2.5	-	0.025	-	16.5	-	5	1.5 HA	1.8	32
B 9	1.4	1.5	-	0.040	-	16.5	-	5	1.5 HA	1.8	32
B 10	1.4	2.5	-	0.040	-	16.5	-	5	1.5 HA	1.8	32
B 11	1.2	1.8	-	-	0.003+ 0.002	18	-	3	1.5 HA	1.8	32
B 12	1.2	1.8	-	-	0.006+ 0.005	18	-	3	1.5 HA	1.8	32
B 13	1.2	1.8	-	-	0.056+ 0.045	18	-	3	1.5 HA	1.8	32
B 14	1.2	1.8	-	-	0.011+ 0.008	18	-	3	1.5 HA	1.8	32
B 15	1.2	1.8	-	0.008	0.003+ 0.002	18	-	3	1.5 HA	1.8	32
B 16$^+$	1.2	1.95	-	0.008	0.003 (Ti)	18.8	-	-	1.1 HA	3.4	32
B 17$^+$	1.2	1.95	-	0.008	0.004	18.8	-	-	1.1 HA	3.4	32

	Zn	Mn	Ni	Cu	TiF6 + ZrF6 **	PO_4	NO_2	NO_3	HA etc.	FA	TA
					(Zr)						
B 18	1.4	3.5	-	0.015	-	16.5	-	5	1.5 HA	1.8	32
B 19	1.2	1.3	-	-	0.006+ 0.005	18	-	3	1.5 HA	1.8	32
B 20	1.2	2.5	-	-	0.006+ 0.005	18	-	3	1.5 HA	1.8	32
VB 1	1.2	0.5	-	0.005	-	18	0.1	3	-	1.8	32
VB 2	1.2	0.5	-	0.005	-	16.5	0.1	3	-	1.8	32
VB 3	1.2	0.8	-	0.005	-	18	0.1	3	-	1.8	32
VB 4	1.2	1.0	1.0	-	-	18	0.1	3	-	1.8	32
VB 5	2.5	2.0	-	0.008	-	18	-	3	1.5 HA	1.8	32
VB 6	1.2	1.0	-	-	-	18	0.1	3	-	1.8	32
VB 7	1.4	2.5	-	0.002	-	18	0.1	3	-	1.8	32
VB 8$^+$	1.2	1.95	-	0.005	-	18.8	-	-	1.1 HA	3.4	32

"-" denotes without addition of an additive
"**" denotes calculated as F_6
"+" denotes a content of 3 g/l SiF_6 and 0.13 g/l SO_4

In addition the baths contained a minor amount to a certain amount of sodium as well as, for the pretreatment of aluminium surfaces, an amount of free fluoride in the range from 80 to 250 mg/l by addition of ammonium bifluoride. The total acid is given approximately.

Table 2: Results of the adhesion and corrosion tests on aluminium, steel or galvanised surfaces, on coatings produced according to the invention (B) or in comparison examples (VB), obtained by

1. cross-hatch adhesion test according to DIN/EN ISO 2409 after storage for 40 hours in 5% NaCl solution (BMW specification),

2. stone impact test over 12 cycles according to VW specification, and

3. salt spray/condensation water alternating test over 12 cycles according to VDA 621-415. A= ground, B = unground.

	cross-hatch adhesion test				Stone Impact Test acc. to VW			Alternating Test acc. to VDA 621-415			
	Score				% Paint Loss			mm Creep			
	CRS	EG.	HDG	Al	CRS	EG	HDG	CRS	EG	HDG	Al
				A/B							
B 1	1	1	1	1.1	-	-	-	-	-	-	-
B 2	1	1	1	1.1	-	-	-	-	-	-	-
B 3	1	1	1	1.1	-	-	-	-	-	-	-
B 4	1	1	1	1.1	2	5	8	0.5	2.0	1.8	-
B 5	1	1	2.5	1.1	3	10	10	0.5	2.5	2.0	-
B 6	1	1	1	1.1	3	6	12	0.5	2.0	1.5	-
B 7	1	1	2	1.1	5	10	15	0.5	2.0	1.7	-
B 8	1	1	0	1.1	4	5	6	0.5	2.0	1.5	-
B 9	1	1	1.5	1.1	5	8	10	0.5	2.5	2.0	-
B 10	0	0	0	1.1	3	4	5	0.5	2.0	1.3	-
B 11	1	1	1	1.1	-	-	-	-	-	-	-
B 12	1	0	1	1.1	-	-	-	-	-	-	-
B 13	0	0	1	2.1	-	-	-	-	-	-	-
B 14	0	1	1	1.1	-	-	-	-	-	-	-
B 15	1	1	1	1.0	-	-	-	-	-	-	-
B 16	-	-	0.5	-	-	-	-	-	-	-	-
B 17	-	-	2.5	-	-	-	-	-	-	-	-
B 18	1	1	0	1.1	4	5	6	0.5	2.0	1.5	-
B 19	1	1	2	1.1	-	-	-	-	-	-	-
B 20	1	0	0	1.1	-	-	-	-	-	-	-
VB 1	1	4	3	1.1	4	80	100	0.5	2.5	3.0	-
VB 2	1	4	4	-	8	60	35	1.5	2.0	2.5	-
VB 3	1	3	4	1.1	3	80	25	0.5	2.5	2.4	-
VB 4	1	1	1	1.1	3	4	8	0.5	2.0	1.2	-

VB 5	1	3	4	1.1	10	80	50	2.0	3.5	4.0	-
VB 6	1	3	5	2.1	10	70	90	2.2	3.5	3.5	-
VB 7	1	2	2	1.1	4	8	18	1.0	2.5	2.0	-
VB 8	-		3.8	-	-	-	-	-	-	-	-

In the cross-hatch adhesion test the scores ranged from 0 to 5 for the best and for the worst results respectively. In the stone impact test the percentage paint loss through the layer structure down to the metallic substrate surface is given in area %, while for the salt spray/ condensation water alternating test the corrosive creep of the paint starting from a scratch is given in mm. In all tests the results are mean values over in each case several tested sheets.

In the tests it was found that for all the results given in Table 2, the results of the examples according to the invention were better with an increasing copper content or with a lower Zn:Mn ratio of the copper-containing examples. The same is also true for an increasing hexafluoride content in titanium/zirconium/hafnium and for a reduced Zn:Mn ratio of the copper-free examples. The combination of the copper content with the hexafluoride content in titanium/zirconium/hafnium indicates, at least for the content of titanium hexafluoride, a significantly better improvement in the paint adhesion results, which were tested on the basis of the metal surface (HDG) that behaved most badly. The results vary only slightly however, depending on the type of metal surfaces.

Table 3: Results of the corrosion tests on coatings obtained according to the invention (B) and obtained in

the comparison examples (VB) on the aluminium alloy AlMgSi and on thoroughly annealed steel (CRS) by

1. Filiform test according to DIN EN 3665,

2. salt spray/condensation water alternating test over 12 cycles according to VDA 621-415, and

3. salt spray test according to DIN 50021 for steel,

the following letters identifying the processing state:

A = ground, B = unground

	Filiform Test		Salt Spray/ Humidity Cycle Test		Salt Spray Test
	mm Creep		mm Creep		mm Creep
	AlMgSi				CRS
	A	B	A	B	B
B 1	3.8	3.5	2.5	1.5	<1
B 2	5.0	3.1	1.8	1.2	<1
B 3	5.3	1.3	1.8	0.3	<1
B 5	6.5	3.0	3.5	0.75	<1
B 6	6.0	4.0	4.0	0.5	<1
B 7	6.5	3.0	3.5	1.0	<1
B 8	5.7	1.3	1.75	0.5	<1
VB 1	4.5	43.3	2.2	1.5	<1
VB 2	-	-	-	-	1.5
VB 3	6.1	5.2	3.3	1.0	<1
VB 4	4.0	2.5	2.0	1.0	<1

In the filiform test the mean value of the size of the filiform corrosion phenomena in mm was measured. In the salt spray/condensation water alternating test and in the salt spray test according to DIN 50021 on steel the corrosive creep of the paint starting from a scratch was given in mm on base metal. In all tests the results are mean values over in each case several tested sheets.

Since individual sites of such sheets are still always reground in industrial coating, i.e. individual ground parts occur between the largely unground surfaces, this comparison is significant for practical purposes.

In this connection it was found that when the aluminium alloy was tested by the filiform test, the expected reliability was not obtained, whereas in the salt spray/condensation water alternating test in some cases even better results were obtained in the samples coated according to the invention than in the nickel-containing phosphating.

Overall, the quality of the high nickel content phosphatings was obtained with the tests of Table 2 and Table 3.

It was also found that the layer weight of the HDG sheets coated according to the invention was almost constant, in the range from 2.0 to 2.1 g/cm^2 with a manganese content in the range from 1 to 2.5 g/l, and was almost exactly 1.0 g/cm^2 with a copper content in the range from 5 to 20 mg/l.

In the <u>prephosphating</u> on the one hand compositions with a nitrate acceleration (B 21 - B 23) and on the other hand with a nitrate-free peroxide acceleration (B 24 - B 26) were successfully tested and compared to a nickel-free prephosphating and to a very low copper content or high nickel content phosphating (VB 26 and VB 27). Also, copper-free and relatively high copper content phosphating solutions (VB 21 - VB 24) were used compared to the phosphating solutions according to the invention with a certain copper content. Hydrofluoric acid was added in five tests. The sample sheets were treated, as in the experiments involving Examples B 1 to B20, according to the steps a) to c), though the titanium-containing activator was sprayed on. Layer weights in the range from 1.5 to 1.6 g/m^2 were obtained.

Table 4: Composition of the prephosphating solutions in g/l and points of free acid (FA) and total acid according to Fischer (TAF)

	Zn	Mn	Ni	Cu	F_{total}	PO_4	NH_4	NO_3*	H_2O_2	FA	TAF
B 21	1.74	2.15	-	0.010	-	20	-	15.5	-	2.6	19.2
B 22	1.74	2.15	-	0.020	-	20	-	15.5	-	2.6	19.2
B 23	1.74	2.15	-	0.040	-	20	-	15.5	-	2.6	19.2
B 24	1.74	2.15	-	0.010	0.9	20	-	-	1.0	3.4	19.2
B 25	1.74	2.15	-	0.020	0.9	20	-	-	1.0	3.4	19.2
B 26	1.74	2.15	-	0.040	0.9	20	-	-	1.0	3.4	19.2
VB 21	1.74	2.15	-	-	-	20	-	15.5	-	2.6	19.2
VB 22	1.74	2.15	-	0.060	-	20	-	15.5	-	2.6	19.2
VB 23	1.74	2.15	-	-	0.9	20	-	-	1.0	3.4	19.2
VB 24	1.74	2.15	-	0.060	0.9	20	-	-	1.0	3.4	19.2
VB 25	1.70	2.0	1.3	-	-	18.0	-	12.0	-	2.9	19.0
VB 26	1.95	0.8	-	0.003	3.0**	18.5	0.9	3.2	1.2$^{\#}$	3.0	19.4
VB 27	0.7	1.0	1.0	-	-	17.5	-	2.1	-	0.8	18.0

*as added amount **as SiF_6 $^{\#}$as HA

In the comparison example 25 a nickel-containing prephosphating was applied in a layer weight of about 1.5 g/m^2, whereas in the comparison examples 26 and 27 phosphate layers were applied in a layer weight of about 3 g/m^2. The comparison examples, like the prephosphatings according to the invention of the examples B 21 to B 26 according to the invention (without post-phosphating), were painted with a automobile paint structure according to BMW and tested. In addition the baths contained a very small to a specific amount of sodium. Due to the high nitrate levels a comparatively minor amount of nitrite was formed, which had a strongly accelerating effect.

Table 5: Results of the corrosion tests on electrolytically galvanised steel surfaces, on coatings obtained according to the invention (B) and coatings obtained in the comparison examples (VB) by

1. paint adhesion test by cross-hatch adhesion test method according to BMW test N 600 87.0 after 40 hours' storage in 5% NaCl solution at 40°C,

2. paint adhesion test by cross-hatch adhesion test /condensation water test according to DIN/EN ISO 2409 after 240 hours' storage in condensation water,

3. corrosion alternating test according to General Motors GM-SCAB Test 95-11 over 40 cycles, and

4. corrosion test by weathering in the open air with NaCl acceleration according to VDA 621-414.

	cross-hatch adhesion test acc. to BMW	cross-hatch adhesion test-condensation water Test acc. to DIN EN ISO 2409	GM-SCAB Test 95-11	Open Air Weathering Test acc. to VDA 621-414
	Score	Score	mm Creep	mm Creep
B 21	3.0	2.0	1	0.3
B 22	1.0	1.0	1	0.3
B 23	1.0	1.0	1	0.3
B 24	-	2.5	1.5	-
B 25	-	2.0	1	-
B 26	-	2.0	1	-
VB 21	5.0	5.0	3	0.8
VB 22	4.5	4.0	2	0.6
VB 23	-	4.5	2	-
VB 24	-	4.0	2	-
VB 25	2.0	1.5	1	0.3
VB 26	2.0	-	1	0.3
VB 27	1.5	1.0	1	0.3

Whereas in the two cross-hatch adhesion test scores of 0 to 5 can be awarded, 0 being the best, in the corrosion tests the corrosive creepage of the paint starting from a crack is specified in mm on base metal. In all tests the results are mean values over in each case several tested sheets.

In these tests it was found that the sheets coated according to the invention have approximately the same quality as sheets with high nickel content phosphate coatings.

Patent Claims

1. Process for the coating of metallic surfaces by manganese-zinc phosphating with an aqueous phosphating solution, in which no nickel is intentionally added to the phosphating solution, characterised in that

   the zinc:manganese weight ratio of the phosphating solution is maintained in the range from 0.05:1 to 0.99:1,
   and that the phosphating solution has the following contents:

      zinc in the range from 0.05 to 5 g/l,
      manganese in the range from 0.075 to 5.2 g/l, as well as
      copper in the range from 0.008 to 0.050 g/l, and/or
      a total amount of 0.002 to 0.5 g/l of hexafluoride complexes of boron, aluminium, titanium, hafnium and/or zirconium, calculated as F_6.

2. Coating process according to claim 1, characterised in that the phosphating solution has a content of silver in the range from 0.0001 to 0.05 g/l.

3. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a content of sodium in the range from 0.01 to 10 g/l and/or a content of potassium in the range from 0.01 to 10 g/l.

4. Coating process according to one of the preceding claims, characterised in that the zinc:phosphate

weight ratio of the phosphating solution is maintained in the range from 0.016:1 to 1.33:1, phosphate being calculated as PO_4.

5. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a content of phosphate in the range from 3 to 75 g/l, phosphate being calculated as PO_4.

6. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a chloride content in the range from 0.01 to 6 g/l and/or a chlorate content in the range from 0.01 to 5 g/l.

7. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a content of silicon hexafluoride in the range from 0.1 to 5 g/l.

8. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a content of free fluoride in the range from 0.001 to 0.8 g/l.

9. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a total content of fluoride in the range from 0.01 to 5 g/l.

10. Coating process according to one of the preceding claims, characterised in that the phosphating

solution has a content of at least one accelerator in the range from 0 to 40 g/l.

11. Coating process according to one of the preceding claims, characterised in that the phosphating solution has a content of nitrite in the range from 0.01 to 0.3 g/l, a content of nitrate in the range from 1 to 30 g/l, a content of compounds based on peroxide in the range from 0.001 to 3 g/l calculated as H_2O_2, a total content of nitrobenzenesulfonate (NBS), nitropropane, nitroethane and/or other nitro-organic compounds - with the exception of compounds based on nitroguanidine - with oxidising properties in the range from 0.1 to 3 g/l calculated as NO_2, a content of compounds based on nitroguanidine in the range from 0.1 to 5 g/l, a chlorate content in the range from 0.05 to 4 g/l, a content of reducing sugar compounds in the range from 0.1 to 10 g/l and/or a content of compounds based on hydroxylamine (HA) in the range from 0.1 to 6 g/l, calculated as HA.

12. Coating process according to one of the preceding claims, characterised in that the phosphating solution has the following contents, in particular for parts:

zinc in the range from 0.6 to 1.4 g/l,
manganese in the range from 0.7 to 2.0 g/l,
zinc:manganese weight ratio in the range from 0.6:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 12 to 25 g/l,

zinc:phosphate weight ratio in the range from 0.02 to 0.12,
copper in the range from 0.008 to 0.025 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride, in the range from 0 to 6 g/l, calculated as F,
wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l calculated as SiF_6, and
nitrate in the range from 0 to 22 g/l and/or at least one other accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

13. Coating process according to one of the preceding claims, characterised in that the phosphating solution has the following contents in particular for strip material, particularly preferably for galvanised strip surfaces:

zinc in the range from 0.1 to 4 g/l,
manganese in the range from 0.5 to 5 g/l,
zinc:manganese weight ratio in the range from 0.02:1 to 0.9:1,
phosphate calculated as PO_4 in the range from 10 to 40 g/l,
zinc:phosphate weight ratio in the range from 0.0025 to 0.4,
copper in the range from 0.008 to 0.032 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride in the range from 0 to 6 g/l calculated as F,

wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 to 22 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

14. Coating process according to one of the preceding claims, characterised in that the phosphating solution for the prephosphating has the following contents:
zinc in the range from 1.3 to 2.3 g/l,
manganese in the range from 1.7 to 2.6 g/l,
zinc:manganese weight ratio in the range from 0.5:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 10 to 20 g/l,
zinc:phosphate weight ratio in the range from 0.06 to 0.23,
copper in the range from 0.008 to 0.048 g/l,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride in the range from 0 to 6 g/l calculated as F,
wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 to 22 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds

based on hydroxylamine and/or nitroguanidine, in each case in the range from 0.01 to 2 g/l, or peroxide in the range from 0.01 to 3 g/l.

15. Coating process according to one of the preceding claims, characterised in that the phosphating solution has the following contents:

zinc in the range from 0.6 to 1.4 g/l,
manganese in the range from 0.7 to 2.0 g/l,
zinc:manganese weight ratio in the range from 0.6:1 to 0.95:1,
phosphate calculated as PO_4 in the range from 12 to 25 g/l,
zinc:phosphate weight ratio in the range from 0.02 to 0.12,
total content of fluoride as free fluoride, as bound fluoride and/or as at least one complex fluoride, in the range from 0.012 to 6 g/l, calculated as F,
wherein the total content of complex fluorides of titanium, hafnium and/or zirconium is in the range from 0.002 to 0.5 g/l, calculated as F_6, and wherein the complex fluoride SiF_6 is contained in an amount in the range from 0 to 4.5 g/l, calculated as SiF_6, and
nitrate in the range from 0 to 22 g/l and/or at least one further accelerator selected from the group comprising nitrite or compounds based on hydroxylamine, nitroguanidine and/or peroxide, in each case in the range from 0.01 to 2 g/l.

16. Coating process according to one of the preceding claims, characterised in that the metallic substrates are coated for a time of up to 20 minutes, wherein strip material is preferably coated for a time of 0.1 to 120 seconds and particularly preferably for a time of 0.3 to 60 seconds, and wherein parts are preferably coated for a time from 1 to 12 minutes and particularly preferably for a time from 2 to 8 minutes.

17. Coating process according to one of the preceding claims, characterised in that the temperature of the phosphating solution in the coating procedure is in the range from 10° to 72°C, wherein strip material is preferably coated in the range from 40° to 70°C and wherein parts are preferably coated in the range from 20° to 60°C and particularly preferably in the range from 32° to 58°C.

18. Coating process according to one of the preceding claims, characterised in that the free acid has a value of 0.1 to 10 points, the total acid according to Fischer has a value of 5 to 50 points, and the ratio of the total acid according to Fischer to free acid is in the range from 0.01 to 0.7.

19. Coating process according to one of the preceding claims, characterised in that the pH of the phosphating solution is in the range from 1 to 4.

20. Coating process according to one of the preceding claims, characterised in that the phosphating

solution is applied to the surface of the substrates by knife coating, flow coating, spraying, sprinkling, brushing, dipping, nebulising or rolling, wherein individual process steps may be combined with one another, the application optionally being followed by squeezing off.

21. Coating process according to one of the preceding claims, characterised in that substrates with a metallic surface predominantly containing aluminium, iron, copper, magnesium, tin or zinc are coated with the phosphating solution, in particular surfaces of at least one of the materials based on aluminium, iron, steel, zinc and/or alloys with a content of aluminium, iron, copper, magnesium, tin or zinc.

22. Coating process according to one of the preceding claims, characterised in that a phosphate coating that has a layer weight in the range from 0.2 to 6 g/m^2 is deposited from the phosphating solution.

23. Coating process according to one of the preceding claims, characterised in that the metallic surfaces are cleaned, pickled, rinsed and/or activated before the phosphating.

24. Coating process according to one of the preceding claims, characterised in that the metallic surfaces are galvanised directly before the phosphating.

25. Coating process according to one of the preceding claims, characterised in that the metallic surfaces are prephosphated.

26. Coating process according to claim 25, characterised in that the phosphating solution for the prephosphating has the following contents:

    zinc in the range from 0.4 to 5 g/l,
    manganese in the range from 0.5 to 5.2 g/l,
    copper in the range from 0.008 to 0.050 g/l.

27. Coating process according to claim 25 or 26, characterised in that at least partially prephosphated, optionally at least partially formed/shaped, optionally at least partially welded metallic substrates are phosphated by coating with an aqueous phosphating solution, in which no nickel is intentionally added to the phosphating solution or the coating is carried out only with a nickel content of the phosphating solution of up to 0.3 g/l, wherein the phosphating solution has the following contents:

    zinc in the range from 0.05 to 5 g/l, and
    manganese in the range from 0.075 to 5.2 g/l.

28. Coating process according to one of the preceding claims, characterised in that the phosphated substrates are rinsed at least once and are optionally treated between two rinse procedures with a post-rinse solution to provide additional passivation.

29. Coating process according to one of the preceding claims, characterised in that after the phosphating the metallic surfaces are welded, bonded and/or

formed/shaped, and are then optionally rephosphated.

30. Coating process according to one of the preceding claims, characterised in that the metal parts provided with a first and/or second phosphate layer are coated with a paint, with another type of organic coating, with a film and/or with an adhesive layer and are optionally formed/shaped, wherein the metal parts coated in this way may in addition be bonded or welded to other parts and/or joined together in some other way.

31. Coating process according to one of claims 1 to 30, characterised in that the metal parts provided with a first and/or second applied phosphate layer are coated either before or after the forming and/or assembly with a coating corresponding to claim 29.

32. Use of the metal parts coated by the process according to at least one of claims 1 to 31 as prephosphated metal parts for a renewed conversion treatment or for a renewed conversion pretreatment, in particular before painting, or as pretreated metal parts in particular for the automobile industry, especially before painting, or an end-phosphated metal parts, which may optionally also subsequently be painted, organically coated in another way and/or coated with a film, with an adhesive layer, formed/shaped, assembled and/or welded together.

33. Use of the substrates coated by the process according to at least one of claims 1 to 31 in the production of strip material, for the production of components or car body parts or preassembled

elements in the automobile or aerospace industry, in the building and construction industry, in the furniture industry, for the production of instruments and units, in particular domestic appliances, measuring instruments, control devices, testing devices, structural components, claddings/linings as well as small parts; as wire, wire coiling, wire mesh, metal sheeting, cladding/lining, screening, car bodies or parts of car bodies, parts of vehicles, trailers, mobile homes or missiles, as electronic or microelectronic components, as coverings, housings, lamps, lights, hanging light units, items of furniture or furniture parts, components of domestic appliances, frames, profiled sections, moulded parts of complicated geometry, beam barrier, radiator or sauna parts, automobile bumpers, parts of or with at least one pipe and/or a profiled section, window, door or bicycle frames, or as small parts such as for example screws, nuts, flanges, springs or spectacle frames.