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(54) **ZINC PHOSPHATE CONVERSION COATING COMPOSITION AND PROCESS**

ZUSAMMENSETZUNG UND VERFAHREN FÜR DIE ZINK-PHOSPHATKONVERSIONSBESCHICHTUNG

PROCEDE ET COMPOSITION DE REVETEMENT PAR CONVERSION A BASE DE PHOSPHATE DE ZINC

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(73) Proprietor: **HENKEL CORPORATION**
Plymouth Meeting, PA 19462 (US)

(72) Inventors:
- **NAGASHIMA, Yasuhiko**
  Hiratsuka-shi, Kanagawa-ken 254 (JP)
- **ISHII, Hitoshi**
  Toyoake-shi, Aichi-ken (JP)

(74) Representative:
Sanderson, Laurence Andrew et al
SANDERSON & CO.
European Patent Attorneys
34, East Stockwell Street
Colchester Essex CO1 1ST (GB)

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Description

[0001] This invention relates to zinc phosphate-based conversion treatment baths which can be applied to a variety of metal substrates, for example, steel, steel sheet, glavanized steel sheet, and the like. More particularly, this invention relates to a zinc phosphate-based conversion bath and to a surface treatment method that are able to form a fine, dense, and uniform conversion coating on metal surfaces and that are also able to induce fine-crystal formation in the conversion coating.

[0002] The execution of a zinc phosphate-based conversion treatment on various metals prior to the coating or plastic working thereof is known at present for the purpose of improving the paint adherence and post-paint corrosion resistance and improving the lubrication during plastic working.

[0003] The conversion treatment baths used for zinc phosphate-based conversion treatment are essentially acidic aqueous solutions that contain zinc ions, phosphate ions, and oxidizing agent(s). Nitrite salts, chlorate salts, hydrogen peroxide, organic nitro compounds, hydroxylamine, and the like, are ordinarily considered for this oxidizing agent. These oxidizing agents are typically called conversion "accelerators" because they function to accelerate the conversion reactions. Nitrate salts may be present in conversion baths, but - because, in the concentrations usually present in zinc phosphate-based conversion baths, nitrate ions do not exercise an oxidizing activity sufficient to convert ferrous ions substantially completely to ferric ions - nitrate ions must be distinguished from the conversion accelerators.

[0004] One important role of conversion accelerators during the zinc phosphate based conversion treatment of ferriferous metals is to oxidise the divalent iron ions eluting into the conversion bath to trivalent iron ions. For example, the conversion reactions are inhibited when divalent iron ions accumulate in the conversion bath during the continuous conversion treatment of ferriferous metals, and the role of the conversion accelerator in inhibiting this accumulation of divalent iron ions is thus crucial.

[0005] However, each of these already known conversion accelerators is associated with problems that must be addressed. For example, in the case of the nitrite salts, which are the most widely used conversion accelerators at the present time, these compounds are unstable in the acid region. As a result, these compounds undergo spontaneous decomposition and are thereby consumed even when conversion treatment is not being run (storage period). The maintenance of a constant or prescribed concentration of these compounds therefore requires continual replenishment to make up for the amount lost to this consumption. It is also known that as a result of their oxidative activity and spontaneous decomposition these nitrite salts partially convert to NO_x gas, which diffuses into and pollutes the atmosphere.

[0006] When chlorate salts are used as conversion accelerators, chloride ions are produced as a decomposition product during conversion treatment and accumulate in the conversion treatment bath. The corrosion resistance of the metal substrate is substantially impaired when even a trace of chloride ions from the conversion treatment bath remains on the surface of the metal workpiece. In addition, chlorate salts are ordinarily used in combination with another conversion accelerator, such as nitrite salts, and when used alone provide only a significantly reduced conversion reaction rate.

[0007] Stability in the conversion treatment bath is also a problem for the use of hydrogen peroxide as a conversion accelerator: Hydrogen peroxide is readily decomposed by oxygen dissolved in the conversion bath. In addition, hydrogen peroxide has a narrow optimal concentration range for conversion treatment, which makes it difficult to manage the conversion treatment bath. When the dissolved concentration is too high, a powdery, poorly adherent conversion coating is deposited on the metal surface.

[0008] French Patent Specification No. 2,410,055 concerns the use of hydrogen peroxide as a conversion accelerator in a zinc phosphate conversion coating bath but although mention is made of a peroxide precursor, this is not illustrated. GB Patent Specification No. 828,916 mentions the use of a large range of oxidants including hydrogen peroxide and t-butyl peroxide.

[0009] With regard to the use of nitrogenous organic compounds as conversion accelerators, the following problems are associated with the use of organic nitro compounds such as nitroguanine and sodium m-nitrobenzenesulfonate: Nitroguanine, for example, has a low solubility in water and as a result cannot be formulated as a concentrate for addition to the conversion bath. It is also difficult to control the divalent iron ions concentration in the conversion bath using nitroguanine because this compound has a weak capacity to oxidize the divalent iron ions. On the other hand, sodium m-nitrobenzenesulfonate provides a poor conversion performance when used by itself, and for this reason this compound must ordinarily be used in combination with another, more powerful conversion accelerator. Moreover, its concentration management requires the use of large-scale measurement equipment, such as an ion chromatograph. Another problem with the use of organic nitro compounds is that the accumulation of these compounds and their decomposition products in the conversion bath causes an increase in the chemical oxygen demand ("COD") of the conversion treatment effluent, which unfavorably affects the environment.

[0010] Hydroxylamine compounds are another type of nitrogenous organic compounds used as conversion accelerators. These compounds, however, in order to achieve the best results, must be added to give concentrations of at

least 1,000 parts per million by weight (hereinafter usually abbreviated as "ppm") in the conversion bath, giving rise to the possibility of a large and economically undesirable consumption of the conversion accelerator.

[0011] In addition, results have been reported from an investigation into the use of chromic acid and permanganate salts as conversion accelerators for zinc phosphate-based conversion treatment baths (Norio Sato, et al., *Boshoku Gijutsu* [English title: Corrosion Engineering], Volume 15, No. 5 (1966)). These authors report that the formation of conversion coatings was not observed at concentrations of 5 millimoles per liter (hereinafter usually abbreviated as "mmol/L") or 10 mmol/L.

[0012] Many of the known conversion accelerators as described above are nitrogenous compounds, and as such resist removal by chemical wastewater treatment techniques, so that in practice they are usually removed through microbiological treatments. However, even with the use of microbiological treatments, the elimination of high concentrations of these nitrogenous compounds is highly problematic, while a complete elimination cannot be achieved even at low concentrations. Nitrogenous compounds have recently come to be thought of as one factor in the eutrophication of bodies of water, and the discharge of nitrogenous compounds has therefore become subject to an increasingly strict regulatory atmosphere. In view of these environmental considerations, the development of a nitrogenous compound-free zinc phosphate-based conversion bath would be highly desirable.

[0013] Another drawback to each of the above-described conversion accelerators is that, in order to obtain the thin, uniform, fine, and dense conversion coatings desired as underpaint coatings, the metal surface must in each case be conditioned by treatment with a colloidal titanium system immediately prior to execution of the conversion treatment. In addition to the fact that treatment bath management is quite complicated in the case of surface conditioners, a surface-conditioning step also requires installation of the corresponding treatment facilities and expansion of the space devoted to treatment. As a result, strong demand has recently appeared for the development of a conversion accelerator that is able to from high-quality conversion coatings on metal surfaces even without the implementation of a surface-conditioning step.

[0014] The present invention seeks to solve the problems described above for conversion accelerators. More specifically, the present invention introduces a zinc phosphate-based conversion bath for metals and a metal surface treatment method which are able to deposit a fine, dense, and uniform zinc phosphate-type conversion coating on the surface of the metal substrate and which are able to induce fine-crystal formation in the conversion coating.

[0015] As a consequence of investigations focusing on organic peroxides within the realm of organic oxidizing agents, the inventors discovered that fine, dense, and uniform zinc phosphate-type conversion coatings can be formed through the use of organic peroxides soluble in the conversion bath as conversion accelerators. The following discoveries were also made: organic peroxide conversion accelerators need not be used in combination with nitrate salts or another conversion accelerator and thereby make possible the elimination of nitrogenous compounds from the conversion bath; the use of organic peroxide conversion accelerators yields fine, dense, and uniform crystals in the coating even without the application of a surface-conditioning treatment; and the use of organic peroxide conversion accelerators results in the formation of high-quality conversion coatings on metal substrates without being subject to narrow limitations of temperature, zinc concentration and the like. The present invention was developed as a result of these discoveries.

[0016] Accordingly, the invention provides an acidic aqueous phosphate conversion-coating composition for treating metal surfaces, which composition comprises water, 0.5 to 1.3 g/l zinc ions, 5 to 30 g/l phosphate ions and 50 to 1,500 ppm organic peroxide(s) as a conversion accelerator and which composition has a free acidity of 0.1 to 0.9 points.

[0017] Since nitrogenous compounds are not included among the essential components of conversion baths according to the present invention, treatment baths according to the present invention can also satisfy environmental regulations concerning the amount of nitrogenous compound in the effluent. One should note in this connection that there is very little risk of environmental damage when the nitrogen concentration in a conversion treatment bath is less than or equal to 20 ppm.

[0018] It is preferred to contact the metal surface with the above-described zinc phosphate-based conversion treatment bath according to the present invention after the pH of the conversion bath has been adjusted to 2.0 to 4.0, more preferably 2.5 to 3.5.

[0019] The described zinc phosphate-based surface treatment according to the invention method is preferably carried out by subjecting the preliminary degreased surface of the metal to a water rinse and consecutively thereafter to the conversion treatment.

[0020] The treatment is preferably carried out by contacting the metal surface with the aqueous conversion coating composition at a treatment temperature of from room temperature up to 90°C and for a period of time in the range of from 30 seconds to 15 minutes.

[0021] The appropriate range for zinc ions concentration in a bath according to the invention will vary as a function of the service intended for the conversion coating produced.

[0022] When the conversion treatment bath according to the present invention is to be used to provide an underpaint coating for metals and the zinc ions concentration falls below 0.5 g/L, the resulting zinc phosphate-type conversion coating will exhibit a reduced coverage ratio, which can cause an unsatisfactory post-paint coating adherence and an

unsatisfactory post-paint corrosion resistance. Zinc ions concentrations in excess cause a coarsening of the crystals in the coating, which can in particular cause a reduced post-paint coating adherence.

[0023] The phosphate ions concentration in the conversion bath according to the present invention is preferably 5.0 to 30.0 g/L. Obtaining a normal conversion coating can become problematic at below 5.0 g/L. No additional benefits are obtained at above 30.0 g/L, which makes such values uneconomical. The phosphate ions can be generated by the addition of phosphoric acid or its aqueous solutions to the conversion bath or by dissolving a salt of phosphoric acid, such as the sodium potassium, magnesium, zinc, or the like salt, in a conversion bath.

[0024] The zinc phosphate-based conversion treatment bath according to the present invention is an acidic aqueous solution whose pH preferably is from 2.0 to 4.0 and more preferably from about 2.5 to 3.5. In this pH region, orthophosphoric acid (H_3PO_4) exists in equilibrium primarily with dihydrogen phosphate ions (H_2PO_4), but also with much smaller amounts of hydrogen phosphate ions (HPO_4^{-2}) and phosphate ions (PO_4^{3-}); however, the concentrations specified herein and those of "phosphate ions" are intended to include the stoichiometric equivalent as phosphate ions of any of the chemical species from undissociated orthophosphoric acid to completely ionized phosphate ions. The free acid content, measured as described in the examples below, of the compositions according to the invention is at least, with increasing preference in the order given, 0.1, 0.3, 0.5, or 0.6 point and independently is not more than 0.9 point(s).

[0025] The organic peroxides used by the present invention can be classified into, for example, organoperoxides, such as ethyl hydroperoxides, isopropyl hydroperoxide, tert-butyl hydroperoxide, tert-hexyl hydroperoxide, diethyl peroxide, tert-butyl peroxymaleate, and the like, that contain a peroxy moiety without an adjacent carbonyl group; and percarboxylic acid types such as peracetic acid, monoperphthalic acid, persuccinic acid, and the like.

[0026] Organic peroxide molecules are used at concentrations of 50 to 1,500 ppm in a conversion bath according to the invention. Acceleration of conversion film formation can become unsatisfactory when the organoperoxide concentration in the conversion bath is below 50 ppm. Accordingly, the organic peroxide molecules present in the conversion bath according to the present invention preferably contain C_1 to C_7 alkyl moieties, because a low water solubility is exhibited by organic peroxides containing aromatic or higher molecular weight alkyl moieties, and this can result in a failure to obtain a satisfactory oxidizing activity. On the other hand, no additional effect is obtained at concentrations in excess of 1,500 ppm, and such values are therefore uneconomical.

[0027] Because the conversion treatment bath according to the present invention also functions to induce fine-crystal formation on the part of the depositing zinc phosphate-type crystals, the instant conversion bath can produce a fine, dense, and uniform zinc phosphate-type conversion coating even in the absence of an immediately preceding surface-conditioning treatment for the specific purpose of inducing fine-crystal formation in the coating.

[0028] In addition, the conversion bath according to the present invention does not require the addition of nitric acid, nitrous acid, an organic nitro compound, or the like, and thus can be formulated entirely free of nitrogenous compounds. In this form it therefore offers the advantage of not requiring the inclusion of a treatment step for nitrogenous compounds in the effluent treatment process. Nitrogenous compounds may be added to the conversion treatment bath according to the present invention on an optional basis, but the nitrogen concentration is preferably held to no greater than 100 ppm and more preferably to 20 ppm or less.

[0029] Metal ions other than the zinc ions can be added to the zinc phosphate based conversion bath according to the present invention. These metal ions can act as etchants in order to induce a uniform etch of the surface of the metal workpiece, or can act as paintability improvers when the conversion coating is being used as an underpaint coating.

[0030] Suitable non-zinc metal ions are exemplified by nickel ions, manganese ions, cobalt ions, iron ions, magnesium ions, calcium ions, and so forth. Each of these ions can be provided by dissolution in the treatment bath of the oxide, hydroxide, carbonate, sulfate, phosphate, or the like, of the corresponding metal.

[0031] Fluoride ions or complex fluoride ions, e.g., fluosilicate ions, fluozirconate ions, and the like, can be used as etchant. These ions can be provided, for example, by dissolving in the conversion treatment bath one or more of the following fluorine compounds: hydrofluoric acid, fluosilicic acid, fluozirconic acid, fluotitanic acid, and the corresponding metal salts (e.g., sodium, potassium, magnesium).

[0032] The following process steps preferably should be consecutively executed in the sequence given in order to form a conversion coating on metal surfaces using a zinc phosphate based conversion bath according to the present invention: alkaline degreasing, a water rinse, treatment with the zinc phosphate-based conversion bath, and a water rinse. The degreasing and water rinse processes may themselves each be implemented as multistage processes. A deionized water rinse is preferably used for the final water rinse when the conversion coating will be used as an underpaint coating. Moreover, when the conversion coating is produced on a metal surface for use as an underpaint coating, it is preferred that the conversion treatment be immediately preceded by a surface conditioning process using a colloidal titanium-containing surface conditioner for the purpose of inducing fine-crystal formation in the coating.

[0033] Metals subjected to the above-described conversion treatment can be painted after the final water rinse as described above or after a drying step that follows the final water rinse.

[0034] When plastic working is the intended service for the conversion film formed on a metal substrate using the

conversion bath according to the present invention, after the above-described degreasing and water rinse the metal workpiece is preferably subjected to a pickling step for purposes of descaling. Again with reference to production of the conversion film for plastic working service, the lubricity of the coating can be improved even further by a soap treatment (lubrication treatment) after formation of the conversion film.

[0035] Surface treatment using the zinc phosphate-based conversion bath according to the present invention is generally executed by immersion, spraying, or a combination thereof. When the conversion film is intended as an underpaint coating, the desired coating can be, and preferably is, formed by conversion treatment at a treatment temperature from about room temperature to about 60 °C and at a treatment time from about 0.5 minute to about 5 minutes. When the conversion film is intended for plastic working service, the desired coating can be, and preferably is, formed by conversion treatment at a treatment temperature from about 50 °C to about 90 °C and at a treatment time from about 1 minute to about 15 minutes.

[0036] The invention will be explained in greater detail below with reference to the following working and comparative examples of actual treatment. The scope of the present invention is in no way limited by these examples.

Examples

[0037] The test materials were (1) 0.8 mm-thick cold-rolled steel sheets (SPCC-SD, abbreviated below as "SPC") and (2) galvanized steel sheets (abbreviated below as "plated") prepared by the zinc electroplating (20 g/m^2) of the aforementioned cold-rolled steel sheets. These were in each case cut to 70 x 150 mm and subjected to treatment in the working and comparative examples described below.

[0038] The following treatment process steps, which are a typical example of treatment for the purpose of producing an underpaint coating, were used in the working and comparative examples:

(1) degreasing (alkaline degreaser, brand name: FINECLEANER™ L4460 from Nihon Parkerizing Company, Limited, 20 g/L of constituent A, 12 g/L of constituent B);
43 °C, 120 seconds, immersion;
(2) water rinse (tap water);
ambient temperature, 30 seconds, spray;
(3) surface conditioning (colloidal titanium surface conditioner, brand name: PREPALENE® ZN from Nihon Parkerizing Company, Limited, 1 g/L aqueous solution);
ambient temperature, 30 seconds, spray;
(4) zinc phosphate-based conversion treatment (as described below for the individual working and comparative examples);
43 °C, 120 seconds, immersion;
(5) water rinse (tap water);
ambient temperature, 30 seconds, spray;
(6) deionized water rinse (deionized water, conductivity = 0.2 microS/cm)
ambient temperature, 20 seconds, spray;
(7) drain and dry;
hot air at 110 °C, 180 seconds,

except that the surface-conditioning step was not carried out in Examples 5 and 7 or in Comparative Example 3, and in these cases the zinc phosphate-based conversion treatment step (4) was therefore carried out directly after the degreasing (1) and ensuing water rinse (2) steps.

[0039] The free acidity in the zinc phosphate-based conversion baths in Examples 1 to 8 and Comparative Examples 1 to 4 was adjusted to specific values using sodium hydroxide. The free acidity was measured by titrating 10 milliliters (hereinafter usually abbreviated as "mL") of the particular treatment bath to neutrality with 0.1 N aqueous sodium hydroxide, using bromophenol blue as the indicator. The number of mL of the 0.1 N aqueous sodium hydroxide required for the color change from yellow to blue was determined and is reported as "points" of free acidity. The fluoride ions concentration in the conversion bath was measured using a fluoride sensitive electrode.

[0040] The coating weight was measured as follows: The weight (W1) in grams of the treated sheet after conversion treatment was first measured, and the treated sheet was then subjected to a film stripping treatment using the stripping solution and stripping conditions reported below. The weight of the stripped sheet was measured to give W2 in grams, and the coating weight was calculated from the following equation:

$$\text{Coating weight (in g/m}^2\text{)} = (W1 - W2)/0.021.$$

Treatment for cold-rolled steel sheets	
stripping solution	5 % aqueous chromic acid solution
stripping conditions	75 °C, 15 minutes, immersion

Treatment for galvanized steel sheets	
stripping solution	2 % by weight (hereinafter usually abbreviated as "wt%") of ammonium dichromate + 49 wt% of 28 wt% aqueous solution of ammonia + 49 wt% pure water
stripping conditions	ambient temperature, 15 minutes, immersion.

[0041] The appearance of the coatings was inspected visually, and the morphology and size of the grains in the conversion coating was evaluated by inspection with a scanning electron microscope (SEM).

Example 1

[0042]

Composition of the conversion bath	
phosphate ions	15 g/L (from addition of 75% phosphoric acid)
zinc ions	1.3 g/L (from addition of zinc oxide)
nickel ions	1.0 g/L (from addition of nickel carbonate)
manganese ions	0.5 g/L (from addition of manganese carbonate)
fluoride ions	100 ppm (from addition of 55 % hydrofluoric acid)

[0043] 450 ppm of tert-butyl hydroperoxide (organoperoxide component) was added to the conversion bath with the above composition, and the free acidity of the conversion bath was then adjusted to 0.9 point. A cold-rolled steel test sheetpon was subjected first to the colloidal titanium surface-conditioning treatment and then to conversion treatment (conversion temperature = 43 °C, treatment time = 120 seconds) using the above-described conversion bath. The resulting conversion coating weight was 1.2 g/m^2. The coating crystals were plates with an average grain size of 6 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 2

[0044] A galvanized steel test sheet was subjected first to the same surface conditioning treatment as in Example 1 and then to conversion treatment using the same conversion treatment bath as in Example 1. The resulting conversion coating weight was 2.8 g/m^2. The crystals were plates with an average grain size of 4 micrometers. The conversion coating was grayish white and was uniform, fine, and dense.

Example 3

[0045] A cold-rolled steel test sheet was subjected first to the same surface-conditioning treatment as in Example 1 and then to conversion treatment using the same conversion treatment bath as in Example 1, except that the organoperoxide addition consisted of 80 ppm tert-butyl hydroperoxide and the free acidity was adjusted to 0.6 point. The resulting conversion coating weight was 0.9 g/m^2. The coating crystals were plates with an average grain size of 8 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 4

[0046] A cold-rolled steel test sheet was subjected first to the same surface conditioning treatment as in Example 1 and then to conversion treatment using the same conversion treatment bath as in Example 1, except that 1,200 ppm of tert-butyl hydroperoxide was added as the organoperoxide and sufficient 65.5% nitric acid was added to give a nitrogen component content of 500 ppm. The free acidity of the conversion bath was adjusted to 0.9 point. The resulting conversion coating weight was 1.1 g/m^2. The coating crystals were plates with an average grain size of 7 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 5

[0047] A cold-rolled steel test sheet was subjected to conversion treatment as in Example 1, except that there was no surface-conditioning treatment and only 400 ppm of tert-hexyl hydroperoxide was added as the organoperoxide. The free acidity was adjusted to 0.9 point. The resulting conversion coating weight was 1.0 g/m^2. The coating crystals were plates with an average grain size of 6 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 6

[0048] A cold-rolled steel test sheet was subjected first to the same surface conditioning treatment as in Example 1 and then to conversion treatment using the same conversion treatment bath as in Example 1, except that 100 ppm of peracetic acid was added as the organoperoxide, and the free acidity was adjusted to 0.6 point. The resulting conversion coating weight was 1.3 g/m^2. The coating crystals were plates with an average grain size of 10 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 7

[0049] A cold-rolled steel test sheet was subjected to conversion treatment using the same conversion bath as in Example 1, except that the surface conditioning treatment was not used, 500 ppm of tert-butyl hydroperoxide was added as the organoperoxide, and the free acidity was adjusted to 0.6 point. The resulting conversion coating weight was 1.1 g/m^2. The coating crystals were plates with an average grain size of 10 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Example 8

[0050]

Composition of the conversion bath	
phosphate ions	15 g/L (from addition of 75 % phosphoric acid)
zinc ions	1.3 g/L (from addition of zinc oxide)
nickel ions	1.0 g/L (from addition of nickel nitrate)
manganese ions	0.5 g/L (from addition of manganese carbonate)
fluoride ions	100 ppm (from addition of 55 % hydrofluoric acid)
nitrate ions	7.2 g/L (from addition of sodium nitrate and nickel nitrate) (nitrogen concentration = 1.4 g/L).

[0051] 450 ppm of tert-butyl hydroperoxide (organoperoxide component) was added to the conversion bath with the above composition, and the free acidity of the conversion bath was then adjusted to 0.9 point. A cold-rolled steel test sheetpon was subjected first to the colloidal titanium surface-conditioning treatment and then to conversion treatment (conversion temperature = 43 °C, treatment time = 120 seconds) using the above-described conversion bath. The resulting conversion coating weight was 1.1 g/m^2. The coating crystals were plates with an average grain size of 5 micrometers. The conversion coating was grayish black and was uniform, fine, and dense.

Comparative Example 1

[0052] A cold-rolled steel test sheet was subjected to the same surface conditioning treatment as in Example 1 and was then submitted to the same conversion treatment as in Example 1, except that the organoperoxide addition consisted of 5 ppm of tert-butyl hydroperoxide. The conversion coating weight was 0.5 g/m^2, and the development of yellow rust was observed.

Comparative Example 2

[0053] A galvanized steel test sheet was subjected to conversion treatment as in Example 1, except that the organoperoxide addition consisted of 5 ppm of tert-butyl hydroperoxide. The conversion coating weight was 0.9 g/m^2, the average grain size was 15 micrometers, and the coating was sparse.

Comparative Example 3

[0054] A cold-rolled steel test sheet was subjected to conversion treatment as in Example 8, except that there was no surface-conditioning treatment and 150 ppm of nitrite salt was added to the conversion bath in place of the organoperoxide. The conversion coating weight was 0.1 g/m^2, which indicated that almost no conversion coating deposition had occurred. Yellow rust had developed over the entire surface.

Comparative Example 4

[0055] A cold-rolled steel test sheet was subjected to conversion treatment as in Example 1, except that sodium chlorate was added to the conversion bath in place of the organoperoxide. The sodium chlorate was added to give a chlorate ions concentration of 1.5 g/L. The conversion coating weight was 0.9 g/m^2. The coating crystals were columnar and the average grain size was 15 micrometers. The conversion coating was sparsely deposited, and yellow rust was observed.

[0056] The conditions and results of these examples are summarized in Table 1 below.

[0057] The organoperoxide concentrations used in Examples 1 to 8 were 50 to 1,500 ppm. It was thereby demonstrated that this concentration range produced a good-quality conversion coating on cold-rolled steel sheet as well as galvanized steel sheet. A uniform, dense, and fine coating was obtained even when the surface conditioning treatment was not used.

[0058] In contrast, Comparative Examples 1 and 2 used organoperoxide concentrations below 50 ppm, and it was found that in these cases the oxidation activity by the conversion accelerator was inadequate, resulting in the deposition of scattered coating crystals. The uniformity of the coating on the basis metal was therefore diminished.

[0059] Comparative Examples 3 and 4 used non-organoperoxide conversion accelerators. In Comparative Example 3, a nitrite salt was used as the conversion accelerator and no surface-conditioning treatment was carried out. It was found

TABLE 1

Examples And Comparative Examples	Substrate	Phosphate Ions, g/L	Zinc Ions, g/L	Nitrogen Concentration, ppm	Surface Conditioning	Oxidizing Agent *
Example 1	SPC	15	1.3	0	yes	a
Example 2	plated	15	1.3	0	yes	a
Example 3	SPC	15	1.3	0	yes	a
Example 4	SPC	15	1.3	500	yes	a
Example 5	SPC	15	1.3	0	no	b
Example 6	SPC	15	1.3	0	yes	c
Example 7	SPC	15	1.3	0	no	a
Example 8	SPC	15	1.3	1400	yes	a
Comparative Example 1	SPC	15	1.3	0	yes	a
Comparative Example 2	plated	15	1.3	0	yes	a
Comparative Example 3	SPC	15	1.3	1400	no	d
Comparative Example 4	SPC	15	1.3	0	yes	e

*Type of oxidizing agents added:

a tert-butyl hydroperoxide
b tert-hexyl hydroperoxide
c peracetic acid
d nitrite ions
e chlorate ions

Examples And Comparative Examples	Oxidising Agent Concentration, ppm	Free Acidity Point(s)	Coating Weight g/m^2	Coating Appearance	Shape of Coating Crystals	Average Grain Size (micrometers)
Example 1	450	0.9	1.2	grayish black	plates	6
Example 2	450	0.9	2.8	grayish white	plates	4
Example 3	80	0.6	0.9	grayish black	plates	8
Example 4	1200	0.9	1.1	grayish black	plates	7
Example 5	400	0.9	1.0	grayish black	plates	6
Example 6	100	0.6	1.3	grayish black	plates	10
Example 7	500	0.6	1.1	grayish black	plates	10
Example 8	450	0.9	1.1	grayish black	plates	5
Comparative Example 1	5	0.9	0.5	yellow rust appeared	columnar	13
Comparative Example 2	5	0.9	0.9	sparse coating	columnar	15
Comparative Example 3	150	0.9	0.1	yellow rust appeared	granular	80
Comparative Example 4	1500	0.9	0 9	sparse coating	columnar	15

that in this case conversion coating deposition was entirely absent.

[0060] A chlorate salt was used by itself as the conversion accelerator in Comparative Example 4. It was found that in this case the conversion reaction rate was substantially slowed.

[0061] The zinc phosphate-based conversion bath according to the present invention for application to metal substrates contains 50 to 1500 ppm of organoperoxide as conversion accelerator. In consequence thereof, this bath yields uniform, fine, and dense conversion coatings with coating weights appropriate for the intended applications. This bath at the same time also acts to induce fine crystal formation in the conversion coating. As a result, the bath has such good effects that a surface-conditioning treatment is no longer a necessity.

[0062] We have found that the organic peroxides used by the present invention react under mild conditions and are more stable than the generally used inorganic accelerators, and as a consequence have very good economic attributes. Since the presence of nitrogenous compounds in the conversion treatment bath is also no longer a necessity, environmental regulations relating to the levels of nitrogenous compound discharge can now be fully satisfied, and on this point the conversion bath according to the present invention represents a major practical development.

Claims

1. An aqueous acidic phosphate conversion-coating composition for treating metal surfaces, which composition comprises water, 0.5 to 1.3 g/l zinc ions, 5 to 30 g/l phosphate ions and 50 to 1,500 ppm organic peroxide(s) as a conversion accelerator and which composition has a free acidity of 0.1 to 0.9 points.

2. A composition as claimed in claim 1, in which the concentration of nitrogen containing compounds, calculated as nitrogen, is less than 20 ppm.

3. A composition as claimed in claim 1 or 2 in which the organic peroxide(s) is/are alkyl-substituted organoperoxides wherein the alkyl substituents contain from 1 to 7 carbon atoms.

4. A composition as claimed in any of the preceding claims, having a pH value in the range of from 2.0 to 4.0.

5. A composition as claimed in claim 4, having a pH value in the range of from 2.5 to 3.5.

6. A process for forming a phosphate conversion coating on a metal surface, in which the metal surface is contacted with an aqueous liquid composition as claimed in any of the preceding claims at a treatment temperature of from room temperature up to 90°C and for a period of time in the range of from 30 seconds to 15 minutes.

7. A process as claimed in claim 6, in which prior to the formation of a phosphate conversion coating on the metal surface, it is first degreased and then rinsed with water and after formation of the phosphate conversion coating it is given a further water rinse.

Patentansprüche

1. Wässrige, saure Phosphat-Umwandlungsbeschichtungs-Zusammensetzung zur Behandlung von Metalloberflächen, wobei die Zusammensetzung Wasser, 0,5 bis 1,3 g/l Zinkionen, 5 bis 30 g/l Phosphationen und 50 bis 1500 ppm organisches Peroxid (organische Peroxide) als Umwandlungsbeschleuniger umfasst und wobei die Zusammensetzung einen Gehalt an freier Säure von 0,1 bis 0,9 Punkten aufweist.

2. Zusammensetzung nach Anspruch 1, wobei die Konzentration stickstoffhaltiger Verbindungen - als Stickstoff berechnet - weniger als 20 ppm beträgt.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei es sich beim organischen Peroxid (bei den organischen Peroxiden) um alkylsubstituierte Organoperoxide handelt, wobei die Alkylsubstituenten 1 bis 7 Kohlenstoffatome enthalten.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche mit einem pH-Wert im Bereich von 2,0 bis 4,0.

5. Zusammensetzung nach Anspruch 4 mit einem pH-Wert im Bereich von 2,5 bis 3,5.

6. Verfahren zur Bildung einer Phosphat-Umwandlungsbeschichtung auf einer Metalloberfläche, wobei die Metalloberfläche mit einer wässrigen, flüssigen Zusammensetzung nach einem der vorhergehenden Ansprüche bei einer Behandlungstemperatur von Raumtemperatur bis zu 90 °C und für einen Zeitraum im Bereich von 30 s bis 15 min in Kontakt gebracht wird.

7. Verfahren nach Anspruch 6, wobei vor der Bildung einer Phosphat-Umwandlungsbeschichtung auf der Metalloberfläche die Metalloberfläche erst entfettet und dann mit Wasser gespült und nach der Bildung der Phosphat-Umwandlungsbeschichtung ein weiteres Mal einem Spülen mit Wasser unterzogen wird.

Revendications

1. Composition acide aqueuse de revêtement par conversion à base de phosphate pour traiter des surfaces métalliques, cette composition comprenant de l'eau, de 0,5 à 1,3 g/l d'ions zinc, de 5 à 30 g/l d'ions phosphate et de 50 à 1 500 ppm de peroxyde(s) organique(s) en tant qu'accélérateur de conversion et cette composition ayant une

acidité libre de 0,1 à 0,9 points.

2. Composition selon la revendication 1, dans laquelle la concentration en composés contenant de l'azote, calculée comme azote, est inférieure à 20 ppm.

3. Composition selon les revendications 1 ou 2 dans laquelle le ou les peroxydes organiques est ou sont des peroxydes organiques substitués par un alkyle dans lesquels les substituants alkyle contiennent de 1 à 7 atomes de carbone.

4. Composition selon l'une quelconque des revendications précédentes ayant une valeur du pH dans la plage allant de 2,0 à 4,0.

5. Composition selon la revendication 4 ayant une valeur du pH dans la plage allant de 2,5 à 3,5.

6. Procédé pour former un revêtement par conversion de phosphate sur une surface métallique dans lequel la surface métallique est mise en contact avec une composition liquide aqueuse comme revendiquée dans l'une quelconque des revendications précédentes à une température de traitement allant de la température ambiante jusqu'à 90°C et pendant une période comprise dans l'intervalle allant de 30 secondes à 15 minutes.

7. Procédé selon la revendication 6 dans lequel, avant la formation d'un revêtement par conversion de phosphate sur la surface métallique, celle-ci est d'abord dégraissée, puis rincée avec de l'eau et, après la formation du revêtement par conversion de phosphate, elle est encore rincée à l'eau.