

The invention relates to a process operating free of waste water, for forming phosphate coatings on metal surfaces by means of aqueous zinc phosphate solutions containing iron (II) and nitrate ions.

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In the metal-working industry, the process of forming phosphate coatings by means of aqueous zinc phosphate solutions is used to a large extent. The phosphate coatings produced with this process on the treated metal surfaces serve particularly to facilitate sliding and cold-working, likewise to protect against corrosion and as a base for paints.

Such phosphate baths usually have a ph value of between 1.8 and 3.8 and contain zinc ions and phosphate ions as process-determining ingredients. In addition to the zinc cations, other cations such as ammonium, calcium, cobalt, iron, potassium, sodium, magnesium, manganese, may be present. To accelerate the formation of the phosphate layer, oxidizers such as bromate, chlorate, nitrate, nitrite, organic nitro compounds, perborate, persulfate, hydrogen peroxide, are generally added to the phosphating baths. It is also possible to use an oxygen-containing gas to oxidize iron (II) and iron (III). In order to optimize the formation of the layer on certain materials, additives consisting of for example fluoride, silicon fluoride, boron fluoride, citrate and tartrate, may be used. The large number of individual ingredients and their possible combinations permits a large number of different compositions to be used in the phosphating bath.

The phosphating baths are usually brought into contact with the workpiece surfaces to be treated by dipping, flooding or spraying. During the contact time, which can be from a few seconds to half an hour or more, chemical reaction to the metal results in the formation of crystalline phosphate layers which are firmly intergrown with the metal.

As any residual phosphating solution remaining on the surface would generally interfere with further processing, the phosphating treatment is followed by a thorough rinsing with water. In order to avoid a detrimental enrichment of the phosphating bath contents in the rinsing baths, the latter are replenished with fresh water and contaminated rinsing water is withdrawn as an overflow. The contaminated rinsing water contains pollutants and for this reason must be specially treated before it can be discharged into a sewer or receiving stream.

Because the need for treatment and disposal of spent rinsing water constitutes a disadvantage when using phosphating processes, it has been proposed for example in DE-C-23 27 304, to use a zinc phosphating process in which solutions are so-composed that virtually all components can be precipitated by treatment with $\text{Ca}(\text{OH})_2$. This will greatly facilitate the processing of the rinsing water and will simultaneously achieve the advantage that the processed rinsing water is of good quality and can be re-used in the process. However a disadvantage is that, due to the precipitability requirements, the freedom to adjust the phosphating bath to the requirements needed in practise is greatly restricted.

Additionally, F.Wilhelm (Metalloberflaeche, 33 (1979), pages 301-307) has reported on thoughts to provide a cascade rinsing after the zinc phosphating, and to save so much water that the rinsing water can be used to compensate for the losses from the zinc phosphating zone. However, according to the author, this cannot be put into effect, due to industrial processing and economic reasons.

The aim of the invention is to provide a process for producing phosphate coatings on metals, particularly on steel, galvanised steel, zinc alloy-plated steel, aluminized steel and aluminium, with the aid of zinc phosphate

solutions which contain iron (II) and nitrate ions, which operates free from waste water and from the known disadvantages, particularly those mentioned hereinbefore.

- 5 This task is accomplished, wherein the process mentioned above, in accordance with the invention, is so-developed that the metal surfaces are brought into contact with a phosphating solution which contains

10 0.4 to 30 g/l Zn
 4 to 30 g/l P_2O_5
 5 to 50 g/l NO_3
 up to 10 g/l Fe(II) and
 up to 0.3 g/l Fe(III)

- 15 and in which the weight ratio of free P_2O_5 to total P_2O_5 = (0.04 to 0.50) : is 1, and which is replenished with Zn, NO_3 and P_2O_5 in a weight ratio of

$Zn : NO_3 : P_2O_5 = (0.80 \text{ to } 0.30) : (0.17 \text{ to } 0.4) : 1$
preferably (0.60 to 0.40) : (0.20 to 0.35) : 1,

- whereby no addition of bromate, organic nitro compounds, perborate, persulphate and/or nitrite results, and in which the Fe(II) content is adjusted only by oxidation with nitrate, nitrite derived from nitrate, if need be together with an oxygen-containing gas, H_2O_2 and/or nitrous gases, the phosphating bath is succeeded by a cascade of at least
25 two rinsing baths, low-salt water or preferably salt-free water being fed into that rinsing bath which is last in the direction of travel of the workpieces, the overflowing water being directed into the preceding rinsing bath and phosphating bath respectively, and removing at least so much
30 low-salt or salt-free water from the phosphating bath that it can receive phosphate-enriched rinsing water from the cascade.

- From the point of view of the invention, the term "free of waste water" is understood to mean that no water from the
35 rinsing baths will be delivered to the sewer or the receiving stream, to counteract an enriching of undesired chemicals in the phosphating bath.

The process according to the invention is particularly intended for the surface treatment of iron and steel, low-alloy steel, galvanized steel, zinc alloy-plated steel, i.e. steel plated with ZnAl, ZnFe and ZnNi, aluminized steel, 5 aluminium and its alloys.

The phosphating solutions contain Zn, P_2O_5 and NO_3 as basic ingredients. Other cations and/or anions may also be present. Phosphating solutions which must be replenished 10 during the processing to maintain predetermined concentrations of bromate, chlorate, organic nitro compounds, perborate and/or persulfate are not suited to the waste water process in accordance with the invention. Those processes in which alkali nitrite must be added from time to 15 time or continuously as an accelerator are also unsuitable.

In accordance with a preferred feature of the invention, the metal surfaces are brought into contact with a phosphating solution which additionally contains

20	up to 10	g/l Mg
	up to 20	g/l Ca
	up to 20	g/l Mn
	up to 20	g/l Ni
	up to 10	g/l Co
25	up to 0.02	g/l Cu
	up to 20	g/l Na and/or K and/or NH_4
	up to 8	g/l SiF_6
	up to 8	g/l BF_4
	up to 5	g/l F
30	up to 10	g/l Cl

In accordance with further preferred features of the process according to the invention, the metal surfaces are brought into contact with a phosphating solution in which the weight 35 ratio

$(Mg + Ca + Mn + Ni + Co) : Zn$ is equal to or lower than 4: 1 and which is replenished with the ingredients Mg, Ca, Mn, Fe,

Ni, Co and Cu in a molar ratio

(Mg + Ca + Mn + Fe + Ni + Co + Cu) : Zn which is equal to or lower than 2.

- 5 Of those above-mentioned cations which are optionally contained in the phosphating baths, Fe(II) is not added as a chemical in most cases, but rather during the treatment of iron and steel, becomes enriched as a result of the pickling action unless it is transformed to a trivalent state by
10 oxidizing agents and is precipitated as iron (III) phosphate.

Fe(III) contained in the baths serves, inter alia, to stabilize the equilibrium for the phosphating reaction.

- 15 Through the joint use of Mg and/or Ca and/or Mn, phosphate coatings are obtained which also contain these cations in addition to Zn and if need be Fe(II). Such mixed phosphates distinguish themselves by having a higher resistance to alkali and for this reason are particularly suitable as a
20 base for paints. They have also proved themselves satisfactory as a carrier for lubricants used during cold-working. Ni and/or Co are used in preference to increase the aggressive action of the baths on steel and to improve the phosphating of zinc surfaces. Small amounts of copper
25 have an accelerated effect. Alkali cations and/or ammonium are mainly used to adjust the desired acid ratio. The anions F^- , BF_4^- and SiF_6^{2-} generally increase the phosphating rate and are advantageous in treating zinc surfaces which contain aluminium. The presence of free fluoride (F^-) is
30 essential for the formation of crystalline phosphate coatings on aluminium and its alloys. Cl can be used to adjust the electroneutrality and, in special cases, to increase the aggressive action of the baths. The thickness of the phosphate coatings which are produced and their
35 weight per unit area can be influenced by the addition of polyhydroxycarboxylic acids, e.g. tartaric acid and/or citric acid.

The type and quantity of anions and cations in the phosphating solutions used in the process in accordance with the invention are so-adjusted that the ratio of free P_2O_5 to total P_2O_5 is (0.04 to 0.50): 1. A higher (lower) ratio
5 should be selected in the case of higher (lower) bath temperatures and/or concentrations in the phosphating solution.

To obtain a good coating, the concentration of Fe(II) should
10 not exceed the concentration of zinc, and the total concentration of $Mg + Ca + Mn + Ni + Co$ should not exceed four times the concentration of zinc.

As according to the inventive process, losses from the bath
15 do not arise as a result of mechanical discharge, therefore there is no compensating action. For this reason the proper selection of replenishing substances is of special significance, and the weight ratio of $Zn : NO_3 : P_2O_5$ in the replenishing materials must be kept within the narrow range
20 of (0.60 to 0.30) : (0.2 to 0.4) : 1. Also, if an addition is intended, the molar ratio of $(Mg + Ca + Mn + Fe + Ni + Co + Cu) : Zn$ should not exceed 2:1.

25 The replenishment will be particularly effective if, in accordance with a further preferred feature of the invention, the metal surfaces are brought into contact with a phosphating solution which is replenished by an addition of phosphate in a ratio of free P_2O_5 to total P_2O_5 , is
30 (-0.4 to +0.5): 1 during replenishment. In the above definition of the ratio of free P_2O_5 to total P_2O_5 , the minus sign means that there is no free P_2O_5 , but part of the phosphate is present in the stage of secondary phosphate. For instance, a value of minus 0.19 means that 19% of the
35 total P_2O_5 is present as secondary phosphate.

In accordance with another definition, the phosphate components in the replenishment are located within a range, which is limited on the one hand to 40% secondary phosphate and 60% primary phosphate (calculated as P_2O_5), and on the other hand to 50% primary phosphate and 50% free phosphoric acid (calculated as P_2O_5).

If the ratio of free P_2O_5 to total P_2O_5 in the replenishment is equal to or higher than about 0.2 : 1, the replenishing ingredients will usually be added in the form of acid aqueous chemical concentrate. As liquid replenishing concentrates, having a ratio of free P_2O_5 to total P_2O_5 lower than 0.2 : 1, are unstable, then the replenishing will be carried out by at least two separate concentrates. The additions will be suitably so-timed that the composition of the phosphating solution will remain at least substantially constant even when there are fluctuations in the discharge rate, that means fluctuations in the consumption. Certain parts of the required replenishment may be added to the bath separately from the replenishing concentrate proper. As an example the addition of zinc oxide or zinc carbonate may be mentioned, on the one hand to increase the zinc concentration, and on the other hand to correct the ratio of free P_2O_5 to total P_2O_5 .

The oxidation accelerators used in the process in accordance with the invention consist only of NO_3 , if need be together with oxygen-containing gas, H_2O_2 and/or nitrous gases. In baths which are autocatalytic on the nitrite side, i.e. in baths in which the weight ratio of NO_3 to P_2O_5 exceeds 2:1, a small amount of nitrite, about 0.05 to 0.15 g/l, e.g. as zinc nitrite or calcium nitrite, is preferably added at the beginning of the process. A formation of nitrite from the nitrate may also be initiated by short-time phosphating of zinc, zinc granules or zinc dust or by an initial phosphating of steel at a lower discharge density. Alkali nitrite should only be used to start the bath process in

exceptional cases, as this would result in an enriching of alkali to a disturbing extent. Due to the absence of a surplus of nitrite or H_2O_2 , Fe(II) will become enriched in baths used to treat iron and steel. Enrichment of iron to
 5 above the disturbance boundary can be avoided through intense solution contact with an oxygen-containing gas, such as air, and/or H_2O_2 .

The phosphating step is succeeded by a cascade of at least
 10 two rinsing baths. The principle of the cascade of rinsing baths is that fresh water is fed only to the last rinsing bath and an overflow into the preceding baths is effected. In this manner a flow of rinsing water is produced counter to the workpieces direction of travel. The concentration of
 15 impurities in the several rinsing baths will differ and will depend on the feed rate of fresh water, the fluid conveyance by the workpieces, the number of rinsing baths in the cascade and the concentration of the phosphating solution (see table 1).

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Table 1

- Equilibrium concentration for cascade rinsing in 1-6 stages

- concentration in bath preceding the cascade (g/l): 50

25 - rate of liquid conveyed by workpieces (ml/qm): 30

- rate of counterflowing liquid relative to surface area of workpieces (ml/qm): 200

30 Calculated concentrations of the individual baths (g/l)

bath	cascades					
1	6.522	7.356	7.487	7.497	7.500	7.500
2	---	0.959	1.100	1.121	1.124	1.125
3	---	---	0.144	0.165	0.168	0.169
35 4	---	---	---	0.022	0.025	0.025
5	---	---	---	---	0.003	0.004
6	---	---	---	---	---	0.000

In the process according to the invention, that at least so much low-salt or salt-free water is removed from the phosphating bath by a suitable process, that it can receive the phosphate-rich overflow taken from the cascade.

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The characteristic data of the cascade (number of stages, rate of counterflowing liquid, rate of liquid conveyed by workpieces) must be so-selected that the last rinsing bath has a purity which is sufficient for the technical requirements of further treatments. The effectiveness of a cascade of rinsing baths can be increased if there is no direct overflow from one bath to the preceding one, but the overflow is first sprayed onto the workpiece leaving the preceding bath before the liquid is fed to the rinsing bath.

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Further preferred embodiments of the inventive process reside in that the salt-free or low-salt water is recovered from the phosphating bath by a single or multiple-effect evaporation, reverse osmosis or electrodialysis, and said water is fed back as fresh water to the cascade of rinsing baths.

In accordance with a further preferred embodiment the phosphate-containing rinsing waters from the cascade of rinsing baths are concentrated, particularly by evaporation, electrodialysis or reverse osmosis, before said waters are fed to the phosphating bath.

The phosphating treatment results in a bath sludge, which is removed from the system continuously or from time to time, e.g. by sedimentation, filtration and the like. This wet sludge contains 50 to 90% adhering phosphating solution. In accordance with a further preferred embodiment of the invention, the consumption of chemicals and the rate of waste water are decreased, in that this phosphate sludge which has been removed, is washed with water, which is then fed to the cascade of rinsing baths or directly to the

phosphating bath. The phosphate sludge may be washed with rinsing water from the individual rinsing baths in a plurality of stages, in the form of a cascade, if desired.

- 5 It is particularly advantageous to wash the phosphate sludge in a plurality of stages with the water from the cascade of rinsing baths, and to feed the used wash water into the cascade of rinsing baths or directly to the phosphating bath.

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The invention will be explained by way of example and in more detail with reference to the following Examples.

Example 1

- 15 Bright steel sheets were degreased by being dipped into an aqueous cleaner and were subsequently rinsed with water. The thus-prepared specimens were phosphated for 10 minutes at 90°C by being dipped into an aqueous solution composed of

20	21.6	g/l P_2O_5
	28.6	g/l Zn
	0.028	g/l Ni
	42.2	g/l NO_3
	free P_2O_5	= 7.8
25	total P_2O_5	= 21.6
	free P_2O_5	total P_2O_5 = 0.36
	number of points	: 80

- 30 The phosphating step was succeeded by rinsing in a three-stage cascade. An evaporation of 0.2 l/m² of the treated steel surface was effected from the phosphating bath during the throughput of material. Salt-free water was fed to the last rinsing bath of the cascade at a rate of 0.2 l per m² of treated steel surface. The resulting overflow was fed to
- 35 rinsing bath 2, rinsing bath 1 and finally to the phosphating bath.

To maintain the phosphating bath at a constant number of points, the phosphating bath was replenished with a concentrate composition of

5	25	% P_2O_5
	6.25	% NO_3
	12.5	% Zn
	0.03	% Ni

Free P_2O_5 : total- P_2O_5 = 0.2

Zn : NO_3 : P_2O_5 = 0.5 : 0.25 : 1

- 10 Air was stirred into the phosphating bath during the throughput to keep the Fe(II) concentration at or below 5 g/l.

Under stationary conditions after a throughput of a substantial amount of material, the following numbers of

- 15 points were obtained in the rinsing baths

rinsing bath 1 : 12 points

rinsing bath 2 : 1.8 points

rinsing bath 3 : 0.2 points

- 20 The stationary composition of the phosphating solution was as follows:

20.5 to 23 g/l P_2O_5

22 to 24 g/l Zn

4 to 5 g/l Fe(II)

41 to 43 g/l NO_3

- 25 free P_2O_5 : total- P_2O_5 = 0.32 to 0.46

From the experiment, it is apparent that the process in accordance with the invention can be carried out in such a manner that,

- 30 - satisfactory phosphate coatings are formed,
 - the concentration of the phosphating solution is maintained static,
 - there will be no contaminated waste water from the rinsing baths
 35 - and the last rinsing bath will be operated with a lower salt concentration (0.2 point corresponding to 0.23 g/l salt).

Example 2

Various phosphating bath compositions and replenishing concentrates which can be used in the process in accordance with the invention have been compiled in table 2.

Table 2

		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Bath composition					
Zn	(g/l)	17	10.2	16.8	11
Mn	(g/l)	-	9.2	-	-
Fe	(g/l)	0.03	0.02	0.02	-
Ca	(g/l)	-	-	-	11
Cu	(g/l)	-	-	0.003	-
Na	(g/l)	-	-	2.6	1.1
Fe(II)	(g/l)	2.5	5.0	1.5	-
P ₂ O ₅	(g/l)	23.5	20	14.6	22
NO ₃	(g/l)	24.9	39.2	32	44
F	(g/l)	-	-	0.6	-
Free P ₂ O ₅ : total P ₂ O ₅		0.37	0.31	0.35	0.28

Replenishing concentrates					
Zn	(%)	9	8	10	5.8
Mn	(%)	-	0.8	-	-
Fe	(%)	0.02	0.01	0.01	-
Ca	(%)	-	-	-	1.8
Cu	(%)	-	-	0.02	-
Na	(%)	-	-	-	-
P ₂ O ₅	(%)	18	20	18	19
NO ₃	(%)	4.5	7	6.1	4.9
F	(%)	-	-	0.2	-
Free P ₂ O ₅ : total P ₂ O ₅		0.20	0.43	0.22	0.30

ABSTRACT

A process for forming phosphate coatings on metal surfaces by means of aqueous zinc phosphate solutions containing iron (II) and nitrate ions, can be carried out, operating free of waste water, if the metal surfaces are brought into contact with an aqueous phosphating solution which contains

0.4 to 30 g/l Zn
 4 to 30 g/l P_2O_5
 5 to 50 g/l NO_3
 up to 10 g/l Fe(II) and
 up to 0.3 g/l Fe(III)

and in which the weight ratio of free P_2O_5 to total P_2O_5 = (0.04 to 0.50) : 1 and which is replenished with Zn, NO_3 and P_2O_5 in a weight ratio of Zn : NO_3 : P_2O_5 = (0.60 to 0.30) : (0.2 to 0.4) : 1 and in which the Fe(II) content is adjusted only by oxidation with nitrate, nitrite derived from nitrate, likewise together with an oxygen-containing gas, H_2O_2 and/or nitrous gases. The phosphating bath is succeeded by a cascade of at least two rinsing baths, low-salt water or preferably salt-free water being fed into that rinsing bath which is last in the direction of travel of the workpieces, the overflowing water being directed into the preceding rinsing bath and phosphating bath respectively, and removing at least so much low-salt or salt-free water from the phosphating bath that it can receive phosphate-enriched rinsing water from the cascade.

CLAIMS:

1. A process operating free of waste water, forming phosphate coatings on metal surfaces by means of aqueous zinc phosphate solutions containing irons (II) and nitrate ions, whereby the metal surfaces are brought into contact with a phosphating solution which contains

0.4 to 30 g/l Zn

4 to 30 g/l P_2O_5

5 to 50 g/l NO_3

up to 10 g/l Fe(II) and

up to 0.3g/l Fe(III)

in which the weight ratio of free P_2O_5 to total P_2O_5 = (0.04 to 0.50) : 1 and which is replenished with Zn, NO_3 and P_2O_5 in a weight ratio of Zn : NO_3 : P_2O_5 = (0.80 to 0.30) : (0.17 to 0.4) : 1, whereby no addition of bromate, chlorate, organic nitro compounds, perborate, persulfate and/or nitrite results, and in which the acceleration of the formation of the phosphate layer as also the adjustment of the Fe (II) content through oxidation only results

a) with nitrate or

b) with nitrate and nitrite derived from nitrate

c) with nitrate and at least one of the oxidising agent oxygen-containing gas, H_2O_2 and nitrose gas or

d) with nitrate and nitrite derived from nitrate, likewise with one of the oxidising agent oxygen-containing gas, H_2O_2 , and nitrose gas,

the phosphating bath is succeeded by a cascade of at least two rinsing baths, low salt water being fed into that rinsing bath which is last in the direction of travel of the workpieces, the overflowing water being directed into the preceding rinsing bath and phosphating bath respectively, and removing at least so much low-salt water from the phosphating bath that it can receive phosphate-enriched rinsing water from the cascade.

2. A process according to Claim 1, characterised in that the metal surfaces are brought into contact with a solution which is replenished with Zn, NO₃ and P₂O₅ in the weight ratio of Zn : NO₃ : P₂O₅ = (0.60 to 0.40) : (0.20 to 0.35) : 1.

3. A process according to Claim 2, characterised in that the metal surfaces are brought into contact with a phosphating solution which additionally contains

	up to 10	g/l Mg
	up to 20	g/l Ca
	up to 20	g/l Mn
	up to 20	g/l Ni
15	up to 10	g/l Co
	up to 0.02	g/l Cu
	up to 20	g/l Na and/or K and/or NH ₄
	up to 8	g/l SiF ₆
	up to 8	g/l BF ₄
20	up to 5	g/l F
	up to 10	g/l Cl

4. A process according to Claims 1, 2 or 3, characterised in that the metal surfaces are brought into contact with a phosphating solution in which the ratio of Fe(II) : Zn is equal to or lower than 1:1 and the ratio of

(Mg + Ca + Mn + Ni + Co) : Zn is equal to or lower than 4 : 1.

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5. A process according to Claims 1, 2, 3 or 4, characterised in that the metal surfaces are brought into contact with a phosphating solution which is replenished with the ingredients Mg, Ca, Mn, Ni, Fe, Co, and/or Cu with a molar ratio

(Mg + Ca + Mn + Fe + Ni + Co + Cu) : Zn equal to or lower than 2 : 1.

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6. A process according to any of Claims 1 to 5, characterised in that the metal surfaces are brought into contact with a phosphating solution which is replenished by an addition of phosphate in a ratio of free P_2O_5 to total P_2O_5 is (-0.4 to 0.5) : 1 during replenishment.

7. A process according to any of Claims 1 to 6, characterised in that low-salt or salt-free water is removed from the phosphating bath by a single-effect or multiple-effect evaporation, by reverse osmosis or electrodialysis.

8. A process according to any of Claims 1 to 7, characterised in that the low-salt or salt-free water obtained from the phosphating bath is supplied as fresh water to the cascade of rinsing baths.

9. A process according to any of Claims 1 to 8, characterised in that those substances from the cascade of rinsing baths which are effective for the phosphating are concentrated, particularly by evaporation, electrodialysis or reverse osmosis, before they are introduced to the phosphating bath.

10. A process according to any of Claims 1 to 9, characterised in that the sludge formed in the phosphating bath is washed with water after its removal and the wash water is fed to the cascade of rinsing baths or directly to the phosphating bath.

11. A process according to Claim 10, characterised in that the phosphate sludge is washed in a plurality of stages with water from the cascade of rinsing baths.