FORM 1 APPLICATION NO. 604395 SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Gerhard Collardin GmbH, of Widdersdorfer Strasse 215, 5000 Koln-Ehrenfeld, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of a standard patent for an invention entitled:

Process for Phosphating Metal Surfaces

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
P 38 00 835.1	DE	14 January 1988

The address for service is:-

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DATED this THIRTEENTH day of JANUARY 1989

Gerhard Collardin GmbH

By: M.J. Anderson

Registered Patent Attorney

5004776 13/01/89

TO: THE COMMISSIONER OF PATENTS
OUR REF: 75074
S&F CODE: 55370

5845/2

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Process for Phosphating Metal Surfaces

I/We, Günther Stolzenfels / Dr. Wolf-Achim Roland
[full name of declarant(s)]

of Oppelner Weg 4, 5030 Hürth / Spreestr. 60, 5650 Solingen
[full address of declarant(s) - not post office box]

both in the Federal Republic of Germany

do solemnly and sincerely declare as follows:-

1. ~~I am~~/We are authorised by Gerhard Collardin GmbH, the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in Federal Republic of Germany on 14 January, 1988 by Henkel Kommanditgesellchaft auf Aktien.

3. KURT HOSEMANN and REIHARD OPITZ, of Mozartstrasse 9, 5177 Titz 4 and Wirtelstrasse 35, 5160 Duren both in the Federal Republic of Germany [respectively], are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

   The said applicant is the assignee of Henkel Kommanditgesellschaft auf Aktien which is the assignee of the actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Hurth this 12th day of December 1988

Signature of Declarant

Günther Stolzenfels Dr. Wolf-Achim Roland

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-28508/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 604395

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PROCESS FOR PHOSPHATING METAL SURFACES

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(56) Prior Art Documents
US 4622078

(57) Claim

1. A process for phosphating a metal surface as a pretreatment for cold working, wherein the surface is cleaned and/or mordanted, said process being characterized in that the surface without previous activation is contacted in a temperature range of from 30 °C to 70 °C with an aqueous solution containing
(a) from 10 to 40 g/l of Ca^{2+} ions,
(b) from 10 to 40 g/l of Zn^{2+} ions,
(c) from 10 to 100 g/l of PO_4^{3-} ions
and, as accelerator,
(d) from 10 to 100 g/l of NO_3^- ions and/or
(e) from 0.1 to 2.0 g/l of an organic nitro compound,
said solution exhibiting a pH value in the range of from 2.0 to 3.8 and a ratio of free acid to total acid of from 1:4 to 1:100.

5. The process according to any one of claims 1 to 4, characterized in that said solution additionally contains Ni^{2+} ions in an amount of from 0.01 to 10 g/l.

6. The process according to any one of claims 1 to 5, characterized in that said solution additionally contains simple and/or complex fluorides in amounts of from 0.01 to 10 g/l.

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FORM 10

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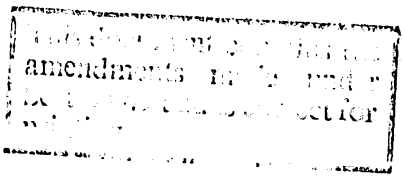
COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:



Priority:

Related Art:

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Complete Specification for the invention entitled:

Process for Phosphating Metal Surfaces

The following statement is a full description of this invention, including the best method of performing it known to me/us

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Abstract of the Disclosure

PROCESS FOR PHOSPHATING METAL SURFACES

The present invention relates to a process for phosphating metal surfaces, and more specifically of surfaces of iron, steel, zinc and the alloys thereof and aluminum as a pretreatment for cold working, wherein the surface is cleaned and/or mordanted in a per se known manner, said process being characterized in that the surfaces without previous activation are contacted in a temperature range of from 30 °C to 70 °C with an aqueous solution containing

(a) from 10 to 40 g/l of Ca^{2+} ions,
(b) from 10 to 40 g/l of Zn^{2+} ions,
(c) from 10 to 100 g/l of PO_4^{3-} ions

and, as accelerator,

(d) from 10 to 100 g/l of NO_3^- ions and/or
(e) from 0.1 to 2.0 g/l of organic nitro compounds,

said solution exhibiting a pH value in the range of from 2.0 to 3.8 and a ratio of free acid to total acid of from 1:4 to 1:100.

PROCESS FOR PHOSPHATING METAL SURFACES

The present invention relates to a process for phophating metal surfaces, and more particularly to zinc-calcium phosphating surfaces of iron, steel, zinc and/or aluminum as pretreatment for cold working.

Processes for phosphating surfaces of iron, steel, zinc and the alloys thereof and of aluminum have been known for long (Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Volume 15 Page 686 et seq.). Phosphating said surfaces serves to increase the adhesion strength of varnish layers and to improve the protection from corrosion.

Of the greatest importance among the phosphating processes are those of zinc phosphating and of alkali phosphating. Zinc phosphating baths may contain, for example, monozinc phosphate, free phosphoric acid, zinc nitrate and oxidants as the main components. The pH value of such solutions conventionally is in the range between 2.8 and 3.4. The process proceeds in two reactions, the mordanting reaction and the formation of a zinc phosphate layer on the surface to be phosphated.

In contrast thereto, the alkali phosphating processes clean and degrease the metal surface and form an

anticorrosive cover layer which mainly consists of iron phosphate. The layer formation is initiated by a mordanting reaction wherein a small amount of the substrate metal is dissolved. The predominant portion of the dissolved surface material reacts with the phosphate ion of the solution to form sparely soluble phosphates which are being deposited as a strongly adhering coating on the surface. Contrary to the zinc phosphation, here the layer-forming cation is derived from the substrate metal itself.

In anticorrosion phosphating basically two layer types may be distinguished: Iron phosphate layers having a low layer weight of about 0.2 to 0.4 g/m^2, and iron phosphate layers having higher area weights of 0.6 to 1.2 g/m^2. The thin phosphate layers are particularly suitable for being coated with a varnish; they provide an excellent varnish adhesion, offer a good protection from interstitial rust formation, electrical insulation, reduction in the sliding resistance and facilitate cold working.

For cold working, phosphate layers having a layer weight of up to 40 g/m^2 are usually deposited. Metal soaps are known to be formed by the reaction of the known phosphate layers for cold working with appropriate sodium stearate soaps. Aluminum, calcium, lithium, zinc and magnesium stearates are known to be water-repellent and when used as solid lubricants in wire-drawing at higher area pressing result in lower frictional values than those provided by conventional alkali soaps.

Since the melting points are lower than those of sodium soaps and the metal stearates alone by themselves

are too fat, in practice carrier materials such as lime are incorporated in order to retain the metal soaps in the lubricant slot. Metal soaps have the advantage over alkali soaps of that they hardly absorb any moisture from the air, retain their lubricating power unchanged due to their high compression stability and enable higher reductions in cross section to be employed, whereas the lubricating effect of alkali soaps may be greatly lowered due to moisture absorption.

The European Patent Specification No. 0 045 110 describes a process for the preparation of phosphate coatings on iron or steel surfaces in the immersion or flow coating process using an aqueous acidic zinc phosphate solution, wherein the surfaces are contacted with a solution containing Zn^{2+} and, in addition thereto, PO_4^{3-}, NO_3^- or an equally acting accelerator which does not oxidize iron(II), in which solution the ratio by weight of $Zn:PO_4$ is greater than 0.8, the ratio of total acid to free acid is at least 5, and the iron(II) content is adjusted to from 0.05 to 1% by weight by adding a suitable amount of ClO_3^- or another equally acting accelerator which oxidizes iron(II) to iron(III).

It was the object of the present invention to provide an improved process for phosphating metal surfaces, and more specifically, surfaces of iron, steel, zinc and the alloys thereof and of aluminum as a pretreatment for cold working.

The object of the present invention is attained by the improved phosphating process based on zinc-calcium phosphate layers.

Subject matter of the present invention is a process for phosphating a metal surface as a pretreatment for cold working, wherein the surface is cleaned and/or mordanted, said process being characterized in that the surface without previous activation is contacted in a temperature range of from 30 °C to 70 °C with an aqueous solution containing

(a) from 10 to 40 g/l of Ca^{2+} ions,

(b) from 10 to 40 g/l of Zn^{2+} ions,

(c) from 10 to 100 g/l of PO_4^{3-} ions

and, as accelerator,

(d) from 10 to 100 g/l of NO_3^- ions and/or

(e) from 0.1 to 2.0 g/l of an organic nitro compound,

said solution exhibiting a pH value in the range of from 2.0 to 3.8 and a ratio of free acid to total acid of from 1:4 to 1:100.

Typically, the metal to be subjected to the process is iron, steel, zinc or the alloys thereof, or aluminium.

Suprisingly, although the Zn:Ca ratio is different from that according to the European Patent 0 045 101 and in spite of the high proportions of calcium, there was found a layer configuration which was not to be expected according to prior art for such a high Ca ion concentration in the phosphating solution.

According to a preferred embodiment of the present invention, the phosphating solution with which the surfaces to be coated are brought into contact may contain Zn^{2+} and Ca^{2+} ions in the ratio by weight of from 1:0.5 to 1:1.5, and preferably in a ratio of 1:1.

Advantageously, preferred embodiments of the present phosphating solution contain further cations of transition metals in addition to the above-mentioned Ca^{2+} and Zn^{2+} cations. Particularly preferred in this place are Ni^{2+} ions. In the case that the phosphating solutions contain Ni^{2+} ions, an amount of from 0.01 to 10 g/l of Ni^{2+} ions is preferred.

In addition to the anions mentioned such as PO_4^{3-} and NO_3^- ions, phosphating solutions according to the invention may contain further additional anions. According to one preferred embodiment, the further anions optionally to be used include simple and/or complex fluorides. These may be used in the phosphating solutions, more particularly, in amounts of from 0.01 to 10 g/l.

While the process according to the invention is regularly carried out in the range of from 30 °C to 70 °C, one preferred embodiment of the present invention consists of adjusting the temperature range to from 50 °C to 70 °C and to contact the metal surfaces with the phosphating solutions.

Phosphating solutions according to the invention may contain from 0.1 to 2.0 g/l of organic nitro compounds in the place of 10 to 100 g/l NO_3^- ions. Organic nitro compounds within the scope of the present invention are selected from m-nitrobenzene sulfonates and/or nitroguanidine. The organic nitro compounds may also be present in an amount of from 0.1 to 2.0 g/l of organic nitro compounds in addition to 10 to 100 g/l NO_3^- ions in the phosphating solutions. According to one embodiment of the present invention, the process for

phosphating metal surfaces, and more specifically surfaces of iron, steel, zinc and the alloys thereof and of aluminum produces zinc-calcium phosphate layers (Scholzite) having an area weight of from 3 to 9 g/m^2.

The zinc-calcium phosphate layers may be produced on the metal surfaces by immersion, spraying and flow coating as well as by combined procedures. Prior to the application of the phosphating process according to the invention the surfaces to be phosphated are degreased according to processes known in the art. Residues of oil, grease and lubricant or of grinding dust left over from preceding manufacturing processes may be removed by organic solvents or organic cleansing agents. Chlorinated hydrocarbons are the most frequently used organic solvents, because they excellently dissolve oils and greases and are not inflammable. However, solid materials and inorganic contaminants are only insufficiently removed. Water-based cleansing agents have a very high cleaning efficiency. They contain surface-active substances emulsifying oil and grease in water and inorganic components such as carbonates, silicates, borates and phosphates which exhibit alkaline reaction and saponify natural fats. A further possibility of pre-cleaning prior to phosphating consists of subjecting the metal surfaces to be cleaned to ultrasonic or mechanical cleaning procedures.

The advantage of the present invention resides in that zinc-calcium phosphate layers are suitable to produce low layer weights on wire in an order of magnitude of from 3 to 9 g/m^2.

The zinc-calcium phosphate layers formed for the most part contain the mineral Scholzite. Upon reaction

of the zinc-calcium phosphate layers with the sodium stearate soaps used in the art there is formed besides zinc stearate and calcium stearate also a mixed soap comprising zinc-calcium stearate.

Zinc-calcium stearate has the advantage under technical aspects of drawing that the use-life of the drawing die is increased by far. Drawing tests in a technical test unit further gave the result that the wire surfaces show an essentially brighter and more uniform optical appearance, more specifically so upon a subsequent polishing draw, than is attainable by conventional procedures run on the accelerator side.

A further advantage of the product is to be seen in that the new zinc-calcium phosphating process for cold working is carried out in a temperature range of from 50 °C to 70 °C. The sludge properties are to be rated as particularly favourable in this process, since even after a bath load of 1.5 m^2 of steel surface per 1 liter of bath solution only a minimum amount of bath sludge on the order of a few milliliters is formed. A still further advantage of the present invention is constituted by that the zinc-calcium stearate mixed soaps formed upon the reaction with drawing soap (sodium stearate) enable the drawing die to have a longer use-life due to the improved properties.

EXAMPLES

EXAMPLE 1

A phosphating solution was prepared which contained
10.3 g l^{-1} of Ca^{2+} ions,
14.0 g l^{-1} of Zn^{2+} ions,
27.8 g l^{-1} of PO_4^{3-} ions,
46.5 g l^{-1} of NO_3^- ions.

The phosphating solution had the following characteristic data:
pH value: about 2.6
acid ratio: about 1:21 (free acid to total acid)

Steel wires which previously had been cleaned with an alkaline cleansing solution by an immersion treatment at 80 °C for 10 minutes and rinsed with water were treated with the above phosphating solution by immersion at 50 °C for 7 min. Then the wires were rinsed with water, and a reactive soap was applied thereonto. Then the wires were drawn through drawing dies. The result was a very bright and shining surface which could not be attained by using phosphating solutions other than those according to the invention.

EXAMPLE 2

A solution was prepared which contained
18.0 g/l of Ca^{2+} ions,
12.0 g/l of Zn^{2+} ions,
2.8 g/l of Ni^{2+} ions,
87.2 g/l of PO_4^{3-} ions,
27.5 g/l of NO_3^- ions.

The pH value was 2.5, and the ratio of free acid to total acid was 1:17.6.

Steel wire which previously had been cleaned in an alkaline immersion bath at 80 °C for 10 minutes and then cold rinsed was treated with the above phosphating solution by immersion at 55 °C for 10 min.

Then the wires were rinsed with water, and a reactive drawing soap was applied thereonto in the immersion bath at 80 °C.

The wire thus coated could be trouble-free drawn through several drawing dies in series to be reduced to the predetermined dimension. Thereby a bright and shining surface was formed.

The claims defining the invention are as follows:

1. A process for phosphating a metal surface as a pretreatment for cold working, wherein the surface is cleaned and/or mordanted, said process being characterized in that the surface without previous activation is contacted in a temperature range of from 30 °C to 70 °C with an aqueous solution containing
(a) from 10 to 40 g/l of Ca^{2+} ions,
(b) from 10 to 40 g/l of Zn^{2+} ions,
(c) from 10 to 100 g/l of PO_4^{3-} ions
and, as accelerator,
(d) from 10 to 100 g/l of NO_3^- ions and/or
(e) from 0.1 to 2.0 g/l of an organic nitro compound,
said solution exhibiting a pH value in the range of from 2.0 to 3.8 and a ratio of free acid to total acid of from 1:4 to 1:100.

2. The process according to claim 1, wherein said metal is iron, steel, zinc or the alloys thereof, or aluminium.

3. The process according to claim 1 or claim 2, characterized in that said solution contains Zn^{2+} and Ca^{2+} ions in the ratio by weight of from 1:0.5 to 1:1.5.

4. The process according to any one of claims 1 to 3, characterized in that said solution contains Zn^{2+} and Ca^{2+} ions in the ratio by weight of 1:1.

5. The process according to any one of claims 1 to 4, characterized in that said solution additionally contains Ni^{2+} ions in an amount of from 0.01 to 10 g/l.

6. The process according to any one of claims 1 to 5, characterized in that said solution additionally contains simple and/or complex fluorides in amounts of from 0.01 to 10 g/l.

7. The process according to any one of claims 1 to 6, characterized in that said metal surface is brought into contact with said solution at from 50 °C to 70 °C.

8. The process according to any one of claims 1 to 7, wherein said organic nitro compound is an m-nitrobenzene sulfonate and/or nitroguanidine.

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9. The process according to any one of claims 1 to 8, characterized in that phosphate layers produced have layer weights of from 3 to 9 g/m^2.

10. The process according to any one of claims 1 to 9, characterized in that said metal surface is treated with said solution by immersion, spraying and flow coating or by combined procedures.

11. A process for phosphating metal surfaces substantially as hereinbefore described with reference to any one of the Examples.

DATED this SIXTH day of September 1990
Gerhard Collardin GmbH

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

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