I/We Metallgesellschaft A.G. of Reuterweg 14, Postfach 3724, D-6000 Frankfurt am Main 1, FEDERAL REPUBLIC OF GERMANY.

hereby apply for the grant of a standard patent for an invention entitled:

PROCESS OF PRODUCING PHOSPHATE COATINGS ON METALS

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: P 36 36 390.1
Convention country in which basic application was filed: FEDERAL REPUBLIC OF GERMANY
Date of basic application: 25 October 1986

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Dated: 21 October 1987

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for: Metallgesellschaft A.G.

By:

Our Ref: 72050
POF Code: 1442/61870

FEE STAMP TO VALUE OF
ATTACHED
MAIL OFFICER

6012q/1
DECLARATION FOR A PATENT APPLICATION

In support of the (a) Convention application made by
(b) METALLGESELLSHAFT A.G.

(hereinafter called "applicant(s)" for a patent (c) for an invention entitled (d)

PROCESS OF PRODUCING PHOSPHATE COATINGS
ON METALS
Dr. Michel and Wolfgang Schneider of
We (d) METALLGESELLSHAFT A.G.
Reuterweg 14, Postfach 3724
D6000, Frankfurt am Main 1, West Germany

do solemnly and sincerely declare as follows:

1. I am/We are-the applicant(s).
   (or, in the case of an application by a body corporate)
2. I am/We are authorized to make this declaration on behalf of the applicant(s).
3. I am/We are-the actual inventor(s) of the invention.
   (or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s) (See headnote*)

(g) Insert FULL name(s) AND address(es) of declarant(s)

(h) Insert country, filing date, and basic applicant(s) for EACH basic application

(i) Insert PLACE of signing

(j) Insert DATE of signing

(k) Signature(s) of declarant(s)

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:

West Germany
Filed October 25, 1986
METALLGESELLSHAFT A.G.

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at (k) West Germany
Dated (l) 5 November 1987

Metallgesellschaft
Aktiengesellschaft

By: [Signature]
Title: [Michel] [Wolfgang Schneider]

To: The Commissioner of Patents

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia
INVENTOR INFORMATION:

Name: Dr. Han Yong Oei
Address: Liebigstrasse 18
       6000 Frankfurt am Main
       West Germany

Name: Gunter Siemund
Address: Im Birkenneck 53
       6056 Heusenstamm
       West Germany

Name: Rudolf Vey
Address: Weitzesweg 13
       6368 Bad Vilbel
       West Germany
1. A process for producing a phosphate coating on metals having surfaces which consist at least in part of iron or steel or coated iron or steel by a treatment with an aqueous phosphatizing solution, which contains zinc ions, manganese ions, $\text{PO}_4$ ions, nitrate ions and iron(II) ions, characterized in that the metals are contacted with a phosphatizing solution which is at a temperature in the range from 30 to 50°C and contains

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc</td>
<td>5 g/l</td>
</tr>
<tr>
<td>manganese</td>
<td>1 g/l</td>
</tr>
<tr>
<td>iron(II)</td>
<td>0.1 g/l</td>
</tr>
<tr>
<td>phosphate</td>
<td>5 g/l</td>
</tr>
<tr>
<td>nitrate</td>
<td>5 g/l</td>
</tr>
<tr>
<td>fluoroborate</td>
<td>0.5 g/l</td>
</tr>
<tr>
<td>tartaric acid</td>
<td>0.05 g/l</td>
</tr>
</tbody>
</table>

and which has been adjusted to weight ratios of $Zn : P_2O_5 = (0.5 \text{ to } 3) : 1$ and of $Mn : Zn = (0.04 \text{ to } 0.5) : 1$ and to a ratio of free acid to total acid of $(0.04 \text{ to } 0.2) : 1$. 


APPLICANT'S REFERENCE: P30,124

Name(s) of Applicant(s):

Metallgesellschaft A.G.

Address(es) of Applicant(s):

Reuterweg 14,
Postfach 3724,
D-6000 Frankfurt am Main 1,
FEDERAL REPUBLIC OF GERMANY.

Address for Service is:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Complete Specification for the invention entitled:

PROCESS OF PRODUCING PHOSPHATE COATINGS ON METALS

Our Ref : 72050
POF Code: 1442/61870

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

6003g/l
PROCESS OF PRODUCING PHOSPHATE COATINGS ON METALS

Background of the Invention

This invention relates to a process of producing phosphate coatings on metals having surfaces which consist at least in part of iron or steel by a treatment with aqueous phosphatizing solutions, which contain zinc ions, manganese ions, P0₄ ions, nitrate ions and if being in working condition, iron(II) ions (dissolved from the workpiece surfaces) and to the use of that process for preparing metals for a subsequent cold working.

It is known to phosphatize metals, particularly iron and steel, by a treatment with phosphatizing solutions which contain manganese and iron(II) and zinc phosphate and are at temperatures from 50 to 98°C. The phosphate coatings thus obtained are suitable for all fields of application which are known in phosphatizing technology, such as rust prevention, priming for the application of paint, electric insulation, reducing sliding friction and facilitating cold working (Published German Application 30 23 479; EP 42 631).

But the performance of the known processes at relatively low temperatures, e.g., between 30 and 50°C, often gives rise to difficulties in the formation of incompletely covering phosphate coatings which become progressively coarser as the iron(II) content in the phosphatizing solution increases. Certain improvements can be obtained by an activating preliminary rinsing step, e.g., with titanium phosphate, but the results thus produced are not entirely satisfactory. On the other hand, low-temperature processes are urgently required because they save energy. Besides, the processes which involve the presence of iron(II) are superior to the use of phosphatizing solutions which are free of iron(II) because much less sludge is formed in the former and the consumption rates are favorable.
It is an object of the invention to provide for the production of phosphate coatings on metals having surfaces which consist at least in part of iron and steel a process which can be carried out at low temperatures and in the presence of iron(II) and without an unusually high process expenditure and which results in the formation of uniformly covering phosphate coatings.

Summary of the Invention

In the process of the kind described first hereinbefore that object is accomplished in that the metals are contacted with a phosphatizing solution which is at a temperature in the range from 30 to 50°C and contains

- 5 to 25 g/l zinc
- 1 to 10 g/l manganese
- 0.1 to 13 g/l iron(II)
- 5 to 40 g/l phosphate (calculated as P₂O₅)
- 5 to 50 g/l nitrate

and which also contains

- 0.5 to 5 g/l fluoroborate (calculated as BF₄⁻)
- 0.05 to 3 g/l tartaric acid or citric acid

and which has been adjusted to weight ratios of Zn:P₂O₅ = (0.5 to 3) : 1 and of Mn : Zn = (0.04 to 0.5) : 1 and to a ratio of free acid to total acid of (0.04 to 0.2) : 1.

The process in accordance with the invention is particularly used to treat iron and steel which contain up to about 5% alloying additions. Besides, it is possible to treat other metals, e.g., of zinc and zinc alloys, together with iron and steel, whether such other metals are in the form of composite workpieces or are merely coating on iron or steel workpieces.
Detailed Description of the Invention

The several components of the phosphatizing solution are jointly predissolved to form an acid phosphatizing concentrate, as is usual in phosphatizing technology, and are added to the phosphatizing solution in that form. The several components are added in such quantities that the required concentration ranges are obtained in the phosphatizing solution. In order to adjust the required ratio of free acid to total acid it may be necessary to use additional ions of the group consisting of the alkali and ammonium ions.

In preferred embodiments of the invention, the metals are contacted with a phosphatizing solution which also contains 0.05 to 2 g/l Ni and/or 0.001 to 0.1 g/l Cu and/or 0.5 to 2 g/l Ca. The nickel content will promote the formation of the layer, particularly on materials which have a relatively high resistance to the attack by the solution and on zinc. An addition of copper ions will accelerate the phosphatizing process. Added calcium ions will modify the phosphate coating and will effect a conditioning of the bath sludge formed in a small amount so that it interferes less in the phosphatizing bath and can be removed from the system more easily.

The phosphatizing solutions used in the process in accordance with the invention need not contain iron(II) ions from the beginning. That component will necessarily become enriched in the bath during the treatment of iron and steel. The phosphatizing solutions are preferably used in such a manner that the concentration of iron(II) ions is not in excess of 10 g/l.

In order to prevent an increase of the concentration above said value, part of the iron(II) ions which have entered the solution as a result of the pickling action are preferably oxidized to form iron (III) ions, which are precipitated as difficultly soluble iron(III) phosphate sludge. In preferred embodiments of the invention, surplus iron(II) is transformed to trivalent iron by a contact with an
oxygen-containing gas (air) or by means of an oxidizing agent such as chlorate and is precipitated as iron(III) phosphate sludge. In the first case, iron(II) can be removed, e.g., in a separate aerating container, which is succeeded by a filter.

During the phosphatizing process, components of the solution are consumed by the formation of the coating, the formation of sludge, and by the mechanical discharge of phosphatizing solution. The components must be replenished in the phosphatizing solution by the addition of separate components or of replenishing concentrates containing a plurality or all of the individual components. The phosphatizing solution can be replenished in a particularly desirable manner by an addition of zinc ions, manganese ions, phosphate ions and nitrate ions in the form of at least one concentrate which has been adjusted to weight ratios of \( \text{Zn} : \text{P}_2\text{O}_5 = (0.3 \text{ to } 0.8) : 1 \), \( \text{Mn} : \text{Zn} = (0.01 \text{ to } 0.05) : 1 \) and of \( \text{NO}_3 : \text{P}_2\text{O}_5 = (0.2 \text{ to } 1) : 1 \). Any other components of the phosphatizing solution to be replenished should be added in weight ratios of \( \text{Ca} : \text{Zn} = (0.005 \text{ to } 0.1) : 1 \), \( \text{Ni} : \text{Zn} = (0.005 \text{ to } 0.05) : 1 \), \( \text{Cu} : \text{Zn} = (0.001 \text{ to } 0.03) : 1 \), of (tartaric acid and/or citric acid) : \( \text{P}_2\text{O}_5 = (0.05 \text{ to } 0.3) : 1 \) and of \( \text{BF}_4 : \text{P}_2\text{O}_5 = (0.008 \text{ to } 0.04) : 1 \).

Manganese carbonate, zinc oxide and/or zinc carbonate can preferably be used to adjust the ratio of free acid to total acid to within the range of the invention. Said components are added to the phosphatizing solution as powder or in an aqueous suspension. To determine the contents of free acid and of total acid, bath samples of 10 ml are titrated with N/10 NaOH to the first and second transitions of phosphoric acid indicated by a color change, e.g., from dimethyl yellow (free acid test) and phenolphthalein (total acid test) used as indicators. The consumption of N/10 NaOH in milliliters corresponds to the points of free acid or total acid.
It has also been found desirable to contact the metals with a phosphatizing solution which contains nitrite-destroying substances, such as urea or sulfamic acid. This will inhibit an autocatalytic formation of nitrite from the nitrate which is present and will preclude a turnover of the bath from the iron side to the nitrite side (absence of Fe(II)).

The metals may be contacted with the phosphatizing solution by dipping, flooding or spraying. In most cases the solution is applied by dipping with treatment times of, e.g., 5 to 15 minutes.

In dependence on the specific composition of the solution, the treating temperature, the treating time and the sequence of operations, the phosphate layers produced by the process in accordance with the invention will have a weight of about 3 to 15 g/m².

Before the phosphatizing process, the metals are pretreated in the conventional manner. For instance, degreasing may be effected by means of aqueous alkaline cleaning solutions, which suitably contain surfactants. Any scale or rust which may be present should be removed by a pickling treatment, e.g., with sulfuric acid or hydrochloric acid.

Before the workpieces are phosphatized, they may be prerinsed in a known manner, e.g., with an activating bath which contains titanium phosphate, in order to promote the formation of finely crystalline phosphate coatings although such a treatment is not essential.

The phosphatizing treatment is usually succeeded by a rinsing with water and by an optional after-treatment and by drying, if required. The resistance to corrosion can be increased by an after-treatment, e.g., with chromic acid and/or corrosion protective emulsions. Workpieces to be cold-worked may be after-treated, e.g., with a soap-aplying bath.
The phosphate coatings produced by the process in accordance with the invention can be used to advantage in all fields in which phosphate coatings are used and are particularly suitable for preparing metals for a subsequent cold working.

The invention will be explained more in detail by way of the following example.

**Example**

Steel wire having a carbon content from 0.5 to 0.9% by weight was dipped into hydrochloric acid to remove rust and scale and was then thoroughly rinsed with water and phosphatized by being treated for 6 to 10 minutes with a phosphatizing solution which was at 45°C and composed as follows:

<table>
<thead>
<tr>
<th>Concentration (g/l)</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9</td>
<td>Zn</td>
</tr>
<tr>
<td>2.1</td>
<td>Mn</td>
</tr>
<tr>
<td>2.0</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>0.5</td>
<td>Ca</td>
</tr>
<tr>
<td>0.5</td>
<td>Ni</td>
</tr>
<tr>
<td>0.01</td>
<td>Cu</td>
</tr>
<tr>
<td>0.3</td>
<td>Na</td>
</tr>
<tr>
<td>24.0</td>
<td>NO₃</td>
</tr>
<tr>
<td>10.6</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>1.6</td>
<td>BF₄</td>
</tr>
<tr>
<td>1.6</td>
<td>tartaric acid</td>
</tr>
<tr>
<td>0.5</td>
<td>urea</td>
</tr>
<tr>
<td>4.7</td>
<td>points free acid</td>
</tr>
<tr>
<td>40.7</td>
<td>points total acid</td>
</tr>
</tbody>
</table>
This was succeeded by another rinsing with water, by a neutralization in a hot aqueous borax solution and by oven-drying. After that sequence of operation the phosphate coating had a weight of 8 to 10 g/m². Although there had been no activating prerinse with titanium phosphate, the phosphate coating provided a uniform coverage and was finely crystalline.

After that treatment the wires could be satisfactorily shaped in up to 10 drawing passes to a maximum reduction in cross-section by 93.5% with a very low wear of the drawing dies. After the drawing the surface of the wire was still provided with a uniform residual phosphate layer and was free of grooves.

Air was blown into the phosphatizing bath during the treatment to maintain the iron(II) ion content in the range from 2 to 7 g/l under the existing conditions. To maintain constant the points of total acid in the bath, the latter was replenished with a replenishing concentrate containing

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>11.4%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.26%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.13%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.11%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.025%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>22.9%</td>
</tr>
<tr>
<td>NO₃</td>
<td>10.3%</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>2.6%</td>
</tr>
<tr>
<td>BF₄</td>
<td>0.38%</td>
</tr>
<tr>
<td>Urea</td>
<td>0.26%</td>
</tr>
</tbody>
</table>

Because the bath was operated on the iron side, bath sludge was formed only in a small amount. Replenishing concentrate was consumed at the very low rate of 20 g per m² of metal surface area.
The claims defining the invention are as follows:

1. A process for producing a phosphate coating on metals having surfaces which consist at least in part of iron or steel or coated iron or steel by a treatment with an aqueous phosphatizing solution, which contains zinc ions, manganese ions, P$_4$O$_5$ ions, nitrate ions and iron(ii) ions, characterized in that the metals are contacted with a phosphatizing solution which is at a temperature in the range from 30 to 50°C and contains

- 5 to 25 g/l zinc
- 1 to 10 g/l manganese
- 0.1 to 13 g/l iron(ii)
- 5 to 40 g/l phosphate (calculated as P$_2$O$_5$)
- 5 to 50 g/l nitrate
- 0.5 to 5 g/l fluoroborate (calculated as BF$_4$)
- 0.05 to 3 g/l tartaric acid or citric acid

and which has been adjusted to weight ratios of Zn : P$_2$O$_5$ = (0.5 to 3) : 1 and of Mn : Zn = (0.04 to 0.5) : 1 and to a ratio of free acid to total acid of (0.04 to 0.2) : 1.

2. A process according to Claim 1, characterized in that the metals are contacted with a phosphatizing solution which also contains 0.05 to 2 g/l Ni and/or 0.01 to 0.1 g/l Cu and/or 0.5 to 2 g/l Ca.

3. A process according to either of claims 1 or 2 characterized in that the metals are contacted with a phosphatizing solution which has been adjusted to an Fe(II) concentration not in excess of 10 g/l.

4. A process according to any one of claims 1 to 3, characterized in that the phosphatizing solution is contacted with an oxygen containing gas to transform surplus iron(II) to Fe(III) and to precipitate the latter as iron(III) phosphate sludge.

5. A process according to any one of claims 1 to 3, characterized in that the metals are contacted with a phosphatizing solution in which surplus iron(II) is reacted
with an oxidizing agent to form iron(III) and to precipitate the latter as iron(III) phosphate sludge.

6. A process according to any one of claims 1 to 5, characterized in that the phosphatizing solution is replenished by an addition of zinc ions, manganese ions, phosphate ions and nitrate ions in the form of at least one concentrate which has been adjusted to weight ratios of Zn : P₂O₅ = (0.3 to 0.8) : 1, of Mn : Zn = (0.01 to 0.05) : 1 and of NO₃ : P₂O₅ = (0.2 to 1) : 1.

7. A process according to any one of claims 1 to 6, characterized in that the phosphatizing solution is replenished by an addition of Zn, Cu, Ca, tartaric acid and/or citric acid as well as fluoborate in weight ratios of Ca : Zn = (0.005 to 0.1) : 1, of Ni : Zn = (0.005 to 0.05) : 1, of Cu : Zn = (0.001 to 0.03) : 1, of (tartaric acid and/or citric acid) : P₂O₅ = (0.05 to 0.3) : 1 and of BF₄ : P₂O₅ = (0.008 to 0.04) : 1.

8. A process according to any one of claims 1 to 7, characterized in that the metals are contacted with a phosphatizing solution having a free acid content that has been adjusted by an addition of manganese carbonate, zinc oxide and/or zinc carbonate.

9. A process according to any one of claims 1 to 8, characterized in that the metals are contacted with a phosphatizing solution which contains nitrite-destroying substances, such as urea or sulfamric acid.

10. A process substantially as hereinbefore particularly described with reference to the Example.

DATED: 22nd October, 1987
PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:

METALLGESSELLSHAFT A.G.