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IMPROVEMENTS IN OR RELATING TO PROCESSES FOR ANODIC
PHOSPHATING OF STEEL SUBSTRATES

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Rafi Marg, New Delhi-1, India, an Indian registered
body incorporated under the Registration of Societies Act.

(Act XXI of 1860)

This is an invention by Kunnattithidal Easthassen RAJAGOPALAN,
Rengachari ERINIVASAN, Narayanaswami KRITHIVASAN, Chakravarthi
RAJAGOPAL, Scientists, Muthuveeran SETHUKUMARI, Malay Priyat
Kochu JAMAKI, Senior Laboratory Assistants and all from
Central Electrochemical Research Institute, Karaikudi: 623006,
Tamil Nadu, India, all Indian.

The following specification describes the nature of this
invention.

PRICE: TWO RUPEES.

This is an invention by Kummattithidal Senthana
RAJAGOPALAN, Rengachari SRINIVASAN, Narayanaswami
KRITHIVASAN, Chakravarthi RAJAGOPAL, Scientists,
Muthuveeran SETHUKUMARI, Moley Eriya Koch[†] JANAKI,
Senior Laboratory Assistants and all from Central Electro-
chemical Research Institute, Karaikudi and Indian citizens.

This invention relates to Improvements in or relat-
ing to Anodic Phosphating.

Hitherto it has been proposed to produce Iron phos-
phate coatings by Anodic Phosphating method employing Tri-
sodium phosphate solutions. (U.K. Patent No. 1090743, U.S.
Patent No. 811061, Indian Patent Nos. 96133, 107624, 132761
and 143411.)

This is open to the objection that the users specifi-
cally demand Iron-Zinc, Zinc phosphate coatings for better
corrosion resistance and hardness and Iron-Manganese and
Manganese phosphates for better performance in drawing
operations.

The object of this invention is to produce zinc-
phosphate, zinc-iron phosphate, manganese phosphate and
manganese-^{iron} phosphate by electrocoating zinc, iron-zinc
alloy, iron-manganese alloy before anodic phosphating and
phosphate the coated surface by anodic phosphating process.

To these ends the invention broadly consists in
treating the pickled steel item in a conventional acid zinc
plating bath, cathodically for a period of 3 minutes or more
so as to get a plating thickness of two microns or more
followed by anodic phosphating as described in I.F.No. 2442/
Cal/74 or treating the pickled item in a conventional
acid manganese-iron alloy plating bath for a period of one
minute or more to get a plating thickness of 1.5 to 3 mi-
crons followed by anodic phosphating as described in
I.P. No. 143411.

The solution employed for phosphating is same as
described in I.F.No. 96133 (1964) or 107624 (1966). The time

of phosphating is 10 minutes or less in order to get a coating weight of 7-20 gms/m². The following typical examples are given to illustrate the invention.

Example I

Phosphating of mild steel plate of size 7.5 x 5 c.m.,

Composition of Steel:	C	=	0.1-0.2%
	Mn	=	0.4-0.5%
	P	=	0.05 to 0.1 %
	& S	=	0.02 to 0.03%

Plating bath composition:-

ZnSO ₄ 7H ₂ O	--	240 g/l
(Al) ₂ (SO ₄) ₃ 10 H ₂ O	--	30 g/l
NH ₄ Cl	--	15 g/l
pH:	--	3-4
Bath capacity	--	400 ml
Cell current	--	1.7 amps
Time of plating	--	3 minutes
Plating thickness	--	2 μ

b) Phosphating:

Current through the resistor -- 6.5 amps.

Cell	Current:	550 mA
	Voltage	1.5 V
Initial potential		-0.10V vs SCE
Final potential		+ 0.2V vs SCE
Time of phosphating		6 minutes
coating weight		8 gms/m ²

Phosphate coating composition:

Zinc: 49.04%

PO₄ : 41.29%

Fe : 1.358%

H₂O : 8.312%

Hardness = 2286 kg/mm² and withstands seven rubbings with the 0/0 emerypaper.

Example 2

Phosphating of mild steel plate of size 15 cm x 10 cm.

Composition of steel :-

C	= 0.1-0.2%
Mn	= 0.4-0.5%
P	= 0.05 to 0.1%
S	= 0.02 to 0.03%

a) Pre coat of Zinc :

Plating bath composition :	As in example I
Bath capacity	= 2.5 L
Cell current	= 6.4 amps
Time of plating	= 3 minutes
Plating thickness	= 2 μ

b) Phosphating:

Current through resistor	= 10 amps.
Cell Current	= 1.3 amps
voltage	= 3 V
Initial potential	= -0.11 V vs SCE
Final potential	= -0.01 V vs S. C. E.
Time of phosphating	= 6 minutes
Coating weight	= 7.5 gms/m ²
Coating composition	as above
Hardness	2083 kg/mm ² and withstands severe rubbings with 0/0 emery paper.

Example 3

Phosphating of mild steel plate of size 7.5 x 5 cm.

Composition of steel as given above.

a) Pre-coat of Manganese - Iron alloy:Plating bath composition:

MnSO ₄ H ₂ O	- 140.3 g/l
FeSO ₄ 7 H ₂ O	- 30 g/l
(NH ₄) ₂ SO ₄	- 75 g/l
Citric acid	- 15 g/l
Hexamine	- 0.5 g/l
pH	- 1-2
bath capacity	- 400 ml
cell current	- 11.25 amps.
Time of plating	- 1 minute
Thickness	- 1.8 μ

8) Phosphating :

Current through the resistor	--	6 amps.
Cell current	--	450 mA
Voltage	--	1 V.
Initial potential =	--	0.5V vs SCE
Final potential =		+ 0.1 V vs SCE
Time of phosphating =		10 minutes
Coating weight =		19 gms/m ²

Composition of the coating:

Fe	=	64.89%
Mn	=	7.062%
PO ₄	=	22.970%
H ₂ O	=	5.078%

Advantages:

The following are the main advantages of the invention:-

- 1) Iron-zinc and zinc phosphate coatings having desired hardness to withstand 5-15 rubbings with 0/0 emery paper and having Knoop hardness from 1000-2500 kg/mm² and better corrosion resistance than iron phosphate coating for specific applications in the industries as in the phosphating of small arms, sprouts and tubes used in inlock bushes in automobiles.
- 2) Iron-manganese-phosphate coatings having better corrosion resistance than iron phosphate coating can be produced.
- 3) The plated and phosphated steel perform better than the plated steel in 3% NaCl immersion test and 100% R. H. test.

Dated this 16th day of December, 1975.

Sd/-

Asstt. Patents Officer,
Council of Scientific & Industrial Research

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

**IMPROVEMENTS IN OR RELATING TO PROCESS FOR ANODIC PHOSPHATING
OF STEEL SUBSTRATES.**

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
Rafi Marg, New Delhi-1, India, an Indian
Registered body incorporated under the Registration
of Societies Act. (Act XXI of 1860).

This is an invention by Kummattithidal Santhanam RAJAGOPALAN,
Kengachari SRINIVASAN, Narayanaswami KRITHIVASAN, Chakravarthy
RAJAGOPAL, Scientists, Muthuveeran SETHUMUMARI, Melay Eriyat
KUCHU JANAKI, Senior Laboratory Assistants- all from Central
Electrochemical Research Institute, Karaikudi-623006, Tamil
Nadu, India and Indian Citizens.

The following specification particularly describes and
ascertains the nature of this invention and the manner
in which it is to be performed.

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This invention relates to improvements in or relating to anodic phosphating of steel substrates.

Hitherto, it has been proposed to produce iron phosphate coatings by anodic phosphating method on steel substrates employing trisodium phosphate solutions (Indian Patents Nos. 96133, 107624, and 132761 and Indian ~~Patent~~ ¹⁴³⁴¹¹ Patent application No. ~~2442/52/74~~).

This is open to the objection that when the users specifically demand zinc-iron phosphate, zinc phosphate or iron-manganese phosphate coatings for better corrosion resistance and hardness and for better performance in drawing operations, these coatings could not be produced by the known processes.

The main object of this invention is to produce coatings such as zinc-iron phosphate, zinc phosphate or iron-manganese phosphate by electroplating zinc or iron-manganese alloy ^{on the substrate} before anodic phosphating and phosphating the coated surface by the known ^{conventional} anodic phosphating process.

The main finding of this invention is that by giving a pre-coat of zinc or iron-manganese alloy, zinc phosphate, zinc-iron phosphate or iron-manganese phosphate coatings can be produced by anodic phosphating process.

The present invention accordingly consists of a process for anodic phosphating of a steel substrate as per our prior Indian patent application No. ~~2442/52/74~~ ¹⁴³⁴¹¹ and is characterised in that a pickled steel substrate is first given a pre-coat of a corrosion resistant layer of zinc or iron-manganese alloy by electroplating. According to another aspect of this invention the pre-coating of the pickled steel substrate may be effected in (a) ^{conventional} acid zinc plating bath cathodically for a period of 30 seconds to 5 minutes (but preferably for a period of 1 to 3 minutes so as to get a

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plating thickness of 0.3 microns to 3 microns or
(b) ~~Iron-Manganese~~ alloy plating bath for a period of
30 seconds to 5 minutes (but preferably for a period of
1 to 3 minutes) to get a plating thickness of 1.5 to 3
microns.

The solution employed for phosphating is same as
described in our Indian Patents Nos 96133 or 107624. The
time of phosphating is six to ten minutes in order to
get a coating of 7-20 gm/m².

Example 1:

200 litres of acid zinc plating solution of composition:-

ZnSO ₄ .7H ₂ O	240 g.p.l.
Al ₂ (SO ₄) ₃ .10 H ₂ O	30 g.p.l.
NH ₄ Cl.	15 g.p.l.

was taken in rectangular P.V.C. container consisting of
two pure zinc anodes of size 35 x 42 cm. The pH of the
bath was maintained by the addition of 1 : 1 H₂SO₄.
Pickled mild steel sheet of size 25 x 60 cm. was kept at
the centre and connected to the negative terminal of the
rectifier and was plated at a current density of 200 amps.
per sq.m. for 3 minutes at room temperature to get a
plating thickness of 2 microns. The treated sheet was
phosphated as described in our Indian Patent application
No. 2448/52/74. 143411.

Phosphating of mild steel sheet of size 60 x 25 cm:

(a) Plating bath composition as described above.

Cell current	--	70 amps.
Voltage	--	6 V
Time of plating	--	3 minutes
Plating thickness	--	2 microns.

(b) Phosphating:

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Current through the resistor	-- 180 amps.
Cell current	-- 15 amps.
Voltage	-- 2 V.
Initial potential	-- -0.1 V vs SCE.
Final potential	-- + 0.05 V vs SCE
Time of phosphating	-- 6 minutes
Coating weight	-- 7 gm/m ²
Hardness	-- 2286 kg/mm ² and withstands 7 rubblings with 0-0 emery paper.

Phosphate coating composition:

Zn	-- 49.04%
PO ₄	-- 41.29%
Fe	-- 1.358%
Water	-- 8.312%

Example 2

400 ml. of iron manganese alloy plating solution to composition.

MnSO ₄ .H ₂ O	-- 140.3 g.p.l.
FeSO ₄ .7H ₂ O	-- 30 g.p.l.
(NH ₄) ₂ SO ₄	-- 75 g.p.l.
Citric acid	-- 15 g.p.l.
Hexamine	-- 0.5 g.p.l.

was taken in a rectangular P.V.C. container consisting of two M.S. electrodes of 10 x 5 cm. size serving as anodes. The pH of the bath was maintained between 1 and 2 by the addition of 1 : 1 H₂SO₄. Pickled M.S. specimen of size 7.5 x 5 c.m. to be plated was kept at the centre and connected to the negative terminal of the rectifier and was plated at a current density of 1500 amps/m² for one minute at room temperature to get a plating thickness of 1.8 μ. The treated plate was phosphated as described in Indian Patent No. 2419/54. 145411.

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Phosphating of m.s. plate of size 7.5 x 5 c.m.

(a) Plating bath composition as described above.

Cell current -- 11.25 amps.

Voltage -- 3 V

Thickness -- 1.8 μ

(b) Phosphating:

Current through the resistor 6 amps.

Cell current -- 450 mA

Voltage -- 1 V

Initial potential -- -0.5 V vs SCE

Final potential -- + 0.1V vs SCE

Time of phosphating-- 10 minutes

Coating weight. -- 19 gm/m²

Composition of the coating:

Fe -- 64.89%

Mn -- 7.062%

PO₄ -- 22.970%

Water -- 5.078%

Advantages:

1. Production of zinc-iron and zinc phosphating¹ having desired hardness to withstand 5-15 rubbings with 0/0 emery paper and having knoop hardness from 1000-2500 kg/mm² and better corrosion resistance than iron phosphate coating for specific applications in the industries as in the phosphating of small arms, sprouts and tubes used in islock bushes in automobiles.
2. Iron-manganese phosphate coatings having better corrosion resistance than iron phosphate coating can be produced.
3. The plated and phosphated steel perform better than the plated steel in 3% NaCl immersion test and 100% R.H. test

1a claim:-

1. Improved process for anodic phosphating of steel substrates as per our prior Indian Patent No. 143411, characterised in that a pickled steel substrate is first given a precoat of zinc or iron-manganese alloy by conventional electroplating bath to obtain zinc phosphate, zinc iron phosphate or iron-manganese phosphate coatings.
2. Process as claimed in claim 1 wherein the zinc pre-coating is produced by electroplating the steel substrate in a conventional acid zinc plating bath cathodically for a period of 30 seconds to 5 minutes (preferably for a period of 1 to 3 minutes) to get a plating thickness of 0.3 microns to 3 microns.
3. Process as claimed in claim 1 wherein the iron-manganese pre-coating is produced by using a conventional iron-manganese alloy plating bath for a period of 30 seconds to 5 minutes (preferably 1 to 3 minutes) to get a plating thickness of 1.5 to 3 microns.

Dated the 9th day of February, 1977.

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