

PROVISIONAL SPECIFICATION.

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ANODIC PHOSPHATING

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, 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, BALASUBRAMANIA DANDAPANI AND ANANTHAKRISHNAN JAYARAMAN, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, ALL INDIAN CITIZENS.

The following specification describes the nature of this invention.

This invention relates to Anodic Phosphating.

Phosphate coatings on steel are produced by treating metallic articles with phosphoric acid or solutions of primary phosphates of manganese, iron, zinc or cadmium. These have the following valuable properties: (1) these improve the adhesion of paints on metals; (2) these retard the spread of corrosion under the paint film even in those places where the paint has been damaged; (3) these lengthen the useful life of paint coatings; (4) these reduce friction in wire-making, tube-making, body-pressing and other deep-drawings operations; and (5) these reduce wear and galling on mating surfaces. Coating weights vary between 100 mg and 3,000 mg per sq.ft. Besides iron and steel, phosphating is also used for zinc, cadmium and other metals.

On the basis of practical experience as well as of numerous investigations, three main phosphating processes have become known (1) normal phosphating baths working at a temperature between 90 and 100°C and producing a coating during 10 to 60 minutes; (2) accelerated phosphating baths working between 85 and 100°C and producing a coating during 30 seconds to 10 minutes; and (3) cold phosphating. These are variously known in trade by proprietary names such as Parkerising, Bonderising, Walterising, Jenolising, Granodising and so on. All of the above processes are based on the chemical reactions that take place when metal is dipped in the phosphating bath.

A few stray references have appeared in literature on electrolytic phosphating by passing an alternating current through the electrolyte and by making the metal cathode. But these have not been pursued because the methods suggested do not appear to have any valuable advantage since the bath compositions and other conditions employed are the same as in chemical phosphating.

We have found out a new method of electro-phosphating from here onwards called ANODIC PHOSPHATING which has immense advantages over the chemical phosphating processes mentioned above. In this new method put forward by us, the following disadvantages of chemical phosphating, namely, (1) use of temperatures round boiling point for getting heavy coatings; (2) use of heavy metal phosphates as principal ingredients in bath composition; (3) need for ageing of the

bath; (4) frequent check-up of bath composition; (5) excessive influence of surface condition of metal on the quality of coating produced, have all been overcome.

The following are among the noteworthy features of the invention:—

1. ANODIC PHOSPHATING employing a critical potential range above the equilibrium potential is proposed by us for the first time.

2. Phosphate coatings of any desired weight and thickness and other characteristics can be produced from the same bath by anodic phosphating as defined under (1).

3. Phosphate coatings in the range of 0 to 5,000 mg/sq.ft. can be produced by anodic phosphating as defined under (1).

4. Phosphate coatings by anodic phosphating as defined under (1) can be produced from bath compositions in the formulation of which no heavy metal phosphate is needed.

5. Physical and chemical characteristics of phosphate coating by anodic phosphating as mentioned under (1) can be modified by small additions of heavy metal salts as well as by changing the potential drop at the metal-solution interface.

6. Phosphating by anodic phosphating as defined under (1) can be carried out as speedily as by any of the known methods.

7. Frequent check-up of bath composition as in chemical phosphating is not necessary in anodic phosphating as defined under (1).

8. Ageing of the bath as in chemical phosphating is not necessary.

9. Phosphate coating of any desired weight and thickness and other characteristics can be produced at room temperature by anodic phosphating as defined under (1).

R. BHASKAR PAI

Patents Officer,

Council of scientific and Industrial Research.

Dated this 6th day of October 1964.

COMPLETE SPECIFICATION

Anodic Phosphating

THIS IS AN INVENTION BY KUMMATTITHIDAL SANTHANAM RAJAGOPALAN, BALASUBRAMANYA DANDAPANI, BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA, BOTH INDIAN CITIZENS.

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

This invention relates to Anodic Phosphating.

Phosphate coatings on steel are produced by treating metallic articles with phosphoric acid or solutions of primary phosphates of manganese, iron, zinc or cadmium. These have the following valuable properties: (1) these improve the adhesion of paints on metals; (2) these retard the spread of corrosion under the paint film even in those places where the paint has been damaged; (3) these lengthen the useful life of paint coatings; (4) these reduce friction in wire-making, tube-making, body-pressing and other deep-drawing operations; and (5) these reduce wear and galling on mating surfaces. Coating weights vary between 100 mg

and 3,000 mg per sq.ft. Besides iron and steel, phosphating is also used for zinc, cadmium and other metals.

On the basis of practical experience as well as of numerous investigations, three main phosphating processes have become known (1) normal phosphating baths working at a temperature between 90 and 100°C and producing a coating during 10 to 60 minutes; (2) accelerated phosphating baths working between 85 and 100°C and producing a coating during 30 seconds to 10 minutes; and (3) cold phosphating. These are variously known in trade by proprietary names such as Parkerising, Bonderising, Walterising, Jenolising, Gra-

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nodising and so on. All of the above processes are based on the reactions that take place when metal is dipped in the phosphating bath.

A few stray references have appeared in literature on electrolytic phosphating by passing an alternating current through the electrolyte and by making the metal cathode. But these have not been pursued because the methods suggested do not appear to have any valuable advantage since the bath compositions and other conditions employed are the same as in chemical phosphating.

We have found out a new method of electrophosphating from here onwards called ANODIC PHOSPHATING—which has immense advantages over the chemical phosphating processes mentioned above. In this new method put forward by us, the following disadvantages of chemical phosphating, namely, (1) use of temperatures round boiling point for getting heavy coatings within a reasonable time; (2) use of heavy metal phosphates as principal ingredients in the bath composition; (3) need for ageing of the bath; (4) frequent check-up of bath composition; (5) excessive influence of surface condition of metal on the quality of coating produced, have all been overcome.

We have discovered that a good phosphate coating can be produced at room temperature by making the metal to be phosphated as anode and by adjustment of the metal-solution potential at an appropriate value by means of a potential controlling instrument (e.g.) Electronic Potentiostat, stabilised D.C. voltage supply.

We have found by the new method, herein called ANODIC PHOSPHATING, that phosphate coatings of any desired weight or thickness in the range of 0 to 6,000 mg/sq.ft. and having other desirable characteristics can be produced from the same bath.

We have found that extremely simple bath compositions made up of very common chemical and having sufficient quantity of phosphate ions can give phosphate coatings of any desired characteristics and any coating weight by the new method, herein called ANODIC PHOSPHATING, as compared to the very complex formulations commonly employed in phosphating by chemical methods.

We have found by the new method, herein called ANODIC PHOSPHATING, that the physical and chemical properties of the phosphate coating can be modified to suit different practical purposes only by changing the potential drop at the electrode-solution interface.

Accordingly, the process of producing phosphate coatings on metal surface by passing an electric current through an electrolyte containing phosphate ions and making the metal anode is characterised in that a critical potential range above the equilibrium potential is employed.

It is well known that the anodic reaction  $Fe \rightarrow Fe + 2e$  i.e. dissolution of metal in acid solution takes place faster when the metal-solution potential is made more positive than the equilibrium potential. It is now discovered that in a solution containing phosphate ions,

at some potential values above the equilibrium potential phosphate coating formation takes place and at still more positive potentials this ceases. Thus, there is a critical potential range of each metal wherein in a solution containing phosphate ions phosphating can be carried out. Some examples of phosphating by the above method are given below:

(i) Phosphate coating as a base for painting:

Prepare a 5 per cent disodium hydrogen phosphate solution by dissolving 5 gms. of the salt in 100 cc of water. Adjust the pH of solution to 5.5 using phosphoric acid. Transfer the solution to a glass or any other non-metallic container. Immerse the polished and degreased steel specimen in the solution and connect it externally to the working electrode terminal of the potentiostat. Introduce the auxiliary electrode, connect to the counter electrode terminal of potentiostat—Introduce the reference electrode and connect it to the reference electrode terminal of the potentiostat—Adjust the potentiometer setting of potentiostat to  $-1.5$  v for 1 minute and change it to  $-0.5$  v. The current measured will be seen to increase and fall to zero. Now, switch off and take out specimen, wash and dry. The specimen is ready for painting. The coating weight will be about 500 mgms/sq.ft.

(ii) Phosphate coating as a protective finish:

Prepare 2.5 per cent disodium hydrogen phosphate, adjust to pH 4 and proceed as before. Change the potentiometer setting from  $-1.5$  v to  $0.05$  v. As soon as the current become zero, switch off the potentiostat, take out the specimen, wash and dry. The coating weight will be 1.4 gms/sq.ft. and the phosphated specimen is ready for sealing with oil or grease.

(iii) Phosphate coating to reduce wear and friction:

Repeat (ii) upto the stage of potentiometer setting at  $-1.5$  v. After one minute change the potentiostat to  $-0.45$  v. As soon as the current comes to zero, switch off, remove the specimen wash and dry. Now the coating weight will be almost of 6 gms/sq. ft. and the specimen is ready to be handled for deep drawing operations.

(iv) Phosphate coating on other metals:

Repeat (ii) using a zinc specimen and change the potentiometer setting from  $-1.5$  v to  $-0.65$  v. As soon as the current comes to zero, switch off the potentiostat, remove the specimen, wash and dry. The coating weight will be 1.35 gms/sq.ft. and this specimen is ready for painting.

The variations in the coating weight with phosphate concentration, pH and metal-solution potential are indicated below:

No.	Bath composition		Temperature °C	Potential above equilibrium potential (in volts)	Coating Weight (gms./sq. ft.)
	PO <sub>4</sub>	Na			
i.	1.7	0.8	R.T.	0.85	0.9
ii.	1.7	0.8	R.T.	0.65	1.8
iii.	1.7	0.8	R.T.	0.6	4.5
iv.	1.7	0.8	R.T.	0.55	6.0

  

No.	Bath composition		Temperature °C	pH	Potential above equilibrium potential (in volts)	Coating Weight (gms./sq. ft.)
	PO <sub>4</sub>	Na				
1.	1.7	0.8	R.T.	3.0	0.5	1.8
2.	1.7	0.8	R.T.	3.5	0.5	3.0
3.	1.7	0.8	R.T.	4.0	0.5	6.0
4.	1.7	0.8	R.T.	4.5	0.5	6.0
5.	1.7	0.8	R.T.	5.0	0.5	3.2

The variations in the appearance of coating with potential, concentration of phosphate and pH are illustrated below:

## (A) At constant potential at room temperature

No.	Bath composition			M	pH	Appearance of Coating
	PO <sub>4</sub>	SO <sub>4</sub>	Na			
1.	1.7	Nil	0.8	..	4.5	White crystalline film.
2.	1.7	Nil	0.8	..	4.0	Black crystalline film.
3.	3.4	Nil	1.6	..	4.0	crystalline White film.
4.	1.7	Nil	0.8	0.1	4.0	White crystalline film.

## (B) At different potentials at room temperature

No.	Bath composition		pH	Potential above equilibrium potential (in volts)	Appearance
	PO <sub>4</sub>	Na			
1.	1.7	0.8	4.0	0.85	Agglomeration of very fine crystals.
2.	1.7	0.8	4.0	0.70	Both very fine crystals and bigger crystals.
3.	1.7	0.8	4.0	0.50	Bigger crystals of the same size
4.	1.7	0.8	4.0	0.35	Fine crystals.

N.B.—'M' refers to heavy metal ion, RT refers to room temperature (30° C.).

## Definitions:

1. "Equilibrium Potential" of a metal may be defined as the potential at which the metal is in dynamic equilibrium with its own ions in the given solution and no change in the metal or solutions takes place with time.

2. "Coating Weight" may be defined as the difference in weight of metal carrying coating and after it has been stripped free of the coating in a suitable solution which dissolves the coating but not the metal.

3. A "Potentiostat" as the name implies, maintains the electrode—solution potential at a present value with respect to reference electrode—If the potential drifts from this value the error signal is amplified and this operates an output stage which sends a current through the system from an auxiliary electrode in such a direction as to annul the change in potential. The output stage can be either electronically or mechanically controlled, the choice resting solely on the amount of current required and the response time desired of the instrument. The potentiostat is described in chapter 18 of New Instrumental Methods in Electrochemistry by Paul Delahay (Interscience Publishers Ltd.).

The following are among the noteworthy features of the invention:

1. ANODIC PHOSPHATING employing a critical potential range above the equilibrium potential is proposed by us for the first time.

2. Phosphate coatings of any desired weight and thickness and other characteristics can be produced from the same bath by anodic phosphating as defined under (1).

3. Phosphate coatings in the range of 0 to 6,000 mg/sq.ft. can be produced by anodic phosphating as defined under (1).

4. Phosphate coatings by anodic phosphating as defined under (1) can be produced from bath compositions in the formulation of which no heavy metal phosphate is needed.

5. Physical and chemical characteristics of phosphate coatings by anodic phosphating as mentioned

under (1) can be modified by small additions of heavy metal salts and various anions as well as by changing the potential drop at the metal—solution interface.

6. Phosphating by anodic phosphating as defined under (1) can be carried out as speedily as by any of the known methods.

7. Frequent check-up of bath composition as in chemical phosphating is not necessary in anodic phosphating as defined under (1).

8. Ageing of the bath as in chemical phosphating is not necessary.

9. Phosphate coating of any desired weight and thickness and other characteristics can be produced at room temperature by anodic phosphating as defined under (1).

## We claim:

1. A process of producing phosphate coatings on metal surface by passing an electric current through an electrolyte containing phosphate ions and making the metal anode characterised in that a critical potential range above the equilibrium potential is employed.

2. A process according to Claim 1 wherein a potentiostat of stabilised D.C. voltage service is used for controlling the potential at the desired range.

3. A process according to any of the preceding claims wherein phosphate coatings in the range of 0 to 6,000 mg/sq.ft. are produced.

4. A process according to any of the preceding claims wherein physical and chemical characteristics of phosphate coatings are modified by adding heavy metal salts to the electrolyte and also by changing the potential drop at the metal solution interface.

5. A process according to any of the preceding claims which is conducted at room temperature.

6. A process of producing phosphate coatings on metal surfaces substantially as hereinbefore described.

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Dated this 16th day of July, 1964.