

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGDISH BOSE ROAD,
CALCUTTA-17.

Complete Specification No. 129510. Application and Provisional Specification filed
on 5th December, 1970. Complete Specification filed on 21st August 1971.
(Acceptance advertised on 27th January, 1973).

Index at acceptance—70C7[LVIII(5)]; 144A[XII(3)]

“PREPARATION OF ELECTRO DEPOSITS ON MILD STEEL FROM AQUEOUS RESIN SYSTEM
OF LINSEED OIL MALEIC ACID/ANHYDRIDE”.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, NEW DELHI 1, INDIA, AN
INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following Specification describes the nature of this invention :—

This is an invention by Dr. Sankaran Guruswamy, Scientist, Central Electrochemical Research Institute, Karaikudi 3, Tamil Nadu, India and Sthanusubramonia Iyer Krishnamoorthy, Senior Laboratory Assistant, Central Electrochemical Research Institute, Karaikudi 3, Tamil Nadu, India, both Indian Citizens.

This invention relates to, improvements in or relating to the electrodeposition of organic coatings on metals. Organic coatings have been extensively used to obtain hard coatings for the protection of metals against corrosion and for electrical insulation. Organic coatings are generally applied to metals from the solutions of organic materials dissolved in organic solvents. Organic solvents serve no purpose other than being a convenient medium for the transfer of organic materials on to metals and there is an element of risk of fire in the large scale use of organic solvents.

The object of this invention is to obviate these disadvantages by (a) depositing with the help of direct electric current, organic polymers and resins from suitably stabilised aqueous colloidal system of the resins and (b) heat treating of the electrodeposit to modify its properties.

To these ends, the invention broadly consists in (a) preparing suitably stabilised colloidal system of the resin, (b) depositing the resins under definite voltage and current conditions and (c) the heat treatment of the deposit to modify its properties.

In our experiments linseed oil was used as a source for conjugated double bonded compounds. It was reacted with maleic anhydride or maleic acid to obtain water dispersible/soluble adduct. Alcohols similar to polypropylene glycol and poly ethylene glycol and amines similar to triethanolamine and other tertiary amines were added to increase the solubilization of the resin in water. The pH of the system was carefully controlled by suitable additions of amines, ammonia and triphenyl phosphate. The right conditions for deposition were obtained by controlling the voltage and the current density. The right shade of colour of the coating was obtained by controlling the pH of the bath, baking time and temperature of the oven.

The following typical examples are given to illustrate the invention :

EXAMPLE 1

30 gms. of maleic anhydride were mixed with 100 c.c. of linseed oil (raw) in a 300 c.c. flask and heated at 220°C for a period of two hours when a homogeneous adduct was formed. The flask was cooled. 30 c.c. of polypropylene glycol was added to the cooled product and heated again to 200°C. The flask was cooled. A viscous, opaque product was obtained which was water solubilised as follows :

500 mg. of triphenyl phosphate was dissolved in 5 c.c. of polypropylene glycol in a 250 c.c. beaker by warming. 10 c.c. of the adduct was added and stirred well to get a homogeneous, viscous solution. 100 c.c. of distilled water was then added to it and again stirred when a suspension of the adduct in water was obtained. To this was added 5 c.c. triethanolamine and stirred when a white fine emulsion of the resin was obtained. The emulsion was quite stable (stable over two hours) and was used for electrodeposition over mild steel.

The following gives the current, voltage and other conditions for deposition over mild steel :

Area of the deposit	4 × 5 cms. (one side)
Distance between electrodes	= 4.7 cms.
Voltage	50 V, D. C.
Current	120 to 40 mA (current decreases during deposition)
Time of deposit	2 minutes

A dark brown, opaque, glossy, smooth coating was obtained by baking the electrodeposit in an air oven at 110°C for two hours.

A reddish brown, thin, translucent, glossy, smooth and non-porous coating was obtained by using 5 c.c. of the linseed oil-maleic anhydride adduct instead of 10 c.c. as above.

Coatings varying slightly in the shade of colour are obtained by using maleic acid in the place of the maleic anhydride in the above example.

EXAMPLE

30 gms. of maleic acid and 100 c.c. of linseed oil (raw) were heated in a flask. A pinch of benzoyl peroxide was added as a polymerisation catalyst. The temperature was maintained at 220°C. for 15 minutes and after the reaction, the flask was allowed to cool down to 100°C. 30 c.c. of polypropylene glycol was added to the above in order to facilitate water solubility of the resin. The flask was again heated to 200°C and again cooled. The resulting adduct was a viscous red resin.

The linseed oil maleic acid resin obtained by the above procedure was water dispersed/solubilised by partial esterification of the resin. Triethanolamine was used as a neutralising base; the necessary adjustment in pH was done by quantitative addition of triethanolamine.

(A) An yellow, transparent, thick, uniform and glossy coating was obtained by baking the electrodeposit at 150°C for one hour. The electrodeposit was prepared by passing current for 3 minutes at an initial current density of 10 mA/sq. cm. through linseed oil-maleic acid resin suspension prepared as above and maintained at a pH of 6.8.

PRICE : TWO RUPEES.

(B) A reddish brown, opaque, uniform, thick and glossy coating with good hiding power was obtained by heat treatment (150°C for one hour). The electrodeposit was prepared by passing current at an initial current density of 10 mA/sq. cm. for three minutes through linseed oil-maleic acid resin dispersion maintained at pH 6.9.

(C) A black, smooth, opaque and glossy coating was obtained by heat treatment of the electrodeposit (200°C for 30 minutes). The electrodeposit was prepared by passing D. C. at a stable current density of 3.3 mA/sq. cm. through a bath as in (B) above. The current generally falls during deposition and a stable current was maintained by adjusting the voltage manually during deposition.

It can generally be stated that deposits tend to become glossier and smoother as the temperature of baking is increased from 100°C and the time of baking at higher temperatures (upto 240°C) is correspondingly reduced.

The following are among the main advantages of the invention :

1. The process has the advantages of speed and ease of production of organic coatings with minimum damage to the underlying metal.
2. The process is capable of being adapted to the needs of continuous coating of metal articles in the industry and commerce.

Dated this 28th day of November, 1970.

Sd.

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Complete Specification—Section 4.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This is an invention by Dr. Sankaran Gurswamy, Scientist, and Sthanusubramonia Iyer Krishnamoorthy, Senior Laboratory Assistant both of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India both Indian citizens.

This invention relates to improvements in or relating to the electrodeposition of organic coatings on metals. Organic coatings have been extensively used to obtain hard coatings for the protection of metals against corrosion and for electrical insulation. Organic coatings are generally applied to metals from the solutions of organic materials dissolved in organic solvents. Organic solvents serve no purpose other than being a convenient medium for the transfer of organic materials on to metals and there is an element of risk of fire in the large scale use of organic solvents.

The object of this invention is to obviate these disadvantages by (a) depositing with the help of direct electric current organic polymers and resins from suitably stabilised aqueous colloidal system of the resins and (b) heat treating of the electrodeposit to modify its properties.

According to the present invention, there is provided a process for the preparation of electrodeposits on mild steel from aqueous resin system of linseed oil maleic acid/anhydride which consists in water-solubilising malenized linseed oil resin by the partial neutralisation of the acid groups of the resin by a base of the type triethanolamine to yield a negatively charged polyelectrolyte of the resin which is deposited on a mild steel anode by the passage of direct current and by baking the electrodeposit to develop colour and adhesion.

Alcohols like polypropylene glycol are incorporated at the preparation stage into the malenized linseed oil resin structure to aid the water solubility of the resin.

Amines like triethanolamine and dispersing agents like triphenyl phosphate are added to disperse and solubilise the malenized linseed oil resin.

In our experiments, we have taken advantage of the malenisation of raw linseed oil to prepare the resin and the addition of alcohols like polypropylene glycol to increase the solubility of the resin structure in water. The solubilization of the resin is carried out by dispersing the resin with dispersing agents like triphenyl phosphate and by partial neutralization of the acid groups in the resin with amines like triethanolamine to yield a negatively charged polyelectrolyte of the resin which deposits on the anode by the passage of a direct current through the system. The

right conditions for deposition were obtained by controlling the voltage and the current density. The right shade of colour of the coating was obtained by controlling the pH of the bath, baking time and temperature.

In the invented process of preparing organic coatings over mild steel, the linseed oil maleic anhydride resin is solubilized in water by partial neutralization of the acid groups in the resin to yield a negatively charged polyelectrolyte of the resin which is deposited on the anode by the passage of direct current through the resin system and the deposited resin is baked to develop colour and adhesion.

The following typical examples are given to illustrate the invention :

EXAMPLE 1

30 gms. of maleic anhydride were mixed with 100 c.c. of linseed oil (raw) in a 300 c. c. flask and heated at 220°C for a period of two hours when a homogeneous adduct was formed. The flask was cooled. 30 c.c. of polypropylene glycol was added to the cooled product and heated again to 200°C. The flask was cooled. A viscous, opaque product was obtained which was water solubilised as follows :

500 mg. of triphenyl phosphate was dissolved in 5 c.c. of polypropylene glycol in a 250 c. c. beaker by warming. 10 c. c. of the adduct was then added and stirred well to get a homogeneous, viscous solution. 100 c.c. of distilled water was added to it and again stirred when a suspension of the adduct in water was obtained. To this was added 5 c. c. triethanolamine and stirred when a white fine emulsion of the resin was obtained. The emulsion was quite stable (stable over two hours) and was used for electrodeposition over mild steel. The stability of the emulsion is increased by controlling the amount of triethanolamine added.

The following gives the current, voltage and other conditions for deposition over mild steel :

Area of the deposit	4 × 5 cms. (one side)
Distance between electrodes	4.7 cms.
Voltage	50 V D. C.
Current	120 to 40 mA
	(current decrease during deposition)
Time of deposit	2 minutes

A dark brown, opaque, glossy, smooth coating was obtained by baking the electrodeposit in an air oven at 100°C for two hours.

A reddish brown, thin, translucent, glossy, smooth and non-porous coating was obtained by using 5 c.c. of the linseed oil-maleic anhydride adduct instead of 10 c.c. as above.

Coatings varying slightly in the shade of colour are obtained by using maleic acid in the place of the maleic anhydride in the above example.

EXAMPLE 2

30 gms. of maleic acid and 100 c.c. of linseed oil (raw) were heated in a flask. A pinch of benzoyl peroxide was added as a polymerisation catalyst. The temperature was maintained at 220°C., for 15 minutes and after the reaction, the flask was allowed to cool down to 100°C. 30 c. c. of polypropylene glycol was added to the above in order to facilitate water solubility of the resin. The flask was again heated to 200°C and again cooled. The resulting adduct was a viscous red resin.

The linseed oil maleic acid resin obtained by the above procedure was water dispersed/solubilised by partial esterification of the resin. Triethanolamine was used as a neutralising base; the necessary adjustment in pH was done by quantitative addition of triethanolamine. Stable emulsions were prepared by controlling the amount of triethanolamine added.

(A) An yellow, transparent, thick, uniform and glossy coating was obtained by baking the electrodeposit at 150°C. for one hour. The electrodeposit was prepared by passing current for three minutes at an initial current density of 10 mA/sq. cm. through linseed oil-maleic acid resin suspension prepared as above and maintained at a pH of 6.8.

(B) A reddish brown, opaque, uniform, thick and glossy coating with good hiding power was obtained by heat treatment (150°C for one hour). The electrodeposit was prepared by passing current at an initial current density of 10 mA/sq cm. for three minutes through linseed oil-maleic acid resin dispersion maintained at pH 6.9.

(C) A black, smooth, opaque and glossy coating was obtained by heat treatment of the electrodeposit (200°C for 30 minutes). The electrodeposit was prepared by passing D.C. at a stable current density of 3.3 mA/sq.cm. through a bath as in (B) above. The current generally falls during deposition and a stable current was maintained by adjusting the voltage manually during deposition.

It can generally be stated that deposits tend to become glossier and smoother as the temperature of baking is increased from 100°C and the time of baking at higher temperature (upto 240°C) is correspondingly reduced.

The following are among the main advantages of the invention :

1. The process has the advantages of speed and ease of production of uniform organic coatings over articles of widely different size and shapes with minimum damage to the underlying metal.

2. The process is capable of being adapted to the needs of continuous coating of metal articles in the industry and commerce.

A baked electrodeposit of raw linseed oil maleic acid/anhydride resin is prepared by electrodepositing the resin on the anode by the passage of electric current through a bath containing an aqueous colloidal electrolyte of the resin and baking the electrodeposit to develop colour and adhesion. The aqueous system is prepared by solubilizing the maleinized raw linseed oil by partial neutralization of the acid groups by amines like triethanolamine. Alcohols like polypropylene glycols and dispersing agents like triphenyl phosphate are added to aid the water solubility and dispersion of the resin structure.

We Claim :

1. A process for the preparation of electrodeposits on mild steel from aqueous resin system of linseed oil maleic acid/anhydride which consists in water-solubilising maleinized linseed oil resin by the partial neutralisation of the acid groups of the resin by a base of the type triethanolamine to yield a negatively charged polyelectrolyte of the resin which is deposited on a mild steel anode by the passage of direct current and by baking the electrodeposit to develop colour and adhesion.
2. A process as claimed in Claim 1 wherein alcohols like polypropylene glycol are incorporated at the preparation stage into the maleinized linseed oil resin structure to aid the water solubility of the resin.
3. A process as claimed in Claims 1 and 2 wherein amines like triethanolamine and dispersing agents like triphenyl phosphate are added to disperse and solubilize the maleinized linseed oil resin.

Dated this 17th day of August, 1971.

Sd.
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