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PROVISIONAL SPECIFICATION

"IMPROVEMENT IN OR RELATING TO ELECTROPOLISHING OF MILD STEEL"

COUNCIL OF SCIENTIFIC & 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
BALKUNJE ANANTHA SHENOI, Scientist and ARUMUGAM PALAMALAI, Junior Scientific Assistant, both are Indian Nationals employed in the Central Electrochemical Research Institute, Karaikudi-3, India.

The following specification describes the nature of :—

This invention relates to improvements in or relating to electropolishing of mild steel.

Hitherto it has been proposed to adopt the foollowing electrolytes/processes for electropolishing of mild steel:

(1) Phosphoric-sulphuric-chromic acid solutions
(2) Phosphoric-sulphuric acid solutions (Faust)
(3) Phosphoric-sulphuric-lactic acid electrolyte (Levin's bath and its modifications)
(4) Mixtures of sulphuric and phosphoric acid+Inhibitors.

The processes employing electrolytes are open to the objections as described below:

Chromic acid baths (1) have to be operated at a higher temperature (65–75°C). The use of hot electrolytes leads to corrosion of th lead cathode and cell-lining due to slow attack on prolonged use. Evaporation of solution components is harmful to the health of the operators. Short-service life due to cathodic reduction of Cr^{6+}, use of diaphragm to prevent this reduction and additional operating steps in the regeneration of the bath are other disadvantages.

In the simple phosphoric-sulphuric acid solutions (2), water content is critical. Hence evaporation at the high operating temperature (40–80°C, preferable one being 55–75°C) requires control of the bath composition. The results are not satisfactory in that the surface obtained is not very bright (about 20% reflectivity). Relatively, longer time of polishing is required (5–40 minutes).

Levin's bath (3) in spite of being operated at low temperature (18°–27°C) and current density (0–7 Amp/in^2), requires 1–2 hours and the high concentration of lactic acid (33% by wt.) makes it costly. Even the modified ones with smaller amounts of lactic acid (about 20 ml/1) are operated at relatively high temperatures (46°–60°C) and requires initlal ageing, to the extent of 5 g/1 of iron.

Electrolytes (4) are operated at higher temperatures (excepting, one two baths employed in foreign countries, containing proprietary inhibitor). Thus, solutions containing "dextrose" or "teepol" are operated at 60°C–70°C and those containing glycerol, at 50°–70°C.

The object of this invention is to obviate disadvantages by adding inhibitors which could be easily prepared from its constituents by conventional methods to the phosphoric-sulpuric acid solutions for electropolishing mild steel.

To these ends, the invention broadly consists in adding any one of the condensation products of formaldehyde with a number of aromatic primary amines, such as p-tolunidine, beta naphthalamine to mixture of phosphoric and sulphuric acids. This enables these baths to be used for electropolishing mild steel, even at lower temperatures (20–30°C) and relatively at lower current densities (25–75 A/dm^2) as compared with the plain baths (viz. phosphoric-sulphuric acid mixtures without inhibitors). The addition of inhibitors enables that A.C can also be used for polishing.

Derusting and mechanical polishing from the necessary pretreatment before electropolishing.

The composition of the electrolyte and the anodic polishing conditions are as follows:

Composition

Phosphoric acid (Sp. gr. 1.75):	55–75% (v/v)
Sulphuric acid (Sp. gr. 1.84):	45–25% (v/v)
Water	: 0–5% (v/v)
Inhibitor	: 0.01–3% (v/v)

Polishing conditions

Temperature	: 3+_3°C
Time	: 5–10 minutes
Bath voltage	: 8–23 V (approx.)
Current density	: 10–150 A/dm^2
Range of current density giving the best polishing	: 25–75 A/dm^2
Cathode	: Lead

First, the inhibitor is added to the measured amount of sulphuric acid, stirred and to this rest of the components are added and stirre i vigorously. The heat of mixing itself may be sufficient to dissolve the inhibitor. If not dissolved, the bath may be heated to be about 80°C.

The specular reflectivity of the polished mild steel surfaces is meusured using a gloss meter, with a silver mirror as the standard and the percentage reflectivity is calculated in each case.

The reflectivity of the polished specimens in the new baths ranges from 30–45%. This is somewhat relatively less than that obtainable from the chromic acid bath (40–60% approx.). In view of the fact that the mild steel is electropolished mainly as a preplating treatment rather than as a finishing for appearance, the reflectivity obtainable with the new baths may be sufficient for practical purposes. Air agitation and cooling arrangements are required. To obtain good quality of the polished surface, agitation may be stopped in the last one or two minutes.

Price : TWO RUPEES

The following typical examples are given to illustrate the invention:

EXAMPLE 1

Specimens of mild steel are derusted and mechanically polished and degreased with trichloroethylene. It is then anodically polished in the following electrolyte:

Phosphoric acid	: 65% (v/v)
Sulphuric acid	: 30% (v/v)
Water	: 5% (v/v)
Inhibitor B (condensation product of HCHO and beta naphthylamine)	: 0.2% (w/v)

The polishing is carried out at 30±3°C for 5 minutes using the current densities of 50 and 75 A/dm². The specullar reflectivities at these current densities are respectively 39% and 45%

EXAMPLE 2

Mild steel specimens are pretreated as in Example 1 and anodically polished in the following electrolyte :

Phosphoric acid	: 60% (v/v)
Sulphuric acid	: 40% (v/v)
Inhibitor B	: 0.2% (w/v)

The polishing is carried out at 30 ±3°C for 10 minutes, under the current densities of 37.5 A/dm² and 50 A/dm² the reflectivities, under these two conditions being respectively 34% and 42%.

EXAMPLE 3

Mild steel specimens are treated as in Example 1 and electrolytically polished in the following bath:

Sulphuric acid	: 35% (v/v)
Phosphoric acid	: 65% (v/v)
Inhibitor B	: 0.15% (w/v)

At 30 ±3°C, they are polished for 10 minutes at a current density of 25 A/dm² and for 5 minutes, at 50 A/dm² the specular reflectances being 31% and 40% respectively.

EXAMPLE 4

Specimens of mild steel are pretreated as in Example 1 and polished anodically in the following bath :

Phosphoric acid	: 65% (v/v)
Sulphuric acid	: 32% (v/v)
Water	: 3% (v/v)
Inhibitor A (condensate of HCHO and p-toluidine)	: 0.2% (w/v)

At the same temperatures as in Example 1 these are polished at 37.5 A/dm² for 10 minutes and at 50 A/dm² for 5 minutes. The reflectances under these conditions are 36% and 41% respectively.

EXAMPLE 5

As in example 1, miled steel specimens are pretreated and electropolished in the following bath using both AC and DC:

Phosphoric acid	: 70% (v/v)
Sulphuric acid	: 30% (v/v)
Inhibitor B	: 0.2% (w/v)

Polishing conditions:

Temperature	: 30±3°C
Time	: 10 minutes

Type of current	Current density (A/dm²)	Specular ot reflectance (%)
AC	60	39
AC	75	42
DC	50	41

The following are among the main advantages of the invention.

1. The new baths employ inhibitors which could be easily prepared from its constituents by conventional methods.
2. The new baths can be operated at room temperature using either DC or AC.
3. The use of room temperature enables that cheap non-metallic materials like plastics may be used for cell-linings due to the relatively lower corrosiveness.

PATENT OFFICER
Sd. Illegible
Council of Scientific and Industrial Research.

Dated this 1st day of April, 1972.

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & 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
BALKUNJE ANANTHA SHENOI, SCIENTIST AND ARUMUGAM PALAMALAI, JUNIOR SCINTIFIC ASSISTANT, BOTH ARE INDIAN NATIONALS EMPLOYED IN THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, INDIA.

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 improvements in or relating to electropolishing of mild steel.

Hitherto it has been proposed to adopt the following electrolytes/processes for electropolishing mild steel.

(i) phosphoric-sulphuric-chromic acid solutions
(ii) phosphoric-sulphuric acid solution (Faust)
(iii) phosphoric-sulphuric-lactic acid electrolyte (Levin's bath and its modifications)
(iv) Mixtures of sulphuric and phosphoric acids+inhibitors

The processes employing these electolytes are open to the objections are described below :

Chromic acid bath (1) have to be operated at a higher temperature (65-75°C). The use of hot electrolytes leads to corrosion of the lead cathode and cell linings due to slow attack on prolonged use. Fumes from the solution components are harmful to the health of the operators. Short service life due to cathodic reduction of Cr^{6+}, use of diaphragm to prevent this reduction and additional operating steps in the regeneration of the bath are the disadvantages.

In the simple phosphoric-sulphuric acid solutions (2), water content is rather critical. Hence, evaporation at the high operating temperature (40–80°C) requires rigorous control of the bath composition. The results are not satisfactory in that the surface obtained is not very bright (about 20% reflectivity). Relatively longer time of polishing is required.

In Levin's bath (3), in spite of the low operating temperature at 0–7 A/sq. in current density, it requires longer time (1–2 hrs) and moreover, the higher lactic acid content (33% by wt) makes it very costly. Even the modified composition with smaller amounts of lactic acid (about 20 ml/litre) are operated at relatively high temperatures (40–60°C) and requires initial ageing, to the extent of 5 gpl of iron.

While bath (iv) comprising mixture of sulphuric acid and phosphoric acid with inhibitor overcomes the disadvantages of the bath's explained in the prior art (bath (i) to (iii)), it still has the disadvantage that the inhibitors used in the bath are to be imported.

The object of the present invention is to overcome the disadvantages cited above by using a bath comprising sulphuric acid and phosphoric acid with an inhibitor prepared indigenously for the electropolishing mild steel after derusting and mechanical polishing in order to obtain a surface suitable for electroplating.

The main finding underlying the invention is for the preparation of indigenous inhibitors which can be easily prepared from its constituents and to use these inhibitors in the phosphoric acid sulphuric acid electrolyte for electropolishing of mild steel at room temperature 30±3°C.

In the present invention, the condensation products of formaldehyde with an aromatic amine, such as para toluidine or beta naphthylamine are used as inhibitors in the phosphoric acid sulphuric acid mixed electrolyte for electropolishing of mild steel.

The electropolishing bath thus obtained by using the inhibitors of this invention can be operated at lower temperature (20–35°C) and at relatively lower current densities (25–75 A/dm²) as compared with the plain baths (viz. phosphoric acid sulphuric acid mixture without inhibitors) to get good electropolishing of mild steel with good reflectivity.

Other new finding of this invention is that alternating current can also be used in addition to direct current for electropolishing mild steel using the above bath. Moreover, the polishing time required is lower for this new bath compared with the baths known earlier.

The present invention consists in adding any one of the condensation products of formaldehyde with aromatic primary amines, such as para toluidine or beta naphthylamine to a mixture of phosphoric and sulphuric acids. This enables these baths to be used for electropolishing mild steel at lower temperature (20–35°C) and at lower current densities 25–75 A/dm²) as compared with the plain bath (viz. phosphoric-sulphuric acid mixture without the inhibitor of this patent). The addition of inhibitors of the present invention enables the use of AC for electropolishing mild steel after derusting and mechanical polishing.

The composition of the electrolyte and the anodic polishing are as follows :

Composition :

Phosphoric acid (sp. gr. 1.75) :	55–75% (v/v)
Sulphuric acid (sp. gr. 1.84) :	45–25% (v/v)
Water :	0– 3% (v/v)
Inhibitor :	0.01– 3% (v/v)

Polishing conditions :

Temperature :	20–35°C
Time :	5–10 minutes
Bath voltage :	8–23V (approx)
Current density :	10–150 A/dm²
Range of current density giving the best polishing :	25–75 A/dm²
Cathode :	Lead

To the measured amount of sulphuric acid, the inhibitor is added and stirred well till complete dissolution. Later, the other ingredients of the bath are added and stirred vigorously. The heat of mixing itself may be sufficient to dissolve the inhibitor. Otherwise, the bath is heated to about 80°C.

The specular reflectivity of the polished mild steel surfaces is measured using a glossmeter, with a silver mirror as the standard and the percentage reflectivity is calculated in each case. The reflectivity of the specimens after mechanical polishing ranges from 10 to 15%. The reflectivity of the polished specimens in the new baths ranges from 30–45%. This is somewhat relativily less than that obtainable from the chromic acid bath (40–60% approx.). Since mild steel is electropolished only as a preplating operation, the reflectivity obtained from the inventive bath is sufficient for practical purposes. Air agitation and cooling arrangements are required for maintaining optimum temperature. To obtain good quality of the polished surface, agitation may be stopped in the last one or two minutes.

The following are the typical examples given to illustrate the invention and not to limit the scope of this invention :

Example 1

Specimens of low carbon mild steel are derusted and mechanically polished (reflectivity 12%) and degreased with trichlorethylene. It is then anodically polished in the following electrolyte :

Phosphoric acid :	65% (v/v)
Sulphuric acid :	30% (v/v)
Water :	5% (v/v)
Inhibitor B (condensation product HCHO and beta naphthylamine)	0.2% (w/v)

The polishing is carried at 30±3°C for 10 minutes, under the current densities (d.c) of 37.5 A/dm² and 50 A/dm² the reflectivities, under these two conditions being respectively 34% and 42%.

Example 2

Mild steel specimens are pretreated as in Example 1 and anodically polished in the following electrolyte :

Phosphoric acid :	60% (v/v)
Sulphuric acid :	40% (v/v)
Inhibitor B :	0.2% (w/v)

The polishing is carried out at 30±3°C for 10 minutes, under the current densities of 37.5 A/dm² and 50 A/dm² the reflectivities, under these two conditions being respectively 34% and 42%.

Example 3

Mild steel specimens are treated as in Example 1 and electrolytically polished in the following bath :

Sulphuric acid :	35% (v/v)
Phosphoric acid :	65% (v/v)
Inhibitor B: condensation product of HCHO and beta naphthylamine :	0.15% (w/v)

At 30±3°C they are polished for 10 minutes at a current density (d.c) of 25 A/dm² for 5 minutes, at 50 A/dm² the specular reflectances being 31% and 40% respectively.

EXAMPLE 4

Specimens of mild steel are pretreated as in Example 1 and polished anodically in the following bath :

Phosphoric acid :	65% (v/v)
Sulphuric acid :	32% (v/v)
Water :	3% (v/v)
Inhibitor A : (condensation product of HCHO and p-toluidine)	0.2% (w/v)

At the same temperature as in Example 1, these are polished at a current density (a.c) of 37.5 A/dm² for 10 minutes and at 50 A/dm² for five minutes. The reflectances under these conditions are 36% and 41% respectively.

EXAMPLE 5

As in Example 1, mild steel specimens are pretreated. Electropolishing is done in the following bath using AC or DC :

Phosphoric acid :	70% (v/v)
Sulphuric acid :	30% (v/v)
Inhibitor B :	0.2% (w/v)

Polishing condition :

Temperature :	30±3°C
Time :	10 minutes

Type of current	Current density (A/dm²)	Specular reflectance
AC	60	39
AC	75	42
DC	50	41

The following are among the main advantages of the invention :

1. The new baths employ inhibitors which could be easily prepared from their constituents by conventional methods.
2. The new baths can be operated at room temperature using either DC or AC.
3. The use of room temperature enables the use of cheap non-metallic materials like plastics for cell-lining. In this invention condensation products of formaldehyde with beta naphthylamine or para toluidine are used as inhibitors in the conventional phosphoric and sulphuric acid bath for electropolishing of mild steel. This enables the bath to operated at room temperatures (30–35°C) unlike the conventional baths and AC or DC can be used at comparatively low current densities to get polishing suitable for electroplating.

We Claim :

1. A process for electropolishing of mild steel in a bath comprising sulphuric acid and phosphoric acid characterised in that an inhibitor is added which is a condensation product of formaldehyde and beta naphthylamine or formaldehyde and para toluidine.
2. A process for electrpolishing of mild steel using a bath as claimed in Claim 1 wherein the sulphuric acid concentration ranges from 25–40% phosphoric acid 60–75%, Water 0–5% and the inhibitor concentration ranges from 0.01% to 3% w/v
3. A process as claimed in claims 1 and 2 wherein the electropolishing bath is operated at 20-35°C using a current density of 25–75 A/dm².
4. A process as claimed in claims 1 to 3 wherein electropolishing of mild steel can be carried out using direct or alternating current.

PATENTS OFFICER,
Council of Scientific & Industrial Research

Dated this 25th day of April, 1973.

Prabhat Press, Meerut/Patent/73—150.