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"AN IMPROVED PROCESS FOR THE PRODUCTION OF NICKEL ELECTROFORMS".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-
110001, India, an Indian Registered body incorporated under the
Registration of Societies Act (Act XII of 1960).

The following specification describes the nature of this invention.

PRICE : TWO RUPEES

This is an invention by Balkunje Anantha Shenoi, Scientist; Subbaih John, Senior Technical Asst; Nandagopal Varadappa Shanmugam, Kumandur Srinivasan, and Mariappan Selvam, Junior Scientific Assts., all of the Central Electrochemical Research Institute, Karaikudi, 623006, all Indian nationals.

This invention relates to an improved process for activation of nickel electroforms for further plating with nickel or chromium.

One of the problems encountered by the nickel electroformers is the poor adhesion between layers of nickel in thick deposits and electroforms. This results because of accidental or deliberate interruptions of current during the plating period. The poor adhesion between layers of nickel results in the embrittlement of the nickel electroforms is particularly deleterious.

Hitherto it has been proposed to activate nickel deposits in the following ways:

- 1) Anodic treatment in 25% H₂ SO₄ at room temperature at a C.D. of 2 to 20 A/dm² for 2- 10 minutes.
- 2) Anodic treatment in low pH watts type or chloride nickel plating bath at 55 - 60°C at a c.d. of 1- 2 A/dm² for 10 minutes and reverse current and plating under normal conditions.
- 3) Anodic for 2 minutes and then cathodic for 6 minutes both at 3A/dm² in acid nickel chloride bath and plating is continued without rinsing.
- 4) Dip in 50% HF(by wt) at room temperature for 10 seconds.
- 5) Dip in 30-50 % (by volume) perchloric acid (S.G. 1.53) at 30°C for 2-60 Secs.
- 6) Electrolytic activation either anodic or cathodic in copper cyanide baths at 60-80°C for 1-3 minutes at a c.d. of 1-2 A/dm².

The main drawbacks of the hitherto known processes are that electrolytic treatment in solutions 1 to 3 produce non uniformity of thickness of the nickel electroform especially for nickel foils and screens whereas the use of solutions 4 and 5 are hazardous and corrosive and not generally used. Moreover the use of solution (3) requires the reversing the polarity during activation necessitating additional units. Use of electrolytic cyanide activation requires a cyanide waste treatment for the electroformer

increasing the cost of the electroforms.

The main object of the present invention is to obviate the above difficulties in the activation of nickel foils and screens by employing a suitable chemical immersion treatment to remove the oxide layer on the nickel surface and thereby produce a cleaned oxide free surface to prevent the layers formation during further plating with nickel or chromium.

The main finding underlying the present invention consists in immersion treating the nickel electroforms in any one of the following three solutions containing (a) hydrochloric acid (S.G.1.18) 200-300 ml/litre, Nitric acid (S.G.1.42) 200-400 ml/l and formic acid 20-100 ml/l (b) Hydrochloric acid 150-300 ml/l, nitric acid (S.G.1.18) 200-400 ml/l and acetic acid 100-200 ml/l (c) Ferric chloride 100 - 200 gms/l, Ferric nitrate 100 - 300 gms and hydrochloric acid (S.G.1.18) 100-200 ml/l at room temperature for a period of 1-10 minutes to remove the oxide layer for prevention the poor adhesion between the nickel electroform to further nickel or chromium deposits.

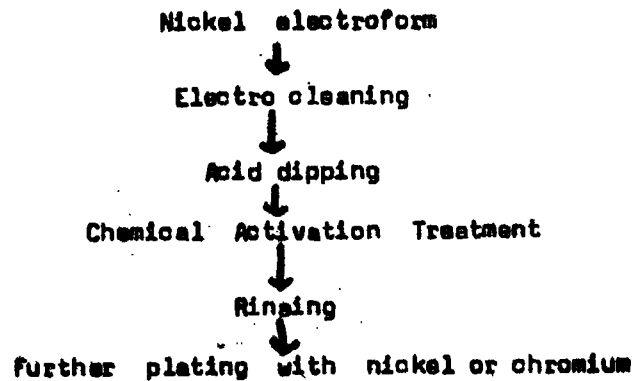
The new result flowing from the new finding is that nickel electroforms activated in the above solutions produce highly adherent and sound deposits without any lifting of deposits.

The present invention consists of a process for activating the nickel electroforms suitable for further plating with nickel or chromium which consists in alkaline cleaning, acid dipping, chemical immersion treating with and electroforming with nickel or chromium in their acid electrolytes wherein the nickel electroform is immersion treated in any one of the solutions containing (a) hydrochloric acid 200 - 300 ml/l (S.G.1.18), nitric acid 200 - 400 ml/l and formic acid 20 - 100 ml/l (b) hydrochloric acid (S.G.1.18) 150 - 300 ml/l, nitric acid (S.G.1.42) 200 - 400 ml/l and acetic acid (S.G.1.42) 100 - 200 ml/l (c) Ferric chloride 100-200 gms/l

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Ferric nitrate 100 - 300 gms/l, hydrochloric acid (S.G.1.18) 100-200 ml/l at room temperature for a period of 1-10 minutes which is characterised in that the said immersion treatment produce a clean, oxide free nickel surface to obtain a sound adherent deposits of nickel or chromium without any lifting of deposits.

The following is the flow chart of the process



The following typical examples are given to illustrate how the invention is carried out in actual practice but not to limit the scope of this invention.

Example 1

Electroformed nickel foil (35 μ) of size 15 cm x 20 cm was alkaline cleaned and rinsed with tap water and acid dipped in 10% sulphuric acid. After rinsing with tap water the foil was chemically activated with a solution containing

Hydrochloric acid (S.G. 1.18)	250 ml/l
Nitric acid (S.G. 1.42)	200 ml/l
Formic acid	80 ml/l

for a period of 5 minutes and rinsed with tap water and distilled water. The foil is further plated with nickel in a sulphamate nickel bath for a predetermined time to a thickness of 100 μ . The foil was having no layer formation and a sound deposit was obtained.

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Example 2

Electroformed nickel centrifugal filter screen of thickness 40 with the mandrel was alkaline cleaned and acid dipped in 10% sulphuric acid. After rinsing the mandrel with the screen was chemically activated in a solution containing ferric chloride 200 gms/l; ferric nitrate 400 gms/l and hydrochloric acid (S.G. 1.18) 150 ml/l for about 10 minutes and after rinsing electroforming was continued in a sulphamate nickel bath for a predetermined time. The screen was inspected for the peeling of deposit and hole size variation and found to be unaffected.

Example 3

Electroformed nickel screen was pretreated as per example 2 and chemically activated in a bath containing

Conc. hydrochloric acid (S.G. 1.18)	300 ml/l
Conc. nitric acid (S.G. 1.14)	200 ml/l
acetic acid (S.G. 1.047)	100 ml/l

for a period of 1 minute and then chromium plated on the bright side of the screen to 8 μ . The chromium plate was having very good adhesion without any peeling.

Example 4

Electroformed nickel foil of thickness 40 μ of size 10 cm x 10cm was alkaline cleaned, rinsed, acid dipped in 5% sulphuric acid and chemically activated in the following bath for 10 minutes.

Hydrochloric acid (S.G. 1.18)	300 ml/l
Nitric acid (S.G. 1.42)	200 ml/l
Formic acid	80 ml/l

After rinsing with tap water and distilled water the foil is plated in a nickel sulphamate bath to a thickness of 200 μ . The foil was found to have no layer formation.

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The following are the main advantages of this invention:

1. The layer formation between nickel deposits is prevented
2. The solutions used produce cleaned and oxide free nickel surface
3. No rectifier and polarity reversing switch is needed
4. The chemicals used are indigenously available
5. Thickness variation of thicker foil and screens due to electrolytic treatment is prevented
6. The solutions used are not hazardous as perchloric acid and hydrofluoric acid
7. Cyanide waste treatment system is not required.

Dated this 25th day of October, 1980.

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section-10)

"AN IMPROVED PROCESS FOR THE PRODUCTION OF NICKEL ELECTROFORMS".

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New
Delhi-110001, India, an Indian Registered body incorporated under
the Registration of Societies Act (ACT XXI of 1860).**

**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 Balkunje Anantha Shenoi, Subbiah John, Nandagopal Varadappa Shanmugam, Kumandur Srinivasan and Mariappan Selvam, Scientists of Central Electrochemical Research Institute, Karaikudi - 623006, Tamilnadu, India and all Indian nationals.

This invention relates to an improved process for the production of nickel electroforms. These are further treated for plating with nickel or chromium.

One of the problems encountered in the production of nickel electroforms is the poor adhesion obtained between successive layers of nickel in thick deposits on the foils. This is the result of generally accidental or deliberate interruptions of current during the plating process. The poor adhesion between layers of nickel results in the embrittlement of the nickel electroforms and that is particularly deleterious in their use.

Hitherto it has been proposed to activate nickel deposits on nickel foils in the following ways :

- 1) Anodic treatment in 25% H_2SO_4 at room temperature at a current density (c.d.) of 2-20 A/dm^2 for 2-10 minutes.
- 2) Anodic treatment in low pH Watt's type or chloride nickel plating bath at 55-60°C at a c.d. of 1-2 A/dm^2 for 10 minutes and reverse current and plating under normal conditions.
- 3) Anodic treatment for 2 minutes and then cathodic treatment for 6 minutes both at 3 A/dm^2 in acid nickel chloride bath and plating is continued without rinsing.
- 4) Dip in 50% HF (by wt) at room temperature for 10 seconds.
- 5) Dip in 30-50% (by volume) perchloric acid (S.G. 1.53) at 30°C for 2-50 seconds.
- 6) Electrolyte activation either anodic or cathodic in copper cyanide baths at 60-70°C for 1-3 minutes at a c.d. of 1-2 A/dm^2 .

The main drawbacks of the hitherto known processes

is that the electrolytic treatment in solutions 1) - 3) produces non-uniformity of thickness of the nickel electroforms obtained especially in respect of nickel foils and screens while the use of solution 4) and 5) is hazardous and corrosive and these are not generally used. Moreover the use of solution (3) requires the reversing of the polarity during activation step necessitating use of additional units. Use of cyanide electrolyte activation requires a cyanide waste treatment plant which leads to a net increase in the cost of the electroforms produced.

The main object of the present invention is to obviate the above difficulties in the activation of nickel foils and screens by employing a suitable chemical immersion treatment to remove the oxide layers on the nickel surface and thereby produce a clean oxide free surface to prevent the layer formation during further plating of the same with nickel or chromium.

The other advantages of this invention are that;

the layer formation between nickel deposits is prevented, the solutions used produce cleaned and oxide free nickel surface,

no rectifier and polarity reversing switch is needed,

the chemicals used are indigenously available,

thickness variation of thicker foil and screens due to electrolytic treatment is prevented,

the solutions used are not hazardous as perchloric acid and hydrofluoric acid, and that the

cyanide waste treatment system is not required.

The main finding underlying the present invention consists in activation of the Ni foil by immersion treating the nickel electroform in a chemical solutions to remove the oxide layer for preventing the poor adhesion between nickel electroform for further nickel or chromium deposition.

The new result flowing from the new finding is that nickel electroforms activated in the above solutions produce highly adherent and sound deposits without any lifting of deposits.

The essential steps of the process for the production of nickel electroforms are cleansing the nickel foils—rinsing—chemical activation treatment—rinsing and electroplating the thus treated foils with nickel or chromium and the step of treating the foil by immersion of the nickel electroforms in the activation solution at room temperature for 4-10 minutes as the distinctive feature of this invention.

Thus the characteristic novelty of the invented process is the immersion treatment of the nickel electroforms in the activation solutions at room temperature for 4-10 minutes to prevent poor adhesion of the nickel or chromium deposits to the nickel electroforms.

The new result achieved due to the presence of the invented step is the activated nickel electroforms for further plating with nickel or chromium with good adhesion of plated deposits to nickel electroform.

Accordingly this invention provides an improved process for the production of nickel electroforms which comprises cleansing the nickel foils, rinsing, chemical activation treatment, rinsing and further electroplating the thus treated foils with nickel or chromium characterised in that the cleansed nickel foils are subjected to chemical activation treatment by immersion in a solution consisting of hydrochloric acid admixed with nitric acid and carboxylic acid like formic acid, acetic acid or with ferric chloride and ferric nitrate.

The cleansing of the nickel foils, rinsing and electroplating of the treated foils with nickel or chromium in the process of the present invention is carried out according to methods known per se.

According to a feature of the invention the activation

solution consists of 200-300ml/L of hydrochloric acid admixed with 200-400 ml/L of nitric acid and 20-100 ml/l of formic acid.

According to another feature of the invention the activation solution consists of 150-300 ml/l of hydrochloric acid admixed with 200-400 ml/l of nitric acid and 100-200 ml/l of acetic acid.

According to a further feature of the invention the activation solution consists of 100-200 gms/l of ferric chloride, 100-300 gms/l ferric nitrate and 100-200 ml/l of hydrochloric acid.

According to a still further feature of the invention the activation is carried out by dipping the cleansed foil in the activation solution for a period of 1-10 minutes at room temperature.

The present invention thus consists of a process for activating the nickel electroforms suitable for further plating with nickel or chromium which consists of cleansing the nickel foils, rinsing, chemical activation treatment and electroplating with nickel or chromium in their acid electrolytes wherein the cleansed nickel foil is immersed in any one of the chemical activation solutions containing (a) hydrochloric acid 200-300 ml/l (S.G. 1.18) admixed with nitric acid (200-400 ml/l) and formic acid 20-100 ml/l (b) hydrochloric acid (S.G. 1.18) 150-300 ml/l admixed with nitric acid (S.G. 1.42) and acetic acid (S.G. 1.047) 100-200 ml/l (c) ferric chloride 100-200 g/l admixed with ferric nitrate 100-300 g/l and hydrochloric acid (S.G. 1.18) 100-200 ml/l at room temperature for a period of 1-10 minutes which is characterised in that the said immersion treatment produce a clean, oxide free nickel surface to obtain sound adherent deposit of nickel or chromium without any lifting of deposits.

The following is the flow chart of the process:

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Nickel electroform
  ↓
Cleaning
  ↓
Rinsing
  ↓

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↓
Chemical Activation treatment

↓
Rinsing

↓
Further plating with nickel or chromium

The following physical characteristics were tested to assess the quality of the activation treatment,

a) Adhesion :

Since adhesion tests cannot be made on thin foils and screens, the following experiments were carried out to assess the adhesion on nickel plated panels under identical conditions.

1. Tape test: Nickel plated specimen was pretreated, activated and nickel/chromium plated, rinsed and dried. 1" width colourless cellotape was applied on the panels and pulled at 90°C. No peeling of nickel layer indicates a good adhesion.
2. Bend Test : The end products were tested by bending to 180° twice, using a vice bench and visualised through a microscope at 20 X for any lifting of deposits in the fracture portion.
3. Thermal cycling : The end products were heated to 200°C in the furnace for one hour and immediately quenched in ice cold water. The test was repeated for three times and no blistering could be observed.

b) Porosity :

Foils and screens were examined by illumination with a light source from one side and visualised for any pores. This test was carried out for raw material, activated substrate and the end product. In all the cases pores could not be observed.

The following typical examples are given to illustrate how the invention is carried out in actual practice but not to

limit the scope of this invention.

Example 1

Electroformed nickel foil (35 micron) of size 15 cm x 20 cm was alkaline cleaned, rinsed and chemically activated in the solution containing

Hydrochloric acid (S.G. 1.18)	250 ml/L
Nitric acid (S.G. 1.42)	200 ml/L
Formic acid	80 ml/L

for a period of 5 minutes and rinsed with tap water and distilled water. The foil is further plated with nickel in a sulphamate nickel baths to a thickness of 100 micron. The foil was having no layer formation, no porosity and a sound deposit was obtained.

Example 2

Electroformed nickel centrifugal filter screen of thickness 40 micron with the mandrel was alkaline cleaned, rinsed and chemically activated in a solution containing.

Ferric chloride	200 g/L
Ferric nitrate	100 g/L
Hydrochloric acid (S.G. 1.18)	150 ml/L

for about 10 minutes and after rinsing, electroforming was continued in Watt's nickel bath for a desired time. The screen was inspected for the peeling of the deposit and hole size variation and found to be unaffected. The screen was free from pin holes.

Example 3

Electroformed nickel screen was pretreated as per example 2 and chemically activated in a bath containing

Hydrochloric acid (S.G. 1.18)	300 ml/L
Nitric acid (S.G. 1.14)	200 ml/L
Acetic acid (S.G. 1.047)	100 ml/L

for a period of 1 minute and then chromium plated on the bright

side of the screen to 8 micron. The chromium plating was having very good adhesion without any lifting of deposit and was free from porosity.

Example 4

Electroformed nickel foil of thickness 40 micron of size 10 cm x 10 cm was alkaline cleaned, rinsed and chemically activated in the following bath for 10 minutes.

Hydrochloric acid (S.G. 1.18)	300 ml/l
Nitric acid (S.G. 1.42)	200 ml/l
Formic acid	80 ml/l

After rinsing with tap water and distilled water the foils are plated in a nickel sulphamate bath to a thickness of 200 micron. The foil was found to have no layer formation and free from pin holes

We Claim :

1. An improved process for the production of nickel electroforms which comprises cleansing the nickel foils, rinsing, chemical activation treatment, rinsing and further electroplating the thus treated foils with nickel or chromium characterised in that the cleansed nickel foils are subjected to chemical activation treatment by immersion in a solution, consisting of hydrochloric acid admixed with nitric acid and carboxylic acid like formic acid, acetic acid or with ferric chloride and ferric nitrate.
2. Process as claimed in claim 1 wherein the activation solution consists of 200-300 ml/l of hydrochloric acid admixed with 200-400 of nitric acid and 20-100 ml/l of formic acid.
3. Process as claimed in claims 1 and 2 wherein the activation solution consists of 150-300 ml/l of hydrochloric acid admixed with 200-400 ml/l of nitric acid and 100-200 ml/l of acetic acid.

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4. Process as claimed in any of the preceding claims wherein the activation solution consists of 100-200 gms/l of ferric chloride, 100-300 gms/l of ferric nitrate and 100-200 ml/l of hydrochloric acid.
5. Process as claimed in any of the preceding claims wherein the activation of the nickel foils is carried out by dipping the cleansed foil in the activation solution for a period of 1-10 minutes at room temperature.
6. An improved process for the production of nickel electroforms substantially as herein described and illustrated.

Dated this 14th day of January 1982



(A.N.NAGPAUL)

OF NAGPAUL & ASSOCIATES

Agent for the applicants.

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