RIAG Oberflächentechnik AG · Postfach 169 · CH-9545 Wängi TG

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DURNI-COAT® DNM-4

Semi-bright electroless nickel plating bath for increased wear and corrosion resistance

DNM-4 is an electroless process for the deposition of nickel-phosphorus alloys, which has been specially developed for the deposition of metallic semi-bright plating on magnesium alloys.

The phosphorus content of the deposits ranges between 5 and 8 %.

Both rack and barrel articles can be treated with the **DNM-4** process. The deposition rate (assuming that the permitted operating tolerances are observed) is around 13 – 16 µm/h.

DNM-4 is supplied in 3 liquid concentrates:
DNM-4 Make up solution, DNM-4 Replenisher 1 and **DNM-4 Activator salt** are required for a new bath make up, while **DNM-4 Replenisher 1** and **2** and concentrated or diluted Ammonia are used for replenishing.

Tank and equipment

DNM-4 can be used in existing plants designed for electroless nickel plating, provided heat-resistant plastics (95 °C) or stainless steel tanks with anodic protection are used.
Heating should be carried out using a PTFE or stainless steel steam coil, or an electric immersion heater (casing: stainless steel with anodic protection, glass or PTFE).
An exhaust ventilation system must be provided for the extraction of spray-mist and steam. A cover should be placed over the bath during breaks in production to stop evaporation loss at working or near working temperatures. It will also prevent the entry of dirt or other impurities from the surrounding air.

Filtration and tank agitation

The continuous filtration on the **DNM-4** electrolyte during the operation helps to ensure of optimum deposits. The parts of the filter unit which come into contact with the **DNM-4** electrolyte should be made of heat resistant plastic or stainless steel, anodically protected. The filter unit should consist of a rotary submersible pump with following filter housings, the submersible pump being used for movement of the bath. In order to ensure optimum mixing of the regenerative solutions flowing into a bath continuous operation, a bath recirculation of 15 – 20 bath volumes/h is necessary. As filters, we recommend 3 µm cartridge filters of polypropylene in the case of continuous operation, 1 µm for intermittent operation.

Operating conditions

Make up:	distilled or demineralised water (electrical conductivity < 5 µS/cm)	60 vol.-%
	DNM-4 Make up solution	10 vol.-%
	DNM-4 Replenisher 1	5 vol.-%
	Ammonia solution up to pH value 10	
	DNM-4 Activator salt	15 g/L (pre-dissolved)

The required quantity of **DNM-4 Activator salt** for 100 L of electrolyte is first to be dissolved in demineralised water to make up 10 L. After the make up of the bath, the pH value is to be adjusted to the specified value at approx. 90 °C by means of concentrated chemically pure ammonia.

Replenishing:	**DNM-4 Replenisher 1**	100 g/L nickel
	DNM-4 Replenisher 2	648 g/L sodium hypophosphite monohydrate 360 mg/L stabiliser (lead acetate)
	pH value correction solution	ammonia (conc. or diluted)

Dosage ratio: **Repl.1** : **Repl.2** = 1 : 0.733

Working temperature: 86 – 94 °C

pH value: 8.0 ± 0.2 (measured at 20 °C), (electrometric)
corresponding to a value of approx. 7.0 ± 0.2 at 90 °C

Nickel content: 5.0 ± 0.5 g/L

Reducing agent: 18 ± 3 g/L

Stabiliser content: 2.7 mg/L (2 – 4 mg/L)

Bath load: 0.2 – 1.2 dm^2/L

Deposition speed: 13 – 16 µm/h (according to pH value, temp.), after approx. 2 – 3 MTO, the deposition speed is held between 10 and 15 µm/h by increasing the working temperature.

Agitation: Agitation of the parts is useful, but not absolutely necessary.

Bath make up

Before the new or first make up of a **DNM-4** bath, all plant parts which come into contact with the **DNM-4** electrolyte solution are to be treated with concentrated nitric acid. After thorough rinsing of the aggregates concerned with water and distilled water, the water quality leaving the filter must be checked. The electrical conductivity should not exceed 5 µS/cm.

The volume of distilled water (conductance < 5 µS/cm) required for the make up of the bath is prepared in advance. After the filter circulation has been switched on, the **DNM-4** make up chemicals (**DNM-4 Make up solution** and **DNM-4 Replenisher 1**) are added first. Now the pH value is set to 10 using conc. ammonia followed by adding the pre-dissolved **DNM-4 Activator salt**. After heating to working temperature, the pH value must be checked (see pH check).

Instructions

After careful pretreatment, the parts to be electroless nickel plated are simply immersed in the **DNM-4** solution long enough to reach the required plating thickness. In order to achieve optimum adhesion, a heat treatment should be carried out. Optimum values have been found to be a temperature of 180 °C and a treatment time of 30 minutes.

A plating thickness of at least 4 µm is required as the basis for the deposition of further galvanic layer systems.

For pretreatment of the **DNM-4** plated parts after the heat treatment, and also in the case of plating interruptions in cyanide copper plating, it is essential to follow the procedure below:

Hot degreasing (Procedure, see DNM-4 Process)	Treatment time:	280 – 320 seconds
Activator (Procedure, see DNM-4 Process)	Treatment time:	55 – 65 seconds

Warning: Do not use electrolytic degreasing! Do not exceed treatment time in activator!

Layer thickness of the galvanic cyanide copper plate

The layer thickness should be at least 8 – 10 µm, depending on the roughness of the material to be plated. Greater copper plate thickness increase process reliability.

When **DNM-4** is not in use, it is advisable to cool it down (t < 40 °C), in order to achieve maximum bath life (6 – 8 metal turnovers) and stability of the solution.

Base materials

DNM-4 is a specially developed electrolyte for the plating of magnesium alloys.

RIAG will be glad to provide the pretreatment specifications for the application concerned.

Bath maintenance

The safeguarding of optimum deposition rates requires that the specified bath parameters described under "Operating conditions" are maintained. Under normal working conditions, approx. 50 dm^2 at 25 µm layer thickness can be plated with 1 litre of **DNM-4 Replenisher 1**. To one volume unit of **DNM-4 Replenisher 1**, approx. 0.733 volume units of **DNM-4 Replenisher 2** and concentrated ammonia have to be added. Ensure when doing so that the solution does not fluctuate by more than 10 % from the demanded metal-content (see "Operating conditions"). Additions should be made slowly, at regular intervals and in small quantities, or – in the case of large bath volumes – by means of an automatic pH-value and (particularly) nickel-content control system.
We recommend twice a day (morning and evening) analysis of the amounts of nickel and reducing agent present. One metal turnover (MTO) is reached when 5.0 g/L nickel has been deposited from the solution; one metal turnover is also reached after the consumption of 50 mL/L **DNM-4 Replenisher 1**.

In order to increase the nickel content by 1.0 g/L, 10.0 mL **DNM-4 Replenisher 1** / litre electrolyte must be added.

In order to increase the sodium hypophosphite content by 1.0 g/L, 1.54 mL **DNM-4 Replenisher 2** / litre electrolyte must be added.
As a rule of thumb, at a throughput of 1 dm^2 with a layer thickness of 25 µm, 20 mL **DNM-4 Replenisher 1** and 14.6 mL **DNM-4 Replenisher 2** must be added.

Temperature

The normal working temperature is between 86 and 94 °C; Optimum for start: 90 °C. Lower temperatures reduce the deposition rate. Movement of the **DNM-4** solution is necessary during heating and cooling in order to avoid local overheating.

pH value

The working pH range (at t=20 °C) is from 7.8 – 8.2, Optimum 8.0 A newly formulated bath should be started with a pH value of 8.2. The monitoring of the bath solution should be carried out electrometrically, with continuous measurement and corresponding correction. If the pH value measurement is carried out at working temperature, the working pH range is from 6.8 – 7.2. All pH values indicated are based on measurement with temperature compensation.

pH value correction

The pH is lowered by adding approx. 10 % sulphuric acid (60 mL/L conc. sulphuric acid p.a.); for pH increase, approx. 25 % Ammonia. All additions must be made slowly while stirring well. When using ammonia and sulphuric acid, the accident prevention regulations for alkalis and acids must be observed.

Wastewater treatment

DNM-4 and its rinsing water must be detoxified and neutralised before being released into the drainage system. Rinse water and bath concentrates, dilution 1:3, can be passed to the wastewater treatment plant for nickel precipitation by the addition of lime milk and caustic soda at pH 12. After this treatment, the filtrate (< 5 mval Ni/L) is passed through a selective ion exchanger. After adjustment to the initial pH value, the solution leaving the ion exchanger, together with other heavy metal free filtrates, can be released into the drainage system.

Hazard and safety instructions

These details can be found in the material safety data sheets for **DNM-4 Make up solution**, and **DNM-4 Replenisher 1** and **2**. The relevant MSDS for the handling of ammonia can be obtained from the supplier concerned.

The **DNM-4 Make up solution** is acidic, while the **DNM-4 Replenisher 1** is alkaline (pH value 7.8 – 8.2). The **DNM-4 Replenisher 2** is slightly acidic.

The **DNM-4 Make up solution, DNM-4 Replenisher 1** and **DNM-4 Replenisher 2** should be stored at a temperature of 10 – 25 °C.

Should any crystallisation occur as a result of excessive cooling, the solutions must be warmed up to more than 30 ° C, stirring being recommended.

The **DNM-4 Make up solution**, the **DNM-4 Replenishing** solutions and the Ammonia solution should not be allowed to come into contact with the skin or eyes. In the case of an accident, rinse well with plenty of cold water and, in the case of eye injuries, visit or call in a doctor.

Liability

This instruction manual was compiled with reference to the state of the art and all current standards, and is based on the long-term knowledge and experience of RIAG. However, RIAG cannot monitor compliance with this instruction manual and the methods described herein at the customer/end-user's premises. Work carried out with RIAG products must be adapted accordingly to meet local conditions. In particular, RIAG cannot accept liability for damage, loss or cost incurred due to a failure to adhere to this instruction manual, improper application of the methods, unauthorised technical modifications, insufficient maintenance or the absence of maintenance in respect of the requisite technical hardware or equipment, or in the event of use by unqualified personnel. RIAG is not liable for damage or loss caused by RIAG or its employees except where intention or gross negligence can be proved. RIAG furthermore reserves the right to make changes in relation to products, methods and the instruction manual without prior notice.

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RIAG Oberflächentechnik AG
Murgstrasse 19a
CH- 9545 Wängi
Tel. + 41 (0) 52 / 369 70 70
Fax + 41 (0) 52 / 369 70 79
www.riag.ch
info@riag.ch

Analysis – Analytic methods

Nickel

Target value: 5.0 g Ni/L

Required reagents: Na_2EDTA 0.1 mol/L
NH_4OH solution, concentrated (approx. 25 %)
Murexide powder (1 g murexide and 99 g NaCl)
Distilled water

Apparatus required: Erlenmeyer flask, 300 mL
Pipette, 5 mL
microburette (Bang), 10 mL

Method: Pipette to add 5 mL of electrolyte (20 °C) to a 300 mL Erlenmeyer flask. After adding 10 mL of NH_4OH and a spatula-tip of murexide powder, top up to about 150 mL with distilled water. Titration now takes place with Na_2EDTA 0.1 mol/L until there is an abrupt colour-change from yellow to violet.

Calculation: nickel (g/L) = 1.174 x consumed mL Na_2EDTA 0.1 mol/L

This analysis procedure should be carried out at least twice daily. It is also used for checking the function of the flow-rate photometer. Ensure also that each batch of newly made-up electrolyte is checked in this way.

Reducing agent

Target value: 18 g/L sodium hypophosphite

Required reagents: Starch solution 1 %
6 mol/L HCl (600 mL/L 32 % HCl)
0.05 mol/L KJO_3/KJ (iodate-iodide)
0.1 mol/L $Na_2S_2O_3$ (sodium thiosulphate)

Apparatus required Pipette, 2 mL
2 burettes, 50 mL -1/20 division- with
fitting-stopper glass taps or
Teflon tap cocks
automatic tipping device, 20 mL
Erlenmeyer flask with tight-fitting
glass stopper (iodine-count flask)

Method: Pipette 2 mL electrolyte (20 °C) in an Erlenmeyer flask, add 25 mL 0.05 mol/L potassium iodide-iodate and acidify with 20 mL 6 mol/L HCl.

Tightly seal Erlenmeyer flask with stopper and allow sample to react for half an hour in total darkness.

Then titrate with 0.1 mol/L sodium thiosulphate solution until a pale yellowish coloration becomes apparent.

Add two drops of 1 % starch solution to mark the transition point exactly. Now continue to titrate until there is a transition from bluish-violet to colourless.

Calculation: reducing agent (g/L) = (mL 0.05 mol/L KJO_3/KJ – mL 0.1 mol/L $Na_2S_2O_3$) x 2.65

Polarographic analysis of stabiliser content (2 – 4 ppm)

Method:

The lead concentration analysis is performed by inverse voltammetric measurement with the hanging mercury drop mode (HMDE). To do this, the lead in the bath sample is first accumulated at the mercury drop for 70 seconds at – 700 mV. Then a voltage scan is performed from – 550 mV to – 250 mV. This dissolves the lead that has accumulated on the Hg drop electrode again; in this process, a current signal proportional to the lead concentration present is emitted at the half-wave potential of the lead (approx. – 350 to – 450 mV). The actual concentration is then determined by additive calibration with subsequent linear regression. Contamination of the sample vessel and the electrodes from previous measurements plays a very major role; for this reason the blank value must be determined with pure chemicals prior to each sample addition. The blank value must not be higher than 5 nA.

Equipment:

Polarograph (e.g. from Metrohm)
Nitrogen supply
Eppendorf pipette (1 – 1'000 µL)

Reagents:

HNO_3 (suprapur)
Pb^{2+} standard solution 10 mg/L

Procedure:

Pipette 20 mL of deionised water (nano-pure) and 20 µL of HNO_3 into the measurement vessel and perform a control measurement with the parameters adjusted as specified in the operating instructions of the instrument. If the blank value is < 5 nA pipette 500 – 1,000 µL into the measurement vessel (the quantity should be calculated so that approx. 1 µg of lead are in the measurement vessel). Then perform the measurement using the additive calibration procedure, adding 1 µg of lead (100 µL of standard 10 mg/L Pb solution) twice and performing one measurement repetition for each addition. Then multiply the lead concentration value found by the factor 1.83 (calculated on lead acetate) to obtain the stabiliser concentration.

Calculation:

$$\text{Stabiliser (mg/L)} = \frac{\text{Pb quantity [µg]} \times 1.83}{\text{sample quantity [mL]}}$$