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DURNI-COAT®
PTFE-DURNI-DISP N

Electroless nickel plating electrolyte for wear resistant, low-friction, self-lubricating, non-stick coatings

PTFE-DURNI-DISP N is a process for electroless deposition of nickel-phosphorous alloys containing uniformly and homogeneously dispersed PTFE particles with a grain size of 0.1 – 0.5 µm. This coating electrolyte has been developed specifically for the deposition of coatings with very low friction and good non-stick properties. The **PTFE-DURNI-DISP N** process can be used for the coating of ferrous and non-ferrous metals.

The PTFE rate in the layer is 20 – 40 % (by vol.), the phosphorus content is 7.5 – 9 %.
PTFE-DURNI-DISP N coatings have very good tribological properties:

Pin-on-disk-tribometer

The mean coefficient of friction is 0.1 – 0.2 with low wear and a service life of 100’000 to 200’000 revolutions (sliding speed 10 cm/s; load 1 – 5 N, air humidity 50 %; room temperature).

The deposition rate of a newly-prepared electrolyte is approx. 7 – 8 µm/h, which drops to approx. 5 µm/h as the electrolyte ages.

PTFE-DURNI-DISP N is supplied as a set of liquid concentrates:

	Use	
	Make up	Replenishment
PTFE-DURNI-DISP N Make up	X	
PTFE-DURNI-DISP N Replenisher 1	X	X
PTFE-DURNI-DISP N Replenisher 2		X
PTFE-DURNI-DISP N Replenisher 3		X
PTFE-DURNI-DISP N Dispersion	X	X
PTFE-DURNI-DISP N Tenside		X
PTFE-DURNI-DISP N Replenisher 2 (0) stabiliser free		(X)

(X) optional

Plating Tanks and Equipment

PTFE-DURNI-DISP N can be used in ordinary electroless nickel plating systems, preferably with anodically protected tanks made of stainless steel. It is also possible to use tanks made of PP.

The heating should be indirect, with stainless steel steam coils or electrical immersion heating elements (with stainless steel, glass, porcelain or PTFE jackets). Advisable is the use of a heating system with thyristor control. If steam is used, the temperature should not be higher than 105 °C.

The plating installation should be equipped with a circulation system that allows circulation of the electrolyte with minimum solution flow around the parts to be plated.

An air exhaust system is also necessary to remove vapours and spray. However, please note that the **PTFE-DURNI-DISP N** process generates a lot of foam, especially during the coating phase; this means that care must be taken to ensure that the exhaust does not remove too much foam from the electrolyte, as this results in excessive reduction of surfactant levels. When the electrolyte is not in operation it should be cooled down for a better electrolyte life and covered to avoid evaporation losses when it is at or close to operating temperature and drag-in of impurities.

Filtration and Agitation

The electrolyte cannot be filtered continuously through a bag filter (GAF/P200 µm) because the PTFE is filtered out with the time and the filter pressure rises which is not allowed. If a filtration of the electrolyte is necessary one can use a filter for 1 – 2 hours, not more.

If the electrolyte needs to be pumped out it must also be kept in continuous motion in the temporary storage tank.
When you want to restart the system, pump the solution back in through a 20 µm filter and perform a **PTFE** analysis before starting work. If necessary, add **PTFE-DURNI-DISP N Dispersion** to correct the **PTFE** level. In order to maintain **PTFE-DURNI-DISP N Dispersion** stability over longer periods circulation should be restricted to no more than a maximum of two times the electrolyte volume per hour. While components are being coated circulation should be approx. two times the electrolyte volume per hour. Faster circulation can result in a structured appearance or passivities on the coating finish.

Electrolyte make up

Before making up a new or fresh **PTFE-DURNI-DISP N** electrolyte remove any adhering PTFE residues from the tank with ultrasonic equipment or mechanically. Treat all plant components that come into contact with the **PTFE-DURNI-DISP N** electrolyte solution with concentrated nitric acid. After this rinse all these components thoroughly with water and distilled water and check the water quality with the circulation system switched on. Electrical conductivity should be less than 15 µS/cm. Start with approx. 60 % of the volume of distilled water required for the electrolyte set-up. Switch on the filter system, then add the **PTFE-DURNI-DISP N** make up solutions to the water, following the procedure described above. Heat the solution up to working temperature.
Measure the pH value at 85 °C and adjust to the required value with chemically pure ammonia approx. 15 %.

Operating Parameters

Make up

Distilled or de-ionized water	750 mL/L (electrical conductivity max. 5 µS/cm)
PTFE-DURNI-DISP N Make up	180 mL/L
PTFE-DURNI-DISP N Replenisher 1	42 mL/L
Ammonia conc.	Adjust pH value to 4.95
PTFE-DURNI-DISP N Dispersion	10 g/L

After make-up, add conc. ammonia, (chemically pure) to adjust the pH value to approx. 4.95 at 20 °C (consumption approx. 20 – 30 mL/L of electrolyte). After adjusting the pH value, slowly add the **PTFE-DURNI-DISP N Dispersion**, shaking it well first to ensure that it is homogeneously distributed. Allow the electrolyte to mix cold for a minimum of 5 h, circulating at a rate of four times the electrolyte volume per hour. Afterwards heat the electrolyte to operating temperature. At 85 °C adjust pH value to 5.05 with ammonia diluted 1:1. After a further 30 minutes of mixing the electrolyte is ready for use.

Replenishing

PTFE-DURNI-DISP N Replenisher 1	120 g/L nickel
PTFE-DURNI-DISP N Replenisher 2	540 g/L sodium hypophosphite, 70 mg/L stabiliser
PTFE-DURNI-DISP N Replenisher 2 (0) stabiliser free	540 g/L sodium hypophosphite
PTFE-DURNI-DISP N Replenisher 3	600 mL/L ammonia 25%, accelerator
PTFE-DURNI-DISP N Dispersion	600 g/kg PTFE
PTFE-DURNI-DISP N Tenside	24 g/L

Ratio: 1 L **Repl. 1** : 1.32 L **Repl. 2** : 0.50 L **Repl. 3** : 35 g **Dispersion** : 40 g **Tenside**

Operating temperature:	85 ± 1 °C
pH value:	5.05 ± 0.05 (measured at 85 °C with pH-meter) 5.00 (4.95 – 5.05) (measured at 20 °C, with pH-meter) measured with Unitrode/Metrohm
Nickel content:	5.0 g/L (4.3 – 5.2 g/L)
Reducing agent:	20.0 g/L (16.0 – 21.0 g/L)
Stabiliser:	0.3 mg/L (0.2 – 0.4 mg/L), after 0.5 MTO: 0.2 – 0.7 mg/L
Workload:	at 15 µm layer thickness max. 0.8 dm^2/L
Deposition rate:	7 – 8 µm/h, falling to approx. 5 µm/h in the course of electrolyte lifetime

Operating Instructions

After a thorough pre-treatment of the parts to be plated, simply immerse them in the **PTFE-DURNI-DISP N** solution and leave them there until the required coating thickness is achieved. It is not advisable to apply coatings thicker than 15 µm, as no improvement of the specific coating characteristics are achieved beyond this point. If a higher layer thickness or better corrosion resistance is required, first apply a corresponding electroless nickel layer. The **PTFE-DURNI-DISP N** coating must then be applied directly after this coating, from wet to wet. Depending on the used electroless nickel electrolyte it might be necessary to use a special activating system.
The quality of the pre-treatment solutions should also be monitored very carefully, as dispersion coatings are very sensitive to inadequate pre-treatment of the base material, which can lead to adhesion problems.

The coating is carried out at a circulation rate of twice the electrolyte volume per hour. No continuous dosage of replenisher is applied. The nickel content should not be allowed to sink below 14 %. Thus, the electrolyte workload should be adjusted to ensure that the nickel content does not fall below 4.3 g/L, taking the required coating thickness into account.

The stabiliser content has a great influence on the stability of the electrolyte. It is advisable to measure the concentration after each electrolyte and if necessary make a separate addition of stabiliser to reach the right concentration. Especially during the first batches the electrolyte is very sensitive against a too high stabiliser content, so keep the value of 0.3 mg/L. After a electrolyte age of approx. 0.5 MTO higher values are possible.
In the case that no measuring of the stabiliser is possible, it is advisable to do the first replenishment with an amount of **Repl. 2 (0) stabiliser free** to avoid passivations.
For the first replenishment use **Repl. 2** and **Repl. 2 (0) stabiliser free** 1:1
For the second replenishment use **Repl. 2** and **Repl. 2 (0) stabiliser free** 2:1
Do all the following replenishments with **Repl. 2**

Ensure in the start phase of the electrolyte that the pH is always on the target value. (Adjustment after each batch if no automatic pH-measurement and dosage of **Repl. 3** is possible).
The dosage ratio for **Repl. 3** is in the beginning phase of the electrolyte not enough for pH-adjustment.

Replenishment is done following the analytical results or calculated from the coated surface.
It is done between the batches. Allow the solution to mix for approx. 15 – 30 minutes after adding the replenishment solutions.
Continuous replenishment is only possible if the nickel content is monitored continuously, e.g. by using “online” titration as the control parameter.
Automatic Dosation of **PTFE-DURNI-DISP N Replenisher 3** controlled via pH value metering is recommended.
To achieve maximum electrolyte life and stability it is advisable to allow the **PTFE-DURNI-DISP N** electrolyte to cool down (t < 40 °C) when it is not being used.
The life time of the **PTFE-DURNI-DISP N** electrolyte depends to a considerable extent on the volume of impurities dragged-in and the frequency of production pauses. An electrolyte life time of 4 MTO (20 g Ni/L) may be achieved under optimal conditions.

Base Materials

PTFE-DURNI-DISP N can be used for the coating of ferrous and non-ferrous metals.
Detailed pre-treatment instructions for a wide variety of applications are available from riag Oberflächentechnik.

Operating Temperature

The normal operating temperature is 85 °C. Lower temperatures reduce the deposition rate and can lead to passivity of the electrolyte; higher temperatures make the electrolyte instable. Continuous circulation of the **PTFE-DURNI-DISP N** electrolyte is necessary to keep the dispersion in even suspension. This also prevents local overheating during heating and operation.

Maintenance

To achieve and maintain optimum deposition rates and coating quality it is important to maintain the Operating Parameters (see also electrolyte control below). Under normal conditions, with 1 litre of **PTFE-DURNI-DISP N Replenisher 1** a surface area of approx. 148 dm² can be deposited with a layer thickness of 15 µm.

Make sure that the metal content of the solution does not deviate from the limit value by more than 14 % (see Operating Parameters). To replenish properly, perform an analysis after every batch. Precise control of the stabiliser content of the electrolyte is particularly important; if the level falls too low this can lead to instability and premature coagulation of the dispersion. Initially, the stabiliser content should be approx. 0.3 mg/L (determined by polarographic measurement). Later on, levels of up to 0.7 mg/L in the electrolyte are uncritical.

In case of batches with low workload replenish via analysis not later than a total electrolyte load of 0.5 dm²/L (at a layer thickness of 15 µm); otherwise the electrolyte parameters and the deposition rate will both fall too low.

Add per gram of nickel deposited:	8.33 mL	**PTFE-DURNI-DISP N Replenisher 1**
	11.00 ml	**PTFE-DURNI-DISP N Replenisher 2**
	4.17 mL	**PTFE-DURNI-DISP N Replenisher 3**
	0.29 g	**PTFE-DURNI-DISP N Dispersion**
	0.33 g	**PTFE-DURNI-DISP N Tenside**

Due to foam formation, the **PTFE-DURNI-DISP N Dispersion** can only be added by weight.

During the operation of the electrolyte the content of PTFE can drop. If the PTFE content is lower than 5 g/L, a separate replenishment with **PTFE-DURNI-DISP N Dispersion** should be done. It is advisable to add it in portions between the charges of not more than 0.3 g/L to avoid deposits of PTFE on the parts.
One metal turnover (MTO) is achieved when 5.0 g/L of nickel have been deposited from the solution (42 mL/L **PTFE-DURNI-DISP N Replenisher 1**).

Stabiliser concentration

It may be necessary to increase the concentration of the stabiliser due to various working methods, be it the parts to be coated (e.g., rack or barrel), equipment (large or small areas) or customer demand (low or high layer thickness).

DNC XXX Replenisher 2 (70)

Example: Concentration stabiliser: 70% of the common version.
We are happy to advise should a change be necessary.

Determination of Layer Thickness

The layer thickness is determined by measuring the weight increase of coated test panels (0.2 dm²), using the following formula:

$$\frac{[\text{Final weight [g]} - \text{Initial weight [g]}] * 1000}{14.07} = \text{layer thickness in µm}$$

Adjustment of pH Value

To reduce the pH value use 10 % sulphuric acid (60 mL conc. sulphuric acid p.a./L) or better conc. acetic acid. To increase the pH value during electrolyte operation use **PTFE-DURNI-DISP N Replenisher 3**.
Always keep the **PTFE-DURNI-DISP N Replenisher 3** container tightly closed to prevent reduction of the ammonia concentration due to evaporation.
If this happens you will require too much of **PTFE-DURNI-DISP N Replenisher 3** to adjust the pH value which will result in an overdosage of the accelerator. This will lead to layer disturbances. Thus, it is advisable to check the ammonia concentration once a week.
Make additions slowly and carefully, otherwise you may disturb the stability of the **Dispersion**.
In particular, if the pH values becomes too high this can lead to rapid coagulation.
Always observe the safety regulations for bases and acids when working with ammonia and sulphuric acid!

Evaluation of Layers

A test bowed test-panel should always be coated together with every batch for quality control purposes. The panels should have a mat grey appearance, with a smooth, slippery surface. Perform an alternate bending test to check coating adhesion. Check the **PTFE inclusion** rate and the layer quality at regular intervals by cross-section.

Barrel Plating

For the plating of small pieces in a barrel the following cycle rates are the values are for orientation:

3 – 8 min. without moving / 3 sec. moving in alternation

The number of revolutions should be 4 – 5 revolutions/min. A higher revolution rate can cause a higher abrasion and thus an instability of the electrolyte. The right stabilisator content is very important to avoid electrolyte instability.
The timespan without moving can be optimized with the appearance of the working pieces. With flat pieces the time without moving is shorter than with bulky pieces.
The moving time may not be lengthened for the danger of more abrasion and thus an increased electrolyte instability.

Plating with rotation the working piece

To get a very good distribution of the **PTFE**-content in the layer a low rotation movement (2 – 4 rotations/min.) is possible.

Heat Treatment

The adhesion of the Ni/P/PTFE coating to the base material can be improved by a heat treatment at 180 °C within a few hours after applying the coating.

The apparent hardness can be increased by a heat treatment for 3 – 6 h at 300 °C. However, this can also have a negative effect on the antifriction properties.

The anti-stick properties of the coating can be improved by brief heat treatment (15 – 20 minutes) at approx. 340 °C.

Waste Water Treatment

Both **PTFE-DURNI-DISP N** and its rinsing water must be detoxified and neutralised before being released into the drains.
Instructions for waste water treatment are available from riag Oberflächentechnik.

Hazards - and Safety Instructions

These are written in the material safety data sheets for **PTFE-DURNI-DISP N Make up , PTFE-DURNI-DISP N Replenisher 1, 2 and 3.** Those for the handling with sulphuric acid and ammonia are to be required from the supplier. All chemicals should not come in contact with skin and eyes. In case of injury rinse with al lot of cold water and in case of injury of the eyes visit a doctor.

The **PTFE-DURNI-DISP N Make up** and **PTFE-DURNI-DISP N Replenishers 1, 2 and 3** should be stored at 5 – 25 °C.

The **PTFE-DURNI-DISP N Dispersion** should be stored at 10 – 20 °C with constant slow movement to prevent a settling down of the dispersion.

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.
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Electrolyte Control

Nickel Content Analysis

Target value:	5.0 g Ni/L
Reagents:	Na_2EDTA 0.1 mol/L NH_4OH solution, conc. Murexide trituration (1 g Murexide and 99 g Sodium chloride) Distilled or deionized water
Equipment:	1 Erlenmeyer flask 300 mL 1 pipette 5 mL 1 microburette 10 mL (Bang)
Procedure:	Pipette 5 mL of the **PTFE-DURNI-DISP N** electrolyte solution (20 °C) into a 300 mL Erlenmeyer flask. Add 10 mL of NH_4OH and a spatula tip of murexide, then dilute to approx. 150 mL with distilled water. Titrate with Na_2EDTA 0.1 mol/L (10 ml microburette) until the very sudden colour change from yellow to violet occurs. Approx. 3.5 – 4.5 mL of the Na_2EDTA 0.1 mol/L are required
Calculation:	Nickel (g/L) = 1.174 x used mL Na_2EDTA 0.1 mol/L

This analysis should be performed after every batch. You should also use the same analysis method to check every freshly made up electrolyte.

Reducing Agent Analysis

Target Value:	20 g/L sodium hypophosphite
Reagents:	1 % starch solution 6 mol/L HCl 0.05 mol/L KIO_3/KI (iodate-iodide) 0.1 mol/L $Na_2S_2O_3$ (sodium thiosulphate)
Equipment:	1 pipette 2 mL 2 burettes 50 mL with 1/20 division scale – with ground-in glass taps or Teflon stoppers 1 automatic tilting device, 20 mL 1 Erlenmeyer flask with ground-in glass stopper (iodine value flask)
Procedure:	Pipette 2 mL of the electrolyte solution (20 °C) into an Erlenmeyer flask. Add 20 mL of the 0.05 mol/L potassium iodate-iodide solution and 20 mL of the 6 mol/L HCl, then close the Erlenmeyer flask with the ground-in glass stopper and allow it to stand in the dark for 30 min. at room temperature to cause a reaction. Then titrate with the 0.1 mol/L sodium thiosulphate solution until the colour changes to light yellow. To mark the end point precisely, add 2 drops of the 1 % starch solution and continue titration until colour changes from blue-violet to colourless .

Calculation: reducing agent (g/L) = (mL 0.05 mol/L KIO_3/KI – mL 0.1 mol/L $Na_2S_2O_3$) x 2.65

This analysis should be performed after every batch. You should also perform the analysis to check each freshly prepared electrolyte.

A separation of the PTFE from the electrolyte sample (centrifugation for example 15 min. at 5300 rpm) is advisable, because the endpoint is more difficult to see with PTFE in the sample.

Polarographic Analysis of the stabiliser content

Target value: 0.3 mg/L stabiliser

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 electrolyte 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 1,000 µl into the measurement vessel. Then perform the measurement using the additive calibration procedure, adding 1 µg of lead (100 µl of standard 10 ppm Pb solution) twice and performing one measurement repetition for each addition.

Calculation:

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

This analysis should be performed after each batch, as the electrolyte has an extremely sensitive response to the stabiliser content.

pH Value

Adjust the pH value electrometrically whereby the set pH value of 5.05 always refers to a temperature of 85 °C.
It is very important to remember that measurements of cold electrolyte samples will produce different pH values. This pH value - difference between the “hot” and “cold” measurements - depends on the electrolyte composition, the age of the electrolyte and the kind of the pH-value electrode used. This means that this effective difference must always be redetermined if the pH value is measured at lower temperatures.

PTFE Analysis

Target value:	6 g/L PTFE
Method:	The PTFE content of the electrolyte is measured gravimetrically following after centrifugal separation of the **PTFE**.
Equipment:	centrifuge (min. 4’300 rpm)
	pipette (30 mL)
	centrifuge tube (50 mL)
	analytical balance
	drying oven
Procedure:	Weigh the dry centrifuge tube, then pipette 30 mL of the electrolyte solution into the tube and centrifuge for 30 minutes at at least 4,300 rpm. Carefully remove the excess liquid directly after stopping and wash the PTFE residue with deionised water. Then centrifuge again and separate off and discard the washing water. Repeat the same washing procedure one more time, then dry the **PTFE** residue in the drying oven at 100 °C until constant weight is achieved, and weigh (drying time minimum 1 h)
Calculation:	**PTFE** (g/L) = (tube with **PTFE** – empty tube)[g] x 33.3