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PTFE DURNI DISP N

Electroless nickel plating bath 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 bath 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 – 30 % (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 bath is approx. 7 – 8 µm/h, which drops to approx. 5 µm/h as the bath ages.

PTFE Durni Disp N is supplied as a set of six liquid concentrates:

PTFE Durni Disp N Make up solution

PTFE Durni Disp N Replenisher 1

PTFE Durni Disp N Replenisher 2

PTFE Durni Disp N Replenisher 3

PTFE Durni Disp N Dispersion

PTFE Durni Disp N Solution T1a

Optional **PTFE Durni Disp N Replenisher 2 stabilizerfree**

For the make up of a new bath the following is needed: **PTFE Durni Disp N Make up solution**

PTFE Durni Disp N Replenisher 1

PTFE Durni Disp N Dispersion

For the replenishment: **PTFE Durni Disp N Replenisher 1,2 & 3**

PTFE Durni Disp N Dispersion

PTFE Durni Disp N Solution T1a

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 bath 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 bath, as this results in excessive reduction of surfactant levels. When the bath is not in operation it should be cooled down for a better bath life and covered to avoid evaporation losses when it is at or close to operating temperature, and drag-in of impurities.

Bath 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 bath volume per hour. While components are being coated circulation should be approx. two times the bath volume per hour. Faster circulation can result in a structured appearance or passivities on the coating finish.

Operating Parameters

Bath make up

Distilled or de-ionized water	70 % by vol. (electrical conductivity max. 5 µS/cm)
PTFE Durni Disp N Make up Solution	18 % by vol.
PTFE Durni Disp N Replenisher 1	4.2 % by vol.

After bath make-up, add conc. ammonia, (chemically pure) to adjust the pH value to approx. 4.95 at 20 °C (consumption approx. 2.0 – 3.0 L/100 L of bath solution). After adjusting the pH value, slowly add the **PTFE Durni Disp N Dispersion**, shaking it well first to ensure that it is homogeneously distributed. The required quantity is 10 g/L and can be taken from the attached batch certificate supplied with the **PTFE Durni Disp N Dispersion**. Allow the bath to mix cold for a minimum of 5 h, circulating at a rate of two or four times bath volume per hour depending from the sort of mixing and after this heat the electrolyte to operating temperature. At 85 °C adjust pH-value to 5.05 (hot measured) 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 stabilizer
PTFE Durni Disp N Replenisher 2 stabilizerfree	540 g/L sodium hypophosphite
PTFE Durni Disp N Replenisher 3	600 mL/L ammonia 25%
PTFE Durni Disp N Dispersion	60 % **PTFE** by weight
PTFE Durni Disp N solution T1a	24 g/L

Ratio: 1 L **Repl. 1** : 1.32 L **Repl. 2** : 0.50 L **Repl. 3** : 35 g **Dispersion** : 40 g **T1a-solution**

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)
Stabilizer:	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 dm²/L
Deposition rate:	7 – 8 µm/h, falling to approx. 5 µm/h in the course of bath lifetime

Bath make up

Before making up a new or fresh **PTFE Durni Disp N** bath 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** bath 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 bath set-up. Switch on the filter system, then add the **PTFE Durni Disp** set-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. 13 %.

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 bath 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 bath volume per hour. No continuous dosage of replenisher is applied. The nickel content should not be allowed to sink below 14 %. Thus, the bath 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 stabilizer content has a great influence on the stability of the electrolyte. It is advisable to measure the concentration after each batch and if necessary make a separate addition of stabilizer to reach the right concentration. Especially during the first batches the electrolyte is very sensitive against a too high stabilizer content, so keep the value of 0.3 mg/L. After a bath age of approx. 0.5 MTO higher values are possible.
In the case that no measuring of the stabilizer is possible, it is advisable to do the first replenishment with an amount of **Repl. 2 stabilizerfree** to avoid passivations.
For the first replenishment use **Repl. 2** and **Repl. 2 stabilizerfree** 1:1
For the second replenishment use **Repl. 2** and **Repl. 2 stabilizerfree** 2:1
Do all the following replenishments with **Repl. 2**

Take care in the start phase of the bath 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 bath 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 bath 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. A bath 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.

Bath Maintenance

To achieve and maintain optimum deposition rates and coating quality it is important to maintain the Operating Parameters (see also Bath 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 bath 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 bath are uncritical.

In case of batches with low workload replenish via analysis not later than a total bath load of 0.5 dm²/L (at a layer thickness of 15 µm); otherwise the bath 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 Solution T1a**

Due to foam formation, the **PTFE Durni Disp N Dispersion** can only be added by weight.

During the bath operation 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**).

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 bath 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 bath 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 bath 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 solution, 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 solution** 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.

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Bath 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** bath 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 bath.

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 bath 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 bath.

A separation of the PTFE from the bath 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 stabilizer content

Target value: 0.3 mg/L stabilizer

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 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:

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

This analysis should be performed after each batch, as the bath 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 bath samples will produce different pH values. This pH value - difference between the “hot” and “cold” measurements - depends on the bath composition, the age of the bath 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 bath 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 bath 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