DisChem
CHEMISTRY FOR
ADVANCED LITHOGRAPHY

E-Form

ELECTRONIC GRADE SULFAMATE NICKEL

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E-Form is an electronic grade nickel sulfamate electroforming concentrate designed and manufactured specifically for use with microlithography. DisChem's E-form nickel sulfamate and proprietary additives are specified to meet the low internal stress of deposit and high purity requirements of optical disc holographic and micro-electronics applications.

The E-Form product line includes 100% compatible addition agents for process optimization and control.

E-Form contains the highest nickel metal concentration commercially available (180 g / L), free of metallic impurities with only residual amounts of ammonium ion and free sulfur compounds present. This provides for economy in use and transport, while allowing for an operating life far greater than most available products.

SPECIFICATIONS:

Constituent	*Specification*
Nickel Metal	180-185 g / L
Specific Gravity	1.530 - 1.57
pH @ 25°C	4.4-4.8
Purification Technique	Carbon Treatment + Micro-Filtration
Internal Stress of Deposit	0 - 1000 PSI Tensile

Impurities By Weight:	*Maximum*	*Typical*
Chromium (Cr)	Not Detected	N/A
Copper (Cu)	1.0 mg/L	< 0.5 mg/L
Iron (Fe)	2.0 mg/L	< 0.5 mg/L
Manganese (Mn)	0.1 mg/L	Not Detected
Lead (Pb)	1.0 mg/L	Not Detected
Zinc (Zn)	1.0 mg/L	< 0.5 mg/L
Ammonium Ion (NH_4)	175 mg/L	< 80 mg/L
Total Sulfate (SO_4)	150 mg/L	< 20 mg/L
Free Sulfates (SO_x)	<20 mg/L	< 5 mg/L

OPERATING PARAMETERS

E-Form is a highly purified solution concentrate for use in new bath make-up, as well as for periodic maintenance additions. The desired concentration of nickel metal is obtained by simple calculation and dilution of the E-Form concentrate. E-Form is typically operated with a nickel metal concentration between 76 - 105 g/L (10.1 - 14.0 oz / gal). Higher nickel metal concentrations may be desired for high-speed systems where current density exceeds 32.4 A/d^2 (300 ASF).
The recommended operating parameters for the E-Form sulfamate nickel are as follows:

Nickel Metal…90 - 120 g/L
Boric Acid…By Temperature
PH……..3.8 - 4.2
Surface Tension…28 - 33 dynes/cm
Temperature……..50 - 60°C

NEW SOLUTION MAKE-UP

The required volume of E-Form sulfamate nickel concentrate is determined through the calculation:

Required E-Form Addition =

$$\frac{\text{g/L nickel metal desire X bath capacity (L)}}{\text{180 g/L nickel metal (E-Form)}}$$

Liters = Gallons X 3.785

1. Fill the tank to 1/3 of its final volume with DI water.
2. Add the required volume of E-Form determined through the calculation above.
3. Add 30 grams of boric acid for every liter of the final bath capacity (4.0 oz / gallon).

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4. Fill tank to ¾ of the final volume.

5. Heat bath, while agitating, to working temperature.

6. Check pH and adjust to approximately 4.0 using E-Line pH Refined Electronic Grade Sulfamic Acid (99.9% minimum purity).

7. Add remainder of the required amount of boric acid. The required amount of boric acid is proportional to the operating temperature of the bath. Analyze boric acid concentration to determine requirement. (See Analytical Control)

8. Add 0.2 % by volume E-liminate Pit wetting agent.

9. Fill tank to final volume and mix well. Heat solution to operating temperature. Check pH and adjust as needed. Filter solution for a minimum of one hour after reaching operating temperature to insure any precipitated salts are removed from solution.

10. Analyze and adjust chemistry as needed.

DisChem ANALYTICAL SERVICES

DisChem provides analytical services for the complete analysis, optimization and trouble shooting of nickel sulfamate electroforming solutions.

SOLUTION MAINTENANCE

E-Form sulfamate nickel solutions are extremely stable and relatively maintenance free as long as the bath is operated within the recommended parameters. Understanding the functional relationships between the operating variables will allow for the implementation of corrective and preventative actions for enhanced process control. These variable and the chemical characteristics of sulfamate nickel are described in detail in DisChem's guide, *Maintenance, Operating Conditions and Trouble Shooting of Optical Disc Electroforming Solutions.*

ANALYTICAL CONTROL

Nickel Metal - Titration Procedure

A. Required Reagents and Indicators

0.1 Molar EDTA
Ammonium Hydroxide (26° Be')
Murexide Indicator (0.2 g. Murexide + 100 g. sodium chloride)

B. Procedure

1. Pipette 2 mL cooled sulfamate nickel solution into a 250 mL Erlenmeyer flask.

2. Dilute to approximately 100 mL total volume with DI water.

3. Add 10 mL ammonium hydroxide.

4. Add approximately 0.2 grams of Murexide indicator (about the size of a match head, or enough to turn the solution a light brown color).

5. Titrate, while agitating, with 0.1 M EDTA from a light brown to a violet end point.

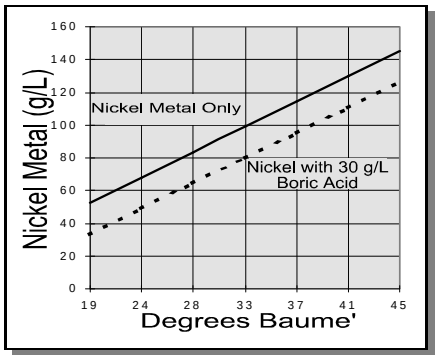
C. Calculation

Oz/gal nickel metal = (mL 0.1 M EDTA Titrated) X (0.391)

g/L nickel metal = (mL 0.1 M EDTA Titrated) X (2.933)

Nickel Metal - Hydrometer Procedure

While titration is the more accurate and recommended method of analysis, the hydrometer provides a simple means of determining the nickel metal concentration. Use a hydrometer capable of reading the degrees Baume' expected for the solution. The nickel concentration may be determined from the Baume' density by comparison against the chart below:



Boric Acid - Titration Procedure

A. Required Reagents and Indicators

0.1 N Sodium Hydroxide
D-Mannitol (powder)
Bromocresol Purple (0.04% aqueous)

B. Procedure

1. Sample is to be taken at operating temperature. If allowed to cool before analyzing, re-heat to 140°F to dissolve any precipitated boric acid.
2. Pipette 5 mL of heated solution into a 250 mL Erlenmeyer flask.
3. Add 2 - 3 drops bromocresol purple indicator.
4. Drop wise, titrate with 0.1 N NaOH until solution turns from green to blue. This step neutralizes residual acids other than boric acid. Re-zero burette.
5. Add approximately 5 grams D-Mannitol powder, or enough to form slurry. Solution will turn back to a pale green.
6. Titrate, while agitating, with 0.1 N sodium hydroxide to a blue endpoint. Note: this endpoint is gradual, turning from green to a light gray to a definite blue.

C. Calculation

Oz/gal boric acid = (mL 0.1 N NaOH titrated) X (0.164)

g/L boric acid = (mL 0.1 N NaOH titrated) X (1.23)

pH - Electrometric

pH should be measured daily with an external temperature compensation probe at the actual bath temperature. Under normal circumstances, the pH of the bath rises with use. This occurs as anode generated oxygen (O_2) couples with cathode generated hydrogen (H_2) to form water (H_2O). The net reaction leaves uncoupled oxygen that, in turn, forms hydroxides:

$$2H_2 + 2O_2 \rightarrow 2H_2O + O_2$$
$$O_2 + H_2 \rightarrow 2OH \text{ (pH } \Uparrow\text{)}$$

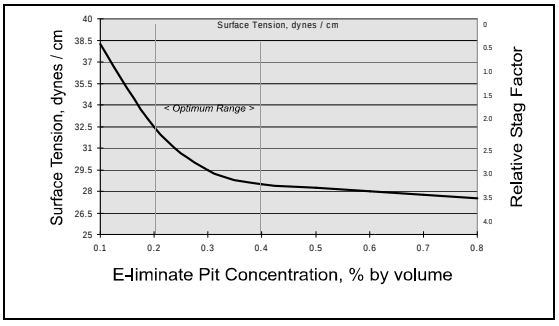
Changes in pH are one of the best tools for evaluating the *health* of the bath. It is necessary to maintain the pH within the defined parameters for normal use: 3.8 - 4.4. A declining pH may indicate a more serious anode problem.

pH should be reduced, as needed, using a high purity sulfamic acid, such as DisChem's E-Line pH Refined Electronic Grade Sulfamic Acid (99.9% min.)

Wetting Agent - Surface Tension

Proprietary wetting agents are added to the bath to prevent pitting by gasses generated during operation. DisChem's E-liminate Pit wetting agent provides excellent surface action with low foaming characteristics. Furthermore, E-liminate Pit is formaldehyde free for complete compatibility with photoresist.

E-liminate Pit may be easily determined through use of a stalagometer or tensiometer (follow the manufacturers instructions of determining surface tension). The relationship between the concentration of E-liminate Pit and bath surface tension is demonstrated below:



Contact your DisChem representative for information on stalagometer and tensiometer testing and equipment.

ANODES

Due to the high efficiency of sulfamate nickel (~ 98%), only sulfur depolarized anode material should be used. Other anodes, such as electrolytic nickel, are prone to passivation in sulfamate nickel, and can result in serious break down products and reduction of bath life. .

In sulfamate nickel electroforming, nickel anodes are the source of metal utilized for deposition; the bath serves as the conductive electrolyte. A gradual decline in the solution nickel metal concentration may result due to drag out by the mandrel. A sudden decline in the nickel concentration may signify a potentially harmful anode problem, such as polarization (passivation). As such, good process control will utilize the nickel metal concentration as a general indicator of bath health.

PHOTORESIST REMOVAL, CLEANING AND ELECTROFORM PASSIVATION

As the surface of an electroforming nickel deposit is quite active, it is necessary to passivate the surface prior to electrolytically growing subsequent generations of electroforms or for use in embossing replication processes.

DisChem's StamperPrep provides high detergency and conductivity for electrocleaning removal of photoresist, organic processing residuals, and for stamper passivation through reverse current electrolysis. Unlike traditional trisodium phosphate and sodium hydroxide cleaners, StamperPrep does not break down with electrolysis virtually eliminating rejects resulting from burning in electrolytic passivation.

DisClean a cationic surface active agent is designed to remove water stains, oxidation products, organic residues and electrostatic contaminants from optical electroforms and substrates. In addition, DisClean lowers the surface charge on nickel electroforms for reduced sticking in injection molding applications.

GRAIN REFINER AND HARDENING AGENTS

E-Line Refiner is an electronic grade grain refiner and hardening agent specified for optical electroforming using sulfamate nickel baths. E-Line reduces the grain size of electrolytically deposited nickel by influencing crystalline structure formation, allowing the creation of smoother, low - stress electroforms with increased hardness. In addition, electroforms such as optical media stampers, that are made using E-Line Refiner have far greater resilience in punching and molding operations.

PRODUCT AVAILABILITY

DisChem offers a complete line of 100% compatible electroforming chemistries and additives:

E-Form Electronic Grade Nickel Sulfamate Concentrate

Unit	*Part Number*
19 L (5 gal) drum	EFM05
55 drum	EFM55

E-Line pH Refined Electronic Grade Sulfamic Acid

Unit	*Part Number*
25 Kg (55.1 lb) drum	EPH50

E-liminate Pit Wetting Optical Media Agent

Unit	*Part Number*
19L (5 gal) pail	EWA05

High Purity Boric Acid, 99.5% Min

Unit	*Part Number*
23 Kg 50 lb. Pail	DBA50

PRODUCT / ORDERING INFORMATION

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DisChem ELECTROFORMING PRODUCTS:

- **E-FORM Electronic Grade Sulfamate Nickel Concentrate (180 g/L)**
- **E-Line pH High Purity Sulfamic Acid, Refined Electronic Grade, 99.9% Min.**
- **E-liminate Pit Optical Media Wetting Agent, 100% photoresist compatible formaldehyde free.**
- **DisChem Ultra-Pure Boric Acid, (99.8% Min.) Fast Dissolving**
- **E-Line Refiner Nickel Sulfamate Grain Refiner / Hardening Agent**
- **StamperPrep Soak / Electroclean / Electro-Passivation Compound**
- **DisChem Analytical Services**

DisChem
CHEMISTRY FOR ADVANCED LITHOGRAPHY

DisChem MISSION STATEMENT

DisChem is dedicated to serving the needs of the microlithography industry through innovative solutions for success. We provide the highest quality products and services available, unmatched cost per quality.

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