A GUIDE TO INDIUM PLATING

INDIUM CORPORATION®

INTRODUCTION

The first commercial indium plating bath was developed in the early 1930s by a group of chemists who founded Indium Corporation. The bath was an alkaline cyanide formulation, used to deposit a thin coating of indium onto aircraft engine bearings. Subsequent diffusion of the indium into the bearing base metallization reduced friction and wear by increasing the lubricity of the bearing, and increased the corrosion resistance of the bearings.

The resulting increase in flight range and payload capacity, and reduction in scheduled maintenance, earned Indium Corporation the coveted “E” Award for manufacturing excellence from the U.S. Government.

While indium is still used to electroplate bearings today, many additional uses have appeared. All take advantage of indium’s unique physical and chemical properties, such as:

- Extreme ductility and softness, even down to temperatures approaching absolute zero
- Cold welding properties
- Resistance to alkaline corrosion
- Ability to rapidly diffuse into certain metals, such as copper, silver, and lead for hardening
- Low melting temperature (157°C)
- Low vapor pressure
- Low oxide formation
- Ability to wet glass, certain metallic oxides, and glazed ceramics
- Ability to alloy with tin, bismuth, silver, and lead metallic layers at low temperatures to form new alloys with different physical properties

Due to toxicity, reclaim, shipping, and environmental concerns, the cyanide-based indium electroplating bath is seldom used today.

The indium sulfamate plating bath has emerged as the standard production-proven approach for high volume indium plating applications.

ADVANTAGES OF THE INDIUM SULFAMATE BATH

The consumable material is the indium anode and not the bath. A properly maintained bath will last for years.

OPERATION AND MAINTENANCE

- One of the easiest plating baths to operate and maintain
- Proven formulation, capable of heavy production
- Extremely stable operation and long life
- Constant plating rate
- Operation at room temperature
- Wide current density range of operation
- High, constant cathode efficiency of 90%
- Easy reclaim of indium from rinse waters
- No additional agents required
- Bath supplied ready to use
- Indium replenishment is from indium anodes, not expensive bath concentrate

PLATING BATH MAINTENANCE

pH

Over time, the pH of the bath will rise and pH should be monitored using a pH meter on a weekly basis. pH is maintained within the recommended range by small additions of a 10% solution of sulfamic acid dissolved in distilled or deionized water.

Metal Concentration and Impurities

Metal concentration and impurities should be analyzed on a routine basis. Since the cathode efficiency is 90% and the anode efficiency is 100%, the metal concentration will rise over time. The rate of rise is dependent on production, but will stabilize at approximately twice the initial metal concentration of the bath. This causes no problem in operation except for a slight increase in drag-out loss. Every attempt should be made to ensure adequate rinses before indium plating to minimize carryover of metallic impurities, particularly if an in-line nickel plating operation precedes indium plating.

Indium Anodes

The bath is designed for use with soluble indium anodes. The use of insoluble inert anodes, such as platinum-plated titanium, is not recommended and may adversely affect bath chemistry. If the bath is idle for a period of time, it is recommended that the indium anodes be removed from the plating bath.

Bath Additives

Since the grain refiners and leveling agents have a wide operational concentration range, they are added to a new bath at the high-end of the concentration range. **No further additions of these additives are required for the life of the bath.** Minor breakdown products from these organics cause the bath to darken over time. While these breakdown products cause no operational difficulties, they can be removed, if necessary, by a short carbon treatment. A standard plating carbon treatment cartridge can be installed in the filter pump system of the tank to achieve this. Carbon treatment is continued until the original amber clarity of the bath is restored.

INDIUM CORPORATION®

INDIUM ANODE FORMS

Strip

Indium anodes can be fabricated in several configurations—most common is the use of indium strip. Since indium metal is soft and pliable, it can be easily bent around the anode bus bar.

To calculate the length, measure the distance from the top of the anode bar to the bottom of the tank. From this measurement, subtract 3-6" to allow for solution circulation at the bottom of the tank and add 2-3" to allow for wrapping the anode strip around the anode bus bar.

The width can be 1-6" depending on the configuration of the part(s) to be plated. Ensure that the anode to cathode area ratio is 1:1 or greater.

The recommended thickness of the strip is 0.125-0.25". A thickness less than 0.125" is not recommended due to possible shorting of anode to cathode by solution movement from filter pump agitation. Thicknesses greater than 0.25" will last longer, but are harder to bend around the anode bus bar.

Cast Anodes

Indium anodes can be cast to customer-specified shapes and dimensions. Holes for Monel hooks can be pre-drilled and Monel hooks can be supplied, if desired.

Indium Shot

Indium shot is teardrop-shaped indium metal. The size is approximately 0.25" diameter. Shot is used where the use of titanium anode baskets is desired.

Special Shapes

Indium can also be fabricated into special shapes, such as rods, balls, cylinders, and other customer-specific shapes.

Contact our engineers today: **metchem@indium.com**

INDIUM SULFAMATE PLATING BATH

Bath Operation	
Indium	30 g per liter
pH	1-3.5 (1.5-2.0 preferred)
Temperature	20-25°C RT
Cathode Efficiency	90%
Anode Efficiency	100%
Throwing Power	Good
Quality of Plate	Smooth, matte finish
Filtration	Constant filtration recommended
Solution Color	Clear when new, darkens to amber color with use due to organic addition agent breakdown. This has no affect on bath operation.
Current Density	10-20 amps per ft^2. Can be increased up to 100 amps per ft^2 if bath temperature is maintained at 20-25°C.
Anodes	Pure indium, 99.99% minimum purity
Anode to Cathode Ratio	1:1 or greater
Routine Bath Analysis	pH, indium metal concentration, survey for metallic impurities

Plating Rates

Theoretical plating rates:

0.3964mg per coulomb
1.4271 grams per amp-hour
12.1 amp-hour to deposit per 0.001” per ft^2

Plating deposit rates at 90% cathode efficiency and 20 amps/ft^2:

15 minutes............................0.3710mils
30 minutes............................0.7434mils
45 minutes............................1.1150mils
60 minutes............................1.4860mils

Indium Content

We recommend using Atomic Absorption (AA) or Inductively Coupled Plasma (ICP) spectroscopy to determine and monitor the indium content of the bath.

PHYSICAL CONSTANTS OF PURE INDIUM

STRUCTURE

Crystal structure: Tetragonal; at °C a=0.32512nm and c=0.49467nm

MASS CHARACTERISTICS

Atomic weight........114.82

Density:

°C	g/cc
20	7.300
164	7.026
194	7.001
228	6.974
271	6.939
300	6.916

Volume change on freezing. 2.5% contraction.

THERMAL PROPERTIES

Melting point........156.61°C

Boiling point........2080°C

Coefficient of thermal expansion........linear, 24.8µm/m/°K at 20°C

Specific heat:

°C	J/kg/°K
25	233
127	252
156.63 (solid)	264
156.63 (liquid)	257
227	256
327	255
427	254

Latent heat of fusion........28.47 kJ/kg
Latent heat of vaporization........1959.42 kJ/kg
Thermal conductivity........83.7 W/mK at 0°C

Vapor pressure:

°C	kPa
1215	0.1013
1421	1.0130
1693	10.1300
2080	101.3000

ELECTRICAL PROPERTIES

Electrical resistivity:

°C	nΩ-m
	3.38°K — Super conducting
20	84
154	291
181	301
222	319
280	348

Electrochemical equivalent........Valence 3,396.4µg/°C

Electrode potential........ $In° \Rightarrow In^{3+}$+3e 0.38V

MAGNETIC PROPERTIES

Magnetic susceptibility..... Volumetric: 7.0 x 10^{-6} mks

NUCLEAR PROPERTIES

Stable isotopes........113,115
Thermal neutron cross section.
For 2.2 km/s
neutrons.... absorption, 190±10b; scattering, 2.2±0.5b

MECHANICAL PROPERTIES

Tensile strength:

°K	MPa
295	1.6
76	15.0
4	31.9

Compressive strength........2.14 MPa

Hardness........0.9 HB

Elastic modulus at 20°C........12.74 GPa in tension

Poisson's ratio at 20°C........0.4498

APPLICATION NOTES

PLATING — AN ALTERNATIVE METHOD OF APPLYING INDIUM

Indium is a versatile metal with the following unique physical properties:

- Has a low melting point of 157°C and a high boiling point of 2080°C
- Has a low vapor pressure, ideal for use in vacuum applications
- Is soft and malleable, even down to cryogenic temperatures approaching absolute zero
- Has relatively low toxicity
- Is a bright, shiny metal that forms a thin (80-100 Angstroms) protective oxide layer
- Will create a hermetic gasket seal between two mating parts. Being soft, indium will deform and fill in the microstructure of two mating parts, pressed together using moderate pressure. Unlike Viton A or other elastomers, indium will retain its plasticity at cryogenic temperatures
- Will cold weld to itself using moderate pressure

Metallic parts can be coated with indium using a solder reflow process. In those instances where a chemical flux cannot be used, or temperature limitations of the parts prohibit reflow coating, electroplating can be an alternate method to deposit indium.

The following three-step operation can be used to electroplate indium:

1. Remove oils, grease, and other contamination using an organic solvent or aqueous alkaline cleaner.
2. Remove oxides from the metallic substrate using a mild mineral acid, followed by a cold DI water rinse.
3. Electroplate the indium ar room temperature from the indium sulfamate bath at a current density of 10-100 amps/ft^2 and rinse. The deposition rate is approximately 1.5mils/hour at a current density of 20 amps/ft^2.

PROTOTYPE PLATING USING THE INDIUM SULFAMATE PLATING BATH KIT

Electroplating indium onto various materials allows the evaluation of indium's unique properties. For example, two metallic substrates can be electroplated with indium and subsequently bonded together simply by pressing the indium-plated surfaces together. This process utilizes the cold-welding property of indium.

The kit is also useful for plating indium onto small prototype parts prior to scale up. Plating can be performed on any properly prepared substrate metallization, such as copper, brass, nickel, gold, tin, or mild steel. As with all electrodeposited metals, indium will not deposit onto high refractory metals such as chromium or tungsten. Stainless steel and aluminum metallizations must have special surface treatments prior to electroplating with any metal. Specific information on these surface treatments can be found in most electroplating textbooks.

Kit Contents

- One 1-liter bottle of ready-to-use indium sulfamate plating bath
- Two 1"-wide x 0.0625"-thick x 12"-long pure indium anode strips
- Guide to Indium Plating booklet

Other Items Required

- A laboratory direct current (DC) rectifier
- A small glass or plastic container to be used as the plating tank
- Plating pretreatment chemicals
- Laboratory stirrer

INDIUM CORPORATION®

APPLICATION NOTES

ACHIEVING A FINER-GRAIN STRUCTURE

The indium sulfamate plating bath is a common method of depositing pure indium onto conductive metallic surfaces. A relatively common misconception about the bath is that the deposit will have a smooth or mirror-like finish. However, a typical bath produces a frosted or matte-like finish. Granular formations can be seen in the deposit using a microscope. Granular growth is common for all soft metals that are electrodeposited, such as tin, lead, tin-lead alloy, and indium. For various reasons, it may be desirable to control the size of the grains that form and, typically, the desire is for smaller grains. (Bath chemistries generally include organic materials that inhibit grain growth.) The following recommendations can be used in conjunction with one another.

Pulse/Periodic Reverse Plating — In this process, the current is cycled from on-to-off-to-reverse in a square wave cycle. Cycle times are generally in milliseconds where the on time is greater than the reverse time to affect a net deposition of metal. When the current is reversed, this causes the indium to “de-plate” off the work piece. The de-plating takes place at areas of high current density. The angular points of a crystal are a prime place for de-plating to occur. Thus, the de-plating tends to smooth out or reduce the size of the grains. This process involves a special pulse plate-rectifier that is specifically designed for periodically reversing the current.

Current Density — Smaller grain size can be achieved by reducing the current density. This is limited by the fact that enough current is still needed to allow for plating to take place. A typical low-end current density would be 10 amps per ft^2.

Anode/Cathode Distance — Increasing the distance between the anode (indium) and cathode (work piece), to a certain extent, will reduce the grain size.

Agitation — Agitation, such as stirring, does not necessarily reduce the size of the grains; however, it can result in a smoother looking

deposit. During the plating process, hydrogen bubbles form on the work piece. In a static bath, the bubble will stick to the work piece until it is large enough to cause buoyancy to pull itself off the surface of the work piece and float to the surface of the solution. While it is stuck to the surface of the work piece, no plating can occur at the site and indium continues to plate around it. This phenomenon produces a "cratering" effect.

With agitation, the bubbles are stripped off sooner, when they are smaller, therefore significantly reducing, if not eliminating, the "cratering."

Note: In order to optimize the performance of the bath, it is important to make sure that certain parameters of the bath fall within the ranges specified by the bath manufacturer.

1. **pH** — Typical bath pH should be 1-3.5 (1.5-2.0 preferred). The pH can be adjusted by making additions of sulfamic acid. If the pH gets too high, the indium will precipitate out in the form of indium hydroxide, which causes the solution to assume a milky-white appearance.
2. **Indium Metal Content** — The bath typically is supplied at a concentration of 30 grams of indium metal per liter of solution. Because the anode efficiency is 100% and the cathode efficiency is 90%, the indium concentration tends to rise over time, leveling off at about 60-75g/l. This is a normal situation and the rise in indium concentration does not impact the operation of the bath.
3. **Current Density** — The bath is typically operated at 10-20 amps per ft^2. The current density can be increased to as high as 100 amps per ft^2 if the temperature can be maintained at 20-25°C. The use of cooling coils may be necessary to keep the bath at this temperature when operating at higher current densities.
4. **Anode Size** — The surface area of the anode should be equal to or greater than the surface area of the work piece(s).

APPLICATION NOTES

PROPER SURFACE PREPARATION

As in all electroplating processes, proper surface preparation prior to actual electroplating of indium is essential to ensure adequate adhesion and coverage of the deposited metal. Indium can be successfully electroplated on most metallic surfaces, such as copper, nickel, silver, platinum, and gold. The electroplating of any metal, including indium, onto stainless steel and high refractory oxide metals, such as aluminum and molybdenum, requires special surface preparation procedures.

Preparation of the base metallization consists of two separate steps — cleaning and activation. The cleaning step removes oils, grease, and other soils from the base metallization surface. The activation step removes oxides from the base metallization surface, which is necessary for proper electrodeposition. The base metal should be cleaned either by ultrasonic solvent vapor degreasing, or by immersion in a commercial alkaline cleaning bath operated at 80-90°C for about 10-15 minutes, followed by a thorough hot water rinse.

The base metal should then be acid-activated by immersion in a 10-15 percent volume of sulfuric or hydrochloric acid solution at room temperature for 3-5 minutes, followed by a quick cold water spray rinse. Commercial proprietary activation solutions can be substituted for the mineral acid solutions. The manufacturer's operational procedures should be followed. For highly passivated metals such as nickel, a Woods nickel strike should be substituted for the acid activation step. The preparation and operation of the Woods nickel strike bath are described in detail in most textbooks on electroplating.

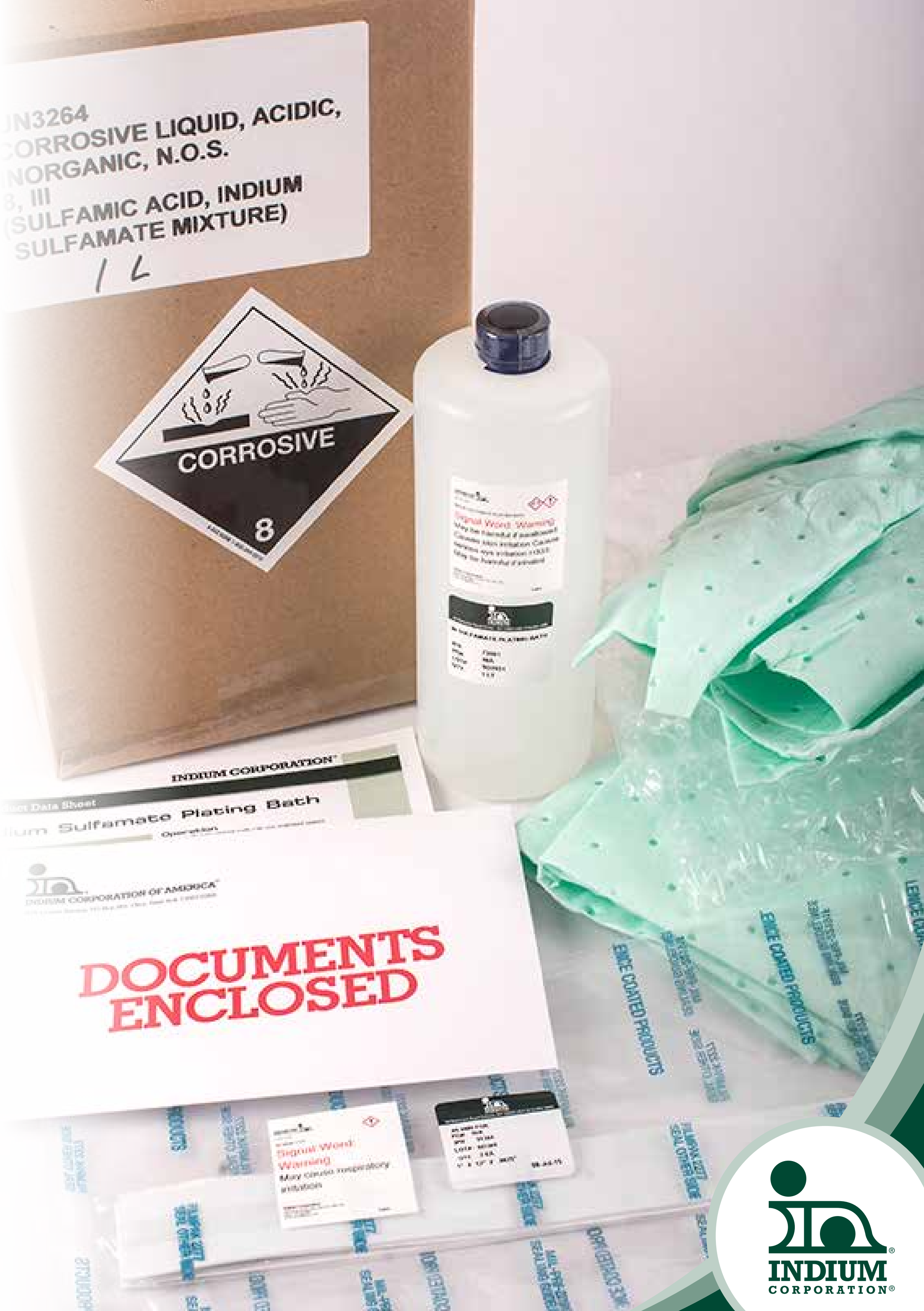
Immediately following the acid activation or Woods nickel strike rinse step, the base metal should then be immersed in a 5 weight percent solution of sulfamic acid solution for 1-3 minutes. This is to ensure that the pH of the base metallization surface remains acidic so no reformation of oxide occurs, and also to protect the indium sulfamate plating bath from drag-in of activator chemicals. The substrate is now ready for indium plating.

RECLAMATION AND DISPOSAL

A properly maintained indium sulfamate plating bath contains 30–60 grams of indium metal per liter of plating bath solution, depending on the solution's age. Due to the high value of indium metal and environmental regulations, it may be desirable to reclaim the indium metal and render the solution environmentally benign for easy disposal. Below are the steps to accomplish this:

1. The pH of the solution should be raised to 7 (neutral) with additions of either NaOH or KOH. At around a pH of 4, indium hydroxide, $In(OH)_3$ (milk-white in color), will begin to precipitate out of solution. The pH can be checked with a pH monitor or pH indicator strips.
2. After allowing the indium hydroxide precipitate to settle, the remaining liquid portion can be decanted off, and depending on local regulations, pumped to drain. Please consult the appropriate environmental agencies in your area for proper disposal.
3. After decanting, a white slurry should be left.
4. Filter the slurry and thoroughly rinse the cake with water to remove as many contaminants as possible.
5. The indium hydroxide cake can then be packaged appropriately (i.e., sealed in a plastic bag) and sent to an indium reclaimer.

Note: In order to reduce shipping charges, the indium cake can be baked to drive off the remaining moisture, thereby reducing the shipping weight.



INDIUM CORPORATION

INDIUM CORPORATION
WORLDWIDE

Our Goal
Increase our customers' productivity and profitability through premium design, application, and service using advanced materials.

Our basis for success:
- Excellent product quality and performance
- Technical and customer service
- Cutting-edge material research and development
- Extensive product range
- Lowest cost of ownership

Business Segments
- Electronics Assembly Materials
- Engineered Solders & Alloys
- Metals & Compounds
- Metal Thermal Interface Materials
- Nanotechnology
- Semiconductor Assembly Materials

Contact our engineers today: metchem@indium.com

Learn more: www.indium.com

From One Engineer To Another®

Form No. 97507 (A5) R6