COPPER GLEAM™ 2001 Acid Copper Process

For PWB Metallization Applications

Regional Product Availability

- N.America
- Asia

Description

The COPPER GLEAM™ 2001 Acid Copper Process is a development in acid copper electroplating technology designed to produce high reliability through-hole copper interconnections in standard and advanced printed circuit board designs.
Specifically, the COPPER GLEAM 2001 Acid Copper Process offers uniform, bright, ductile copper deposits over the range of operating conditions required to optimize throwing power, thickness distribution and productivity.
The excellent thickness distribution and quality of deposits that the technology offers makes the COPPER GLEAM 2001 Acid Copper Process particularly suitable for use in the through-hole copper electroplating of high-aspect-ratio boards.
Analytical procedures for all components facilitate the use of statistical techniques for enhanced process control.

Advantages

- Uniform low current density brightness
- Excellent through-hole micro-leveling
- Excellent throwing power and thickness distribution
- Capable of meeting Mil-P-55110-E and BS 9760
- Complete analytical control

Bath Make-Up

Chemicals Required	Metric	(U.S.)
Deionized (D.I.) Water	350 mL/L	(35% v/v)
Electronic-grade Copper Sulfate ($CuSO_4 \cdot 5H_2O$) or	75 g/L	(10 oz./gal.)
Purified Liquid Copper Sulfate [270 g/L (36 oz./gal.) $CuSO_4 \cdot 5H_2O$]	280 mL/L	(28% v/v)
C.P.-grade Concentrated Sulfuric Acid, 50% w/w C.P-grade (37%)*	252 mL/L	(25.2% v/v)
Concentrated HCl	~0.13 mL/L	~(0.013% v/v)
COPPER GLEAM™ 2001 Carrier	10 mL/L	(1.0% v/v)
COPPER GLEAM 2001 Additive	1 mL/L	(0.1% v/v)

*Actual add to be based on analysis.

High Throw Operation (0.5–2.0 A/dm^2; 5–20 A/ft^2)
The following electrolyte, with reduced copper and increased sulfuric acid concentration, is recommended to obtain maximum throwing power and through-hole thickness uniformity for the plating of narrow bore or high aspect ratio boards.

Chemicals Required	Metric	(U.S.)
D.I. Water	330 mL/L	(33% v/v)
Electronic-grade Copper Sulfate ($CuSO_4$•$5H_2O$) or	30 - 50 g/L	(4 - 7 oz./gal.)
Purified Liquid Copper Sulfate [270 g/L (36 oz./gal.) $CuSO_4$•$5H_2O$]	110 - 185 mL/L	(11 – 18.5% v/v)
Sulfur Free Carbon: Powder Norit SX 4 Granular Norit RO 0.8	 6 g/L 9 g/L	 (0.8 oz./gal.) (1.2 oz./gal.)
C.P.-grade Sulfuric Acid, 50% w/w	450 mL/L	~(0.013% v/v)
C.P.-grade (37%) Concentrated HCl	~0.13 mL/L	~(0.013% v/v)
COPPER GLEAM™ 2001 Carrier	10 mL/L	(1.0% v/v)
COPPER GLEAM 2001 Additive	2 mL/L	(0.2% v/v)

Make-Up Procedure

1. Please refer to the appropriate procedures for the correct preparation of the tank, anodes, filters, anode bags and other related items. Do not proceed until tank has been cleaned and leached according to the instructions in the “Equipment Preparation” section.
2. Fill the tank to approximately 1/3 (33%) of the final bath volume with de-ionized water. Add the required amount of copper sulfate liquid and mix well.
3. SLOWLY, with thorough mixing, add the 50% sulfuric acid. It is recommended that dilute forms of sulfuric acid (such as 50%) be used to minimize heat build-up.

   CAUTION! The sulfuric acid disassociation reaction is exothermic. If concentrated acid is used, heat is generated. A dangerous condition can result if the sulfuric acid is not added very slowly with thorough mixing.
4. Turn on the circulation, filtration and solution agitation. Cool solution to 38°C (100°F) or below before proceeding to the next step.
5. Place pre-bagged anodes (see anode preparation guidelines) into tank and fill to final volume with D.I. water.
6. Analyze the solution for copper sulfate and sulfuric acid and adjust as necessary.
7. Circulate the solution through a carbolator containing pre-rinsed, activated carbon at an approximate loading of 0.36–0.6 kg/100 liters (3–5 lbs./100 gal.) of bath. Activated carbon filters may be substituted if a carbolator is not available. Circulate for 4 to 8 hours per carbon charge.
8. Continue to circulate the solution through activated carbon until a hull cell panel plated at 2A for 10 min. exhibits a matte pink deposit across the entire current density range.

9. When carbon polishing is complete, install pre-leached wound filters (previously prepared according to the procedures in this document).
10. Analyze solution for chloride and adjust to 60 ppm.

    Note:

    For 100 liters of bath

    2.2 mL of concentrated hydrochloric acid (37%) = 10 ppm chloride

    For 100 gallons of bath

    8.3 mL of concentrated hydrochloric acid (37%) = 10 ppm chloride
11. Add COPPER GLEAM™ 2001 Carrier.
12. Electrolysis.

Conditioning of COPPER GLEAM 2001 Solutions by electrolysis is required to film the anodes and produce optimum conditions of operation. Pre-electrolyze using clean copper clad laminate cathodes according to the following schedules.

Standard Operation
(1.5–3.0 A/dm^2; 15–30 A/ft^2)

1. Electrolyze solution for 2 hours at 0.5 A/dm^2 (5 A/ft^2).
2. Electrolyze solution for 2 hours at 2 A/dm^2 (20 A/ft^2).
3. Check chloride and adjust to 60 ppm.
4. Add COPPER GLEAM 2001 Additive and mix thoroughly.
5. Preclean new copper clad cathodes.
6. Electrolyze solution for 2 hours at 2 A/dm^2 (20 A/ft^2).
7. Recheck chloride concentration and adjust to 60 ppm.

High Throw Operation
(0.5–2.0 A/dm^2; 5–20 A/ft^2)

1. Electrolyze solution for 2 hours at 0.5 A/dm^2 (5 A/ft^2).
2. Electrolyze solution for 3 hours at 1.5 A/dm^2 (15 A/ft^2).
3. Check chloride and adjust to 60 ppm.
4. Add COPPER GLEAM 2001 Additive and mix thoroughly.
5. Preclean new copper clad cathodes.
6. Electrolyze solution for 3 hours at 1.5 A/dm^2 (15 A/ft^2).
7. Recheck chloride concentration and adjust to 60 ppm.

Deposit Properties

Structure:	Fine grained equiaxed
Density:	8.9 g/cc
Conductivity:	0.59 megamho/cm
Solderability:	Excellent
Elongation:**	20–28%* Foil thickness 2.0 mil (50 micron) tested in accordance with IPC TM 650
Tensile Strength:**	40–50 KPSI (280–350 N/mm)
Hardness:	80–120 VPN
Thermal Shock Resistance:	5 cycles with no cracking [solder float 288°C (550°F) for 10 sec.]

* Elongation range quoted is based on recommended bath maintenance including periodic carbon purification.

** Tested in accordance with IPC-TM-650 foil thickness 2.0 mil (50 micron).

Operating Conditions (Standard Operation) (1.5–3.0 A/dm^2; 15–30 A/ft^2)—Metric		
Parameter	**Range**	**Recommended**
Copper Sulfate	67.5–90.0 g/L	75.0 g/L
Sulfuric Acid	167–185 g/L	175 g/L
Chloride	40–80 ppm	60 ppm
COPPER GLEAM™ 2001 Carrier	5.0–20.0 mL/L	10.0 mL/L
COPPER GLEAM 2001 Additive	0.5–2.5 mL/L	0.5–1.5 mL/L
Temperature	21–27°C	24°C
Cathode Current Density	1.5–3.0 A/dm^2	2.0 A/dm^2
Anode Current Density	0.5–2.0 A/dm^2	1.5 A/dm^2
Deposition Rate 25 microns in 1 hour at 2 A/dm^2		

Operating Conditions (Standard Operation) (1.5–3.0 A/dm^2; 15–30 A/ft^2)—U.S.		
Parameter	**Range**	**Recommended**
Copper Sulfate	67.5–90.0 g/L	75.0 g/L
Sulfuric Acid	167–185 g/L	175 g/L
Chloride	40–80 ppm	60 ppm
COPPER GLEAM™ 2001 Carrier	0.5–2.0% v/v	1.0% v/v
COPPER GLEAM 2001 Additive	0.05–0.25% v/v	0.05–0.15% v/v
Temperature	70–80°F	75°F
Cathode Current Density	15–30 A/ft^2	20 A/ft^2
Anode Current Density	5–20 A/ft^2	15 A/ft^2
Deposition Rate 1 mil in 1 hour at 20 A/ft^2		

Operating Conditions (High Throw Operation) (0.5–2.0 A/dm²; 5–20 A/ft²)—Metric		
Parameter	Range	Recommended
Copper Sulfate	30.0–50.0 g/L	Dependent upon current density requirements
Sulfuric Acid	300–335 g/L	315 g/L
Chloride	40–80 ppm	60 ppm
COPPER GLEAM™ 2001 Carrier	5–20 mL/L	10 mL/L
COPPER GLEAM 2001 Additive	0.5–2.5 mL/L	0.5–1.5 mL/L
Temperature	21–24°C	24°C
Cathode Current Density	0.5–2.0 A/dm²	1.0 A/dm²
Anode Current Density	0.5–2.0 A/dm²	1.5 A/dm²
Deposition Rate 25 microns in 2 hours at 1 A/dm²		

Operating Conditions (High Throw Operation) (0.5–2.0 A/dm²; 5–20 A/ft²)—U.S.		
Parameter	Range	Recommended
Copper Sulfate	30.0–50.0 g/L	Dependent upon current density requirements
Sulfuric Acid	300–335 g/L	315 g/L
Chloride	40–80 ppm	60 ppm
COPPER GLEAM™ 2001 Carrier	0.5–2.0% v/v	1.0% v/v
COPPER GLEAM 2001 Additive	0.05–0.25% v/v	0.05–0.15% v/v
Temperature	70–80°F	75°F
Cathode Current Density	5–20 A/ft²	10 A/ft²
Anode Current Density	5–20 A/ft²	15 A/ft²
Deposition Rate 1 mil in 2 hours at 10 A/ft²		

Process Sequence

The performance of the COPPER GLEAM™ 2001 Process relies upon two main factors:

1. Maintaining the process at optimum operating parameters
2. Limiting or eliminating the introduction of non-compatible chemistries into the process.

The importance of the interrelationship between these two factors cannot be overemphasized. Dow Electronic Materials has developed a line of proven cleaners and etchants that are fully compatible with the COPPER GLEAM 2001 Process. By reducing the number of influences causing potential plating problems, these products permit easier maintenance and faster, more accurate troubleshooting of the entire copper electroplating line. For these reasons, Dow Electronic Materials strongly recommends the following process sequence:

Bath Operation		
Process	**Temperature**	**Time**
RONACLEAN™ PC 454, 590 or 921 LP-200, SE-250 Cleaner	40°C (105°F)	3 min.
Water Rinse	20–30°C (68–86°F)	1 min.
PREPOSIT™ Etch 748 or RONETCH™ PS Etch	32°C (90°F)	2 min.
Water Rinse	27°C (80°F)	1 min.
10% Sulfuric Acid*	27°C (80°F)	1 min.
COPPER GLEAM™ 2001 Process	24°C (75°F)	**
Water Rinse	20–30°C (68–86°F)	1 min.
Water Rinse	20–30°C (68–86°F)	1 min.
10–20% Acid Pre-dip	27°C (80°F)	2 min.
SOLDERON™ or RONASTAN™ Tin or Tin/Lead	27°C (80°F)	**
Water Rinse	20–30°C (68–86°F)	2 min.

***Note:** Lower concentrations are perferred for low-build electroless copper.

****Note:** Time dependent on current density of operation and thickness requirements.

Note: If rinse water temperatures are below 20°C (70°F), rinse times should be increased accordingly.

Bath Control

Process Control

The solution constituents, with the exception of the Carrier and Additive, are controlled by chemical analysis. The Carrier and Additive are controlled by CVS.

General Assessment of Solution Performance by Hull Cell Test

For Hull cell analysis, use a standard 267 ml cell equipped with air agitation, a phosphorized copper anode and a standard 7 x 10 cm (2.75 x 4 in.) polished brass cathode panel. The cathode panel should be cleaned to produce a water break free surface before plating. Plate panel as follows:

Standard Operation
2 amps for 5 min.
High-throw Operation
1 amp for 10 mins.

Deposit appearance should be semi-bright to bright from right edge (low current density area) across to a minimum of 3x the plating current used in the production bath.

COPPER GLEAM™ 2001 Additive
COPPER GLEAM 2001 Additive should be replenished at a rate of 0.1–0.3 mL/amp hour, dependent on method of operation. The suggested Additive replenishment rate listed is based on use of air agitation. The replenishment rate may be significantly lower for tanks using eductor solution agitation.
Note: COPPER GLEAM 2001 Additive contains the active grain refiners responsible for brightening of the deposits as well as sufficient carrier to maintain loss through drag out. If it is desired to replenish additive without adding carrier, use COPPER GLEAM 2001 Additive NC to replenish the additive.
The COPPER GLEAM 2001 Additive can be controlled by CVS. See Dow Electronic Materials Analytical Procedure AP 30000-A for the determination of COPPER GLEAM 2001 Additive by CVS.
Note: COPPER GLEAM 2001 Additive consumption increases with increased temperature of operation and increased anode area, particularly in combination with titanium anode baskets.

COPPER GLEAM 2001 Carrier
COPPER GLEAM 2001 Carrier should only be replenished on recommendation from Dow Electronic Materials or on the basis of CVS dilution titration analysis. See CVS Analytical Procedure AP 30000-C for the determination of COPPER GLEAM 2001 Carrier by CVS.

Recommended Control Schedule		
Analysis of	**Procedure**	**Frequency**
Copper	Volumetric Analysis Atomic Absorption Stectroscopy	Weekly
Sulfuric Acid	Volumetric Analysis	Weekly
Chloride	Specific Ion Electrode Spectrophotometric Volumetric Analysis	Weekly to twice weekly if using titanium baskets
Metallic Contamination (Fe, Ni, Sn)	Atomic Absorption	Weekly
Process Performance	Hull Cell CVS Thermal Shock	Daily Daily Once every shift

Metallic Impurities

The maximum tolerable level of metallic contaminants are listed below:

Fe plus Ni	1,000 ppm
Sn	100 ppm

General Maintenance

1. Filters should be changed every 2–4 weeks.
2. Anode area should be checked and maintained on a regular basis. For titanium basket/anode slugs, this should include a periodic complete removal of the anodes, thorough cleaning of any sludge build-up, replenishment and reconditioning.
3. Anodes bags should be checked frequently for holes or tears. Replace defective anode bags immediately.

Product Data

COPPER GLEAM™ 2001 Additive

Appearance: Clear, colorless to light yellow
pH: ~2
Specific Gravity: ~1.00

COPPER GLEAM 2001 Carrier

Appearance: Clear, pale blue-green liquid
pH: <2
Specific Gravity: ~1.02

Equipment

Tanks:	Semi-hard PVC, polypropylene
Anodes:	Phosphorus deoxidized copper (0.04%–0.08%P); Slabs with titanium hooks or nuggets in titanium baskets
Anode Bags:	Napped polypropylene or Dynel
Anode to Cathode Distance:	15–30 cm (6–12 inches)
Anode Current Density:	0.5–2.0 A/dm^2 (5–20 A/ft^2)
Heaters:	PTFE coated panel heaters or quartz immersion heaters.
Cooling Coils:	May be required depending on climate. Polypropylene, Teflon fluoropolymer or stainless steel construction
Filtration:	1–5 micron polypropylene filter cartridges; Filter continuously at a rate of 5 tank volume turnovers per hour
Power Supply:	4–6 volt rectifier with a maximum of 5% ripple is required; For optimal plating distribution, split rectification is recommended
Solution Agitation:	Air must be supplied by a blower and free of dirt and oil; A dual air sparge offset from each side of cathode center line is recommended Holes should be drilled facing down at a 45° angle from the vertical; The total area of all holes drilled in sparge should be <50% of the cross sectional area of the feed pipe in order to ensure uniform agitation across the cathode surface Do not put air agitation under the anode.
Air Pressure:	0.035 kg/cm for every meter of solution depth (2 psi/ft.)
Air Flow:	0.09–0.18 m^3/minute for every meter of sparger or (1–2 cfm/foot)
Mechanical Agitation:	Through-hole cathode agitation with a stroke length of 1.5 to 3.0” (4 to 8 cm) at a frequency of 7 to 15 cycles per minute; Total movement should be 20 to 60”/min. (50 to 150 cm/min.)
Vibration:	0.5–1.5 in./sec.—continuous

Equipment Preparation

Tanks and ancillary equipment should be cleaned and leached as follows:

a) Clean tank(s) with 30 g/L (40 oz./gal.) trisodium phosphate and 25 mL/L (3.2 fl. oz./gal.) of 50% sodium hyrdoxide 38–50°C (100–120°F) and recirculate for 4–8 hours.

Note: Not for use with insoluble anodes.

1. Rinse tank and system thoroughly with hot water.
2. Leach tank(s) with a 10% sulfuric acid solution and recirculate through complete system. Leave leaching solution in tank for minimum of 8 hours.
3. Rinse with hot water.
4. Rinse with D.I. water.

b) Anodes should be cleaned and deoxidized prior to use as follows:

1. Immerse anodes in a sulfuric acid/hydrogen peroxide solution or an equivalent Microetch (Dow Electronic Materials Pattern Prep 24, for example).
2. Rinse thoroughly.
3. Immerse anodes in a 10% sulfuric acid solution.
4. Rinse thoroughly with D.I. water.
5. When titanium anode baskets are used, care must be taken to ensure that they are completely filled with anode slugs.

c) Anode bags should be cleaned and leached as follows:

1. Wash thoroughly in hot D.I. water.
2. Leach with a 10% sulfuric acid solution for 2 hours.
3. Rinse thoroughly with D.I. water.

d) Wound polypropylene filter cartridges should be leached as follows:

1. Wash thoroughly in hot D.I. water.
2. Leach with a 10% sulfuric acid solution for 2 hours.
3. Rinse thoroughly with D.I. water.

Handling Precautions

Before using this product, or the analytical reagents required for this control, consult the Material Safety Data Sheet (MSDS)/Safety Data Sheet (SDS) for details on material hazards, recommended handling precautions and product storage.

CAUTION! Keep combustible and/or flammable products and their vapors away from heat, sparks, flames and other sources of ignition including static discharge. Processing or operating at temperatures near or above product flashpoint may pose a fire hazard. Use appropriate grounding and bonding techniques to manage static discharge hazards.

CAUTION! Failure to maintain proper volume level when using immersion heaters can expose tank and solution to excessive heat resulting in a possible combustion hazard, particularly when plastic tanks are used.

Storage

Store products in tightly closed original containers at temperatures recommended on the product label.

Disposal Considerations

Dispose in accordance with all local, state (provincial) and federal regulations. Empty containers may contain hazardous residues. This material and its container must be disposed in a safe and legal manner.

It is the user's responsibility to verify that treatment and disposal procedures comply with local, state (provincial) and federal regulations. Contact your Dow Electronic Materials Technical Representative for more information.

Product Stewardship

Dow has a fundamental concern for all who make, distribute, and use its products, and for the environment in which we live. This concern is the basis for our product stewardship philosophy by which we assess the safety, health, and environmental information on our products and then take approp riate steps to protect employee and public health and our environment. The success of our product stewardship program rests with each and every individual involved with Dow products - from the initial concept and research, to manufacture, use, sale, disposal, and recycle of each product.

Customer Notice

Dow strongly encourages its customers to review both their manufacturing processes and their applications of Dow products from the standpoint of human health and environmental quality to ensure that Dow products are not used in ways for which they are not intended or tested. Dow personnel are available to answer your questions and to provide reasonable technical support. Dow product literature, including safety data sheets, should be consulted prior to use of Dow products. Current safety data sheets are available from Dow.

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