

Technical Information

Hull Cell Plating Tests

INTRODUCTION

The **Hull Cell** (U.S. Patent # 2,149,344) is a miniature test cell designed to produce a plated deposit over a range of current densities. The deposit is dependent upon the condition of the plating bath (i.e. concentration of primary components, addition agents and impurities). The **Hull Cell** is a useful tool for varying chemical composition, determining covering power (the lowest current density at which a deposit is produced), measuring average cathode efficiency, average metal distribution or throwing power, and observing the effects of pH, temperature and decomposition products. A clear Lucite **Hull Cell** enables the operator to observe the plating on the back of the test panel to determine relative covering power at very low current densities.

The **Hull Cell** was originally developed by the R. O. Hull Company, which later became the ROHCO Division of McGean-Rohco, and is now part of Atotech. The **Hull Cell** has become an integral part of plating operations everywhere.

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ADVANTAGES

The Hull Cell enables an experienced operator to determine the following facts about a plating solution:

1. **Approximate Bright Current Density Range.** This is accomplished by comparing the bright plated areas on the panel with current densities given in a chart. If the bright or operable range is between 1-1/4" (3.2 cm) and 2-1/2" (6.4 cm) from the left side of the panel, and the total current applied is 3 Amps, the corresponding respective current densities from a Hull Cell ruler or chart lie between 75 Amps/ft² (7.6 Amps/dm²) and 25 Amps/ft² (2.7 amps/dm²). Since these values represent extreme limits, it does not follow that either of these current densities can be used in a plating bath without obtaining a poor deposit. However, some intermediate current density such as 50 Amps/ft² (5.4 Amps/dm²) should work best.
2. **Approximate Concentrations of Primary Constituents** such as zinc metal content, sodium cyanide content, nickel metal content, etc. Generally, the higher the metal content of a bath, the higher (but not necessarily wider) is the operable bright current density range.
3. **Addition Agent Concentration.** Although a few addition agents can be determined by analysis, the Hull Cell test usually provides the only satisfactory means of controlling the addition of these materials, provided they exhibit a visible effect on the deposit.
4. **Metallic or Organic Impurities** in a plating bath affect the appearance of the Hull Cell deposit, and their presence or absence can be established.

TEST METHODS

Before running a Hull Cell plating test, the following steps must be taken:

1. Bring the solution to be tested to its normal operating level in the plating tank.
2. Either stir the bath thoroughly or use a sampling tube extending to the bottom of the tank and go over the tank uniformly from one end to the other.
3. The temperature of the bath sample should be maintained at the proper operating temperature during the test. The best method for testing samples at high temperatures is by using a Model HT Hull Cell, which is equipped with a heating element and thermostat.
4. Use a clean Hull Cell and clean the cathode panel. If more than one type of plating solution is to be tested regularly, one cell should be used exclusively for each type to avoid cross contamination.
5. Hull Cell plating tests do not eliminate the need for occasional chemical analysis. Such analyses should be made before the plating test so that the bath sample can be adjusted to the optimum composition either prior to or during the sequence of Hull Cell tests.

6. Zinc coated steel cathode panels must be stripped of the zinc by immersing them into a 1:1 solution of hydrochloric acid and water, rinsed and then cleaned with a wet, clean cloth or wet paper towel, just before use. Since the Hull Cell is an actual plating tank, improperly prepared panels will not respond satisfactorily in the cell, just as in commercial practice.
7. For duplication of results, plating times in the Hull Cell should be the same as that used in the production tank. Testing times for different solutions may differ and are specified in the section that follows for the different solutions. A conventional timer can be supplied as an accessory to the Hull Cell set.
8. The correct volumes of solution to use is 267 ml for the 267 ml Hull Cell, 534 ml for the 534 ml Hull Cell and 1000 ml for the 1000 ml Hull Cell. A 2-gram addition to 267 ml, 4-gram addition to the 534 ml or 7.5-gram addition to a 1000 ml Hull Cell is equivalent to a 1 oz/gal (7.5 g/l) addition to the plating tank. To test a hot bath sample, the Model HT Hull Cell should be used. NOTE: A Lucite Hull Cell should never be placed on a hot plate.
9. **CAUTION: DO NOT LEAVE THE HEATER ON OVERNIGHT OR UNATTENDED FOR PROLONGED PERIODS OF TIME. EVAPORATION OF THE SOLUTION COULD CAUSE A MELT DOWN OF THE HULL CELL ITSELF -- A POTENTIAL FIRE HAZARD.**
10. The Filtered Output Rectifier Model B-267 or Model B-534 is the preferred current source. A single-phase rectifier without a properly designed filter circuit must not be used.
11. Steel cathodes have a semi-bright, uniform appearance. Cathodes should only be used once and then filed for future reference. They should not be stripped and reused, as this will change the condition of the surface. Experience has shown that a poor or non-uniform steel surface can cause misleading results. Replacement cathodes that duplicate the original zinc plated cathode panels provided with the set may be ordered from Atotech. Polished brass panels are also available for use with copper, nickel and chromium plating solutions.
12. Do not make too many tests on one sample of plating bath. Generally, six panels cannot be made on a single nickel-plating bath sample unless the pH is checked after each second panel. Here the HT 534 cell is desirable because of the high volume-low current ratio.
13. Conversion Factors:

| <u>Multiply</u> | <u>By</u> | <u>To Obtain</u> |
|-----------------|-----------|------------------|
| grams/liter | 0.134 | oz/gal |
| grams/liter | 0.1 | kg/100 liters |
| oz/gal | 6.25 | lbs/100 gallons |
| oz/gal | 7.5 | grams/liter |

SPECIFIC PLATING BATHS

The Hull Cell plating test is best used to determine the effects of varying each type of plating bath used in production. For example, if a bright nickel bath is to be tested, each parameter (e.g. temperature, agitation, nickel, sulfate, chloride, brightening agents and metallic impurities such as copper, lead, zinc, etc.) should be evaluated individually and the effects noted on the deposit. In conducting such tests, it is helpful to make up dilute solutions of the proprietary addition agents so that unit volumes added to the Hull Cell volume are equivalent to simple additions to the plating bath.

For solid chemicals, the addition of 2 grams to 267 ml, 4 grams to 534 ml, and 7.5 grams to 1000 ml Hull Cells is equivalent to 1 oz/gal (7.5 g/l) to the plating tank. Liquid chemicals such as brighteners or addition agents are normally specified or controlled based on percent (%) by vol. (ml/l) or fl.oz/gal.

When the additive is a liquid, a solution diluted with water is recommended for Hull Cell additions and testing. The material should be diluted to a 20% by volume solution. The addition of one (1.0) ml of a 20% by volume solution to a 267 ml Hull Cell is equivalent to an addition of 0.075% by vol. (0.75 ml/l), 0.1 fl. oz./gal, of the additive to the plating tank.

The value of the Hull Cell test depends upon the experience that the operator has gained in using it. The following generalizations serve as a guide as to what can be expected when testing different types of baths.

BRIGHT NICKEL

Bright nickel baths are probably the most difficult to control when trying to maintain deposit luster. Some brightening agents can be determined by analysis, in which case, Hull Cell tests serve as a check on the operating condition of the bath. Other brightening agents cannot be checked analytically. In this case, the Hull Cell becomes a useful tool for controlling concentration. Testing of bright nickel solutions requires a uniform quality steel cathode panel in order to check the ability of the bath to build brightness.

Before running a Hull Cell test, the bath should be analyzed for nickel, sulfate, chloride, boric acid and pH.

Generally, the current used for the 267 ml or 534 ml Hull Cell is 3 amperes and for the 1,000 ml unit, 5 amperes. For low current density problems, a one-ampere panel is recommended. The plating time should be 5 minutes.

The plating tests should be run on the bath as sampled and then after the salts and pH have been adjusted. Additional Hull Cell tests should then be made to determine the effects of impurities and brightener adjustments.

Solution agitation, if used, is provided by regular movement of a glass-stirring rod parallel to the face of the cathode. This can be done either manually or mechanically using the Atotech Hull Cell Agitator. Air agitation can also be provided by use of the Model HT Hull Cell with a built in air line. Hull Cell tests may not always indicate the slight pitting tendencies of baths.

The temperature should be maintained at the same level as that of the production bath. The Model HT Hull Cell should be used for testing heated baths.

The maximum number of tests that can be run on one sample is three (five in the 534 ml Hull Cell), unless the pH is checked and adjusted.

Interpretation - Bright Nickel

Optimum Composition -- Brilliant, uniform, non-pitted deposits from 5-125 Amps/ft² (0.5-12.5 Amp/dm²).

High pH -- Yellow tinge to deposit, may be irregular and brittle at high current densities.

Low pH -- Gassing at cathode, smoky-blue or brittle deposit.

Low Nickel -- Burned high current densities area.

Low Boric Acid -- Checked deposit at high current density, nickel hydroxide precipitated on cathode panel or a tendency toward pitting.

Low Chloride -- Gassing at the anode, low anode efficiency, higher than normal voltage.

High Anti-pit Agent-- Smoky, irregular deposit.

Low Anti-pit Agent-- Pitting of the deposit, particularly noticeable at high current densities. To check, bend the lower 1/4" (6 cm) edge of the panel to be horizontal and repeat the test. Examine the horizontal edge for pits if boric acid concentration is normal.

High "Primary" or "Carrier" Brightener -- Usually there is no upper limit to this brightener content, except solubility.

Low "Primary" or "Carrier" Brightener -- Dull, non-uniform brittle deposit, usually at higher current densities, poor chrome receptivity.

High "Booster" or "Secondary" Brightener -- Brittle plate, usually poor coverage or black deposit at low current densities, poor chrome receptivity.

Low "Secondary" Brightener -- Semi-bright deposit exhibiting poor leveling.

Organic Contamination -- Brittle, hazy deposit usually over the entire plating range, peeling at high current density, dull low current density range.

Dissolved Air or Oil in Bath -- Pits or orange-peel deposit; splotches that represent thin areas.

High Bath Temperature -- A dull or hazy deposit.

Low Bath Temperature -- A dull or burned deposit at high current density.

Impurities

Shown by dark deposits at low current densities.

Copper or Zinc -- See "Electrolytic Purification".

Chromium -- Black at high current densities, skip plating in low current densities.

Iron -- Slight burning at high current densities, roughness.

ROCHELLE COPPER CYANIDE

Under optimum conditions, the Rochelle Copper Cyanide bath produces deposits that are smooth and semi-bright in appearance. The bath serves two purposes -- one, to produce a flash coating in which variations in bath composition may be tolerated; and second, to build thicknesses up to 0.4 mils (10 microns), where bath composition is more critical.

A current of two amperes for 5 minutes should be used at a temperature that corresponds to that of the plating solution. Steel cathodes are recommended. The anode should be made of pure copper; phosphorized copper should not be used. The best means of heating solutions is in a Model HT Hull Cell.

Interpretation

Optimum Composition for a Still Solution -- Smooth, fairly uniform deposit from 5-45 Amps/ft² (0.5-4.5 Amp/dm²).

Optimum Composition for an Agitated Solution -- Semi-bright from 3-60 Amps/ft² (0.3-6.0 Amp/dm²).

Low Overall Concentration -- Low cathode efficiency, gassing, semi-bright but thin deposit, depending upon actual concentration.

High Overall Concentration -- Same as that for "Optimum Composition".

Low Free Cyanide -- A dull deposit that is not as uniform and smooth as that from the "Optimum Composition". The solution is slightly blue in color.

Slightly High Free Cyanide -- Somewhat lower efficiency than that from the "Optimum Composition", but a somewhat brighter deposit.

Very High Free Cyanide > 2 oz/gal (15 g/l) -- Low efficiency; burnt deposit at high current density.

Low Rochelle Salts -- Dull deposit similar to that from low free cyanide, but solution is not blue-colored.

High Rochelle Salts - Better, brighter, more uniform deposit appearance than from optimum composition, possibly slightly lower cathode efficiency.

Low Carbonate -- No effect on cathode; anode polarization in the plating tank may be noticed.

High Carbonate > 8 oz/gal (60 g/l) -- Appreciable dulling of deposit

Low pH (e.g. 11.0) -- Slightly irregular deposits

High pH (> 13.5) -- Poor anode corrosion, rough deposit, inclusion of particles in deposit

Impurities - Rochelle Copper Cyanide

Lead -- May brighten slightly, also may cause dark deposits; concentration as a brightener is very critical.

Iron (large amount) -- Reduced cathode efficiency; thin deposit.

Zinc -- Brassy, irregular deposit.

Chromium -- Poor coverage, no deposit at low current density end of cathode. The condition may be corrected by small additions [e.g. 0.01 oz/gal (0.075 g/l)] of sodium hydrosulfite powder added to bath (0.02 grams/267 ml in Hull Cell). Additions may be made in these amounts until the problem is corrected. Excessive additions of sodium hydrosulfite should be avoided to prevent rough deposits. Commercial chrome control agents may also be used, as per supplier's recommendation.

HIGH SPEED CYANIDE COPPER

The High Speed Cyanide Copper bath readily lends itself to plating test control, because variations in bath composition are immediately reflected in variations in plating ranges. Moderate differences in copper cyanide content from the amount specified in the bath composition show no effect in the Hull Cell, provided the other components are within the proper range of concentration.

A total current of two (2) amperes for five minutes should be used with the solution at the operating temperature. The Model HT Hull Cell provides the best method for maintaining temperature during tests.

Polished brass panels are the preferred cathode, but steel panels may be used if flash plated with copper from a low efficiency cyanide copper strike or Rochelle copper before use. A pure copper anode should be used. Phosphorized copper should not be used.

To reveal the bright plate range, the solution in front of the cathode must be agitated either by slow movement of a stirring rod while plating or by using an Atotech Hull Cell agitator.

Interpretation

Optimum Composition -- Bright range from 5-60 Amps/ft² (0.5-6.0 Amp/dm²) Current densities of 5-10 Amps/ft² (0.5-1.0 Amps/dm²) show a dull, cherry-red deposit.

High Free Cyanide -- Low bright range with burnt, dark reddish deposits in high current density areas

Low Free Cyanide -- High bright range with narrower burned range than normal at the higher current density areas.

High Wetting Agent -- No effect seen in a Hull Cell; deposit may be difficult to clean before nickel or to buff.

Low Wetting Agent -- Lack of uniformity at medium and low current density range as well as a tendency towards pitted deposits at high current densities.

High Caustic Soda or Caustic Potash -- Overall dulling effect.

Low Caustic Soda or Caustic Potash -- Narrow and low bright range.

High Carbonate -- Deposits are dull and slightly grainy at high current densities.

Impurities - High Speed Cyanide Copper

Lead (> 0.01 g/l) -- Narrow, limited-bright range at high current density end, dark smutty deposits at normal current densities, lead film on the anode.

Zinc (> 1 g/l) -- Bronze to brass appearance at high current densities.

Chromium -- Lack of coverage in lower current densities. (See "Impurities" section of Rochelle Copper)

Organic Contamination -- Narrow bright range at high current densities and a tendency toward mottled and non-uniform deposits in the medium current density range

BRIGHT ACID COPPER

The Hull Cell is an excellent tool for bath control, additive balance, preventive maintenance, and troubleshooting of bright acid copper solutions.

The current normally used is two amperes, 10 minutes, or, for investigations of low current density conditions, one ampere, 10 minutes. A bagged phosphorized copper anode should be used. Polished brass cathode panels are used. Since leveling is a major function of this type of process, a "scratched panel" is often employed. A controlled groove or scratch pattern band should be made across the 3-15/16" (10 cm.) dimension of the panel using steel wool or crocus cloth. The width of this band is normally 1/2-3/4" (1.3-1.9 cm) wide and is made on the bottom most part of the panel. This procedure is performed before cleaning the panel for subsequent plating tests. Air agitation is recommended for bright acid copper evaluations. The temperature of the bath should be controlled within the vendor's recommended range for valid interpretation and correlation of the Hull Cell panels with the production bath.

Interpretation

Optimum Composition -- Full bright panel. If a scratch pattern panel is used, all but the low current density end of the scratch band will have disappeared (leveling).

Low Sulfuric Acid -- Dullness in the low current density area of the panel, lower solution conductivity.

High Sulfuric Acid -- Decreased cathode efficiency, anode polarization and depletion of copper in solution.

Low Chloride -- Dull low current density deposit, decrease in efficiency and lower solution conductivity.

High Chloride -- Loss of leveling, dull to hazy low current density deposits, anode polarization.

Copper Content -- A variation $\pm 25\%$ will show little or no change. Low copper content will cause reduced deposition rates. High copper content will cause a decrease in leveling.

Brighteners -- Low brighteners will cause low current density dullness, HCD burn or striations and hazy deposit throughout the total current density range. Leveling will decrease and brilliance, in general, will be lacking. High brighteners can cause a loss of efficiency and produce dullness in the low current density areas of the panel. Check supplier's recommendations for interpretation and balancing of brightener additives.

Impurities -- Nickel, antimony, arsenic and silicates can cause rough uneven and poor plate distribution. Iron, in addition, can cause reduced cathode efficiency.

Chromium -- Blotchy deposits, haze and blistering.

Organics - Acid copper baths are most sensitive to contamination from foreign organics. They can cause pitting, brittle deposits and hazes because of codeposition of the organic compounds.

BRIGHT CYANIDE ZINC - CONVENTIONAL AND MID-BATHS

Hull Cell tests are valuable for controlling Bright Cyanide Zinc baths since, with experience, the bath balance may be determined as well as addition agent levels and impurities. A total current of one ampere for barrel and three amperes for rack solutions should be used on steel cathodes, with a plating time of five minutes. A zinc anode should be used. These instructions apply to baths containing Atotech zinc brighteners and other proprietary cyanide zinc processes.

Interpretation

Optimum Composition - Uniform, bright deposit.

High Ratio of NaCN to Zinc -- Low bright current density range, low cathode efficiency, as shown by excessive gas evolution.

Low Ratio of NaCN to Zinc Metal -- High bright current density range, gray low current density range.

High Caustic Soda -- Similar to low NaCN/zinc ratio; crystalline appearance of deposit.

Low Caustic Soda -- Similar to high NaCN/zinc ratio; excessive anode polarization.

High Zinc Content > 6.5 oz./gal (48.75 g/l) -- High bright current density range, dullness in low current density areas

Low Zinc Content < 4.0 oz./gal (30.0 g/l) - In conventional baths, poor cathode efficiency, excessive gassing.

Brightening Agent - Controlled best by observation of production work from the tank. Low brightener is usually seen as a dull deposit at low current density.

Low Zinc Purifier - Overall dullness or burning in high current density area.

Impurities - Bright Cyanide Zinc - Conventional and Mid-Baths

Shown by blistered or dark deposits that stain readily

Copper -- Darkens the deposit in 0.25% by vol. nitric acid dip.

Lead -- Dulls the deposit, but does not darken it in 0.25% by vol. nitric acid dip.

Cadmium -- In small amounts, does not dull the deposit directly, but darkens it in a 0.25% by vol. nitric acid dip.

BRIGHT ALKALINE NON-CYANIDE ZINC

Hull Cell tests for control of Bright Alkaline Zinc baths are a valuable tool for control of bath balance, addition agent levels and impurities. Steel cathodes are used with a zinc anode. It is very difficult to recognize changes in the metal content in this type process by Hull Cell tests, therefore, it is necessary to have the analysis of the zinc metal and caustic content for interpretation of the Hull Cell panels. 0.5-1.0 ampere panels are run in barrel baths and 2 or 3 amp. panels are plated from rack baths. These instructions apply for all proprietary processes, not just Atotech systems. Plating time is 10 minutes for 0.5 ampere panels and 10 minutes for other ampere settings. NOTE: Plating times and currents used for Hull Cell tests can be varied depending on conditions being tested.

Interpretation

Optimum Composition -- Uniform, bright surface.

High Zinc Content -- High efficiency and brightness at the high current density end of the panel and a resulting decrease in efficiency, throw and brightness at the low current density end of the panel.

Low Zinc Content - Opposite of the conditions observed with high metal; low current density end of the panel is more uniformly brighter; the high current density end of the panel exhibits a decrease in efficiency and brightness.

NOTE: In alkaline non-cyanide zinc baths, increasing the zinc metal content is similar to reducing the ratio in zinc cyanide systems. Likewise, reducing the zinc metal content is similar to raising the zinc-cyanide ratio.

Low Caustic Content -- Excessive anode polarization (not to be confused with the normal discoloration of the zinc anode characteristic of this type of process). More voltage is required to obtain the testing amperage initially, and during the five-minute plating time, several adjustment increases will be required to maintain the current. Bath efficiency is poor. Metal content may decrease.

High Caustic Content -- Not detectable during the short time of running a Hull Cell panel test. The production bath will show an unusual increase in metal content.

Brightening Agent(s) -- Best controlled by observing the production parts. Follow vendor's recommended addition rates. Low brightener is usually seen as an overall dull deposit and burning at the high current density end of the panel. High brightener content is observed as an overly brilliant deposit, sometimes accompanied by flaking of the deposit.

Impurities - Bright Alkaline Non-Cyanide Zinc

Organic Contamination -- Blistered dull or dark deposits that stain readily.

Iron -- Dull deposits in low current density area that turn blue-black after post dip.

Copper -- Plate deposit darkens in low current density after post dip in 0.25% by vol. nitric acid.

Lead -- Dull deposit that neither darkens nor brightens with a post dip in 0.25% by vol. nitric acid.

Cadmium -- Darkening of the deposits in 0.25% by vol. nitric acid post dip and a cloudy band in the mid-current density area.

Chromium -- Blistering of the deposit in the low current density area. If severe enough, skip plate in this same area.

BRIGHT ACID CHLORIDE ZINC

The Hull Cell is a useful tool for controlling Bright Acid Chloride Zinc baths. Because of the high efficiency of this type of process, variations from recommended chemistry are often masked. It is, therefore, important to adjust the bath chemistry to within the recommended operating range before beginning Hull Cell testing.

pH, temperature and agitation of the solution are important for the same reason when attempting to determine possible impurity problems. For barrel operations, one ampere panels are run. For rack operations 2-3 ampere panels are recommended. In both cases, plating time is 5 minutes. Steel cathode panels are recommended. If an air agitated Hull Cell is not available, vigorous paddle stirring is necessary to reproduce conditions encountered in production air agitated systems.

Interpretation

Optimum Composition -- Full bright panel with less than 1/4" (6 mm) of burning on the high current density edge of the panel.

Low Zinc Content -- Burning along the high current density edge of the panel, extreme roughness in this same area.

High Zinc Content -- Poor throwing power in the low current density end of the panel.

Low Chloride Content -- Low current density efficiency is poor.

High Chloride Content - Not detectable.

Brightening Agents -- Follow the vendor's recommended addition rates.

Low Brightener -- Measure the width of the roughness or burn from the high current density edge of the panel on an "As Is" panel. An addition of brightener that gives a measurable reduction in the rough or burned area is an indication of lower than optimum brightener level.

High Brightener Level -- Extreme bright appearance of the mid-to-high current density areas. In extreme cases, the low current density areas may show a skip plate and high current density blistering.

Impurities - Bright Acid Chloride Zinc

Iron -- Yellowing deposit; blue to black staining in the high current density end of the panel after post dipping in either dilute 0.25% by vol. nitric acid or clear chromate solution.

Copper -- Brown to black stain in the low current density end of the panel when post dipped in either 0.25% by vol. nitric acid or clear chromate solution.

Cadmium -- Overall dullness, black stain in the low current density areas of the panel after 0.25% by vol. nitric acid or clear chromate post dip.

Lead -- Skip plate in the low current density area of the panel.

Chromium -- Overall dullness, first apparent in the low current density areas. Increasing amounts of chromium contamination result in skip plate in the low current density areas and blistering in the high current density areas.

BRIGHT CYANIDE CADMIUM

Bright Cyanide Cadmium baths are highly sensitive to brightening agents and Hull Cell tests provide the best positive evidence of the condition of the plating bath as well as pointing the way in which the bath may be modified to give the best results. The details given below apply to Atotech's ROHCO 20 XL cadmium baths, but the same principles may be applied to the other bright baths.

Cadmium anodes and steel cathodes having a good finish should be used. The bath sample should be between 75-85° F (24-29° C). A total current of one ampere for five minutes for barrel solutions and three amperes for five minutes for rack solutions is used.

The use of the Hull Cell is the simplest and most direct means for determining how much ROHCO 20 XL to add to bath. First, an "As Is" test panel should be plated in a sample of the bath. Then, the sample is adjusted to the proper cadmium and cyanide concentrations. Incremental additions of 0.2 fl.oz/gal (2 ml of 20% vol.) of ROHCO 20XL are made to the Hull Cell to obtain the best bright range or optimum results.

Interpretation

Optimum Composition -- Bright plate from 3-60 Amp/ ft² (0.3-6.0 Amp/dm²) with new 20XL baths, up to 120 Amps/ft² (12.0 Amps/dm²) with used baths.

High Cadmium > 3.5 oz/gal (26.25 g/l) -- Bright high current density range, dull low current density range.

Low Cadmium < 2.0 oz/gal (15.0 g/l) -- Bright low current density range, low cathode efficiency, burning in high current density area.

High Cyanide > 20 oz/gal (150 g/l) with 3.5 oz./gal (26.25 g/l) cadmium or above 17 oz./gal (127.5 g/l) with 2.0 oz/gal (15 g/l) cadmium -- low cathode efficiency, bright range is shifted toward low current density end of panel.

Low Cyanide < 13 oz/gal (97.5 g/l) -- Narrow bright current density range.

High Caustic Soda > 3.5 oz/gal (26.26 g/l) -- Narrows bright current density range, burn or dull HCD.

Low Caustic Soda - Excessive anode polarization; poor conductivity.

High Carbonate > 6 oz/gal (45 g/l) - Dull deposit at high current densities.

Low Carbonate < 2 oz/gal (15 g/l) - Slightly duller deposit than normal.

Excessive Brightener - Dull, off-color, streaked deposit.

Low Brightener - Decreased brightness, especially at high current densities.

Impurities - Bright Cyanide Cadmium

Lead – Slate-colored deposits, narrower bright current density range than normal.

Tin - Dull streaks above 25 Amps/ ft² (2.5 Amp/ dm²)

Chromium - Blisters, skip plate under 25 Amps/ ft² (2.5 Amp/ dm²). See "Impurities" section of Rochelle Copper.

BRASS PLATING BATHS

Hull Cell plating tests of Brass Plating baths provide a very interesting method for learning the fundamental principles underlying the operation of this complex plating system. Some of the reasons for the unusual, but predictable, behavior of brass are as follows:

1. Zinc is plated from the divalent state, while copper is plated from monovalent state.
2. Zinc can exist as complexes of sodium-zinc cyanide or sodium zincate (both present in brass), whereas copper can exist in the form of one or more complexes only with sodium cyanide, dependent upon temperature.
3. Changes in pH change the ratio of copper to zinc deposited, but two ranges are usable.

A description is given for a conventional type brass solution, but the same principles apply to other types of brass baths. For brass plating, a steel panel is used at a total current of one ampere for five minutes. A brass anode should be used. The temperature of the plating bath should be that intended for practical operation, which is usually about 95° F (35° C). When plating flash brass over bright nickel, the test plate time may be shortened.

If the pH is to be measured, the most accurate method is by meter, although pH papers may be used. A satisfactory bath composition produces a bright yellow or greenish yellow deposit from 1-40 Amps/ ft² (0.1-4.0 Amp/ dm²) on the Hull Cell panel.

In the absence of chemical analysis and pH measurement, the simplest method of bath control is to observe the deposit color. If the deposit is the desired yellow or yellow-green color, the composition is approximately 70% to 80% copper, the balance being zinc. A pink or reddish color results from either too high or too low of a proportion of zinc in the deposit.

The first point to determine in correcting a brass bath is whether the zinc content of the deposit is too high or too low. The procedure for this is as follows:

1. Plate an "As Is" test panel, noting color and plating range. If the color is good, but the width of the plating range is narrow, the proportion of constituents is about right. The range can usually be widened by addition of both zinc and copper cyanides with sodium cyanide.
2. If the panel is not a uniform yellow or yellow-green color, take two portions of the bath, add 1.0 oz/gal (7.5 g/l) of sodium bicarbonate to one portion and 0.5 oz/gal (3.75 g/l) of caustic soda to the other. In the first case, the pH is lowered and hence the zinc content of deposit is decreased. The reverse is true of the second portion. This procedure should be repeated in the same portions but with double the respective additions, noting which addition improves the deposit color. High zinc in the deposit produces a characteristic orange-brown powdery deposit at low current densities.

If the bicarbonate addition improves the deposit, the bath can be corrected by any of the following additions to increase the ratio of copper to zinc in the deposit:

1. Adding bicarbonate to lower pH, or
2. Adding copper cyanide, or
3. Adding sodium cyanide to raise the free cyanide content.

If the caustic soda addition improves the deposit, the bath can be corrected by any of the following additions to decrease the ratio of copper to zinc in the deposit:

1. Adding caustic soda to raise pH, or
2. Adding zinc cyanide, or
3. Adding copper cyanide to decrease the free cyanide content.

The zinc content of the deposit can be reduced by (1) decreasing zinc cyanide adds in the bath; (2) lowering the pH of the bath; (3) increasing free cyanide of the bath; and to a lesser degree; (4) raising the temperature; (5) raising the cathode current density; or (6) increasing deposit thickness to about 0.13 mils (3.2 micron). The reverse of these increases the zinc content of the deposit.

The addition of either copper cyanide or zinc cyanide tends to lower the bath pH, whereas sodium cyanide addition tends to raise the bath pH and consequently the pH should be measured and controlled. The best pH value depends chiefly upon the metal cyanide ratio in the bath. For control purposes the following table may be used as a guide.

| <u>Ratio of CuCN/ZnCN</u> | <u>Optimum pH (Electrometric)</u> | <u>Color</u> |
|---------------------------|-----------------------------------|--------------|
| 3/2 for Rubber Bonding | 10.3 (range 10.1-10.5) | Lemon-yellow |
| 3/1 | 12.0 (range 11.5-12.5) | Gold-yellow |

A pH range of 10.5 to 11.5 is not usually used because of the tendency toward streaky, irregular deposits.

Ammonium hydroxide nearly always improves color or deposit unless the bath composition and pH are near ideal. Sodium carbonate should be present, and new baths should have 3-5 oz/gal (22.5-37.5 g/l) included in the formulation.

In general, the above procedure will restore almost any brass bath to operation, even without chemical analysis, since acceptable deposits are obtainable over a wide range of bath compositions. It is very important, however, that only one component is varied in any one plating test, since the multiple functions of some of the ingredients frequently tend to confuse the apparent trend. Thus, adding sodium cyanide tends to raise the pH, which should promote zinc deposition, but this effect is more than counteracted by the decreased cathode efficiency of zinc, so that usually a lower percentage zinc is deposited.

Impurities are rarely encountered. Lead tends to produce a dark, dull deposit. Arsenic (sometimes suggested as a brightener) tends to produce white deposits.

Experience in making such tests will clarify the terms "pink/white" etc. that apply to commercial deposits. By following the above diagnostic plan for brass plating solutions, it is possible to match any required deposit color.

CHROMIUM PLATING BATHS

The Hull Cell affords a rapid, simple and positive method for determining and correcting the chromic acid to sulfate ratio in chromium plating baths. The procedure should be followed carefully, as described below. In conjunction with chromium tests run in the 267 ml porcelain Hull Cell, a Lucite Duplicell is available, in which two panels may be simultaneously plated with a uniform nickel deposit.

Method for Sulfate Ratio

Reagents Required:

0.94 N Sulfuric acid (26.5 ml of 66° Bé Sulfuric acid/liter of deionized water)

Barium Carbonate

Procedure:

1. Using the regular nickel bath, plate two steel cathodes simultaneously in the Lucite Duplicel, so that the cathode panels are adjacent to the long sides, with a standard Hull Cell nickel anode suspended between and attached to a copper rod. Plate for three minutes with nickel using a current of 2-5 amperes. Bright nickel solutions give the widest plating range in chrome. A gallon of known good nickel solution should be stored in a closed bottle exclusively for this use.
2. For control of hard chrome baths, the procedure is the same as for decorative chrome, with nickel plated cathodes and with the chrome bath at the same operating temperature as used in production.
3. Rinse one of the nickel plated panels, transfer to the chromium bath in a 267 ml Hull Cell and immediately turn the current on. Plating should be for 4 minutes at 5 amperes. The bath should be maintained at the temperature of operation. The second nickel plated panel may be left in the nickel solution but not in water for a second test, if necessary. NOTE: Do not use a single phase rectifier without filtered output. Use Rectifier Models B-267 or B-535 as a power source.
4. If the chromic acid to sulfate ratio is optimum and the bath is normal in trivalent chromium, the panel will be covered with chromium to within 3/4 to 1" (75-80 mm) of the low current density end of the panel and will show little or no iridescence on the unplated area.

5. If rainbows or brown oxide are present on the unplated nickel, the sulfate level is low. If the chrome deposit is spotty, the sulfate is very low. Add 1 ml of 0.94 N sulfuric acid solution to the 267 ml Hull Cell or 3.75 ml to the 1,000 ml Hull Cell. Repeat in these increments until the optimum plating range is obtained. With a little experience, the proper addition can be made with one or two tests. Each 1-ml/267 ml or 3.75 ml/1,000 ml Hull Cell addition is equivalent to 34.5 ml of 66° Bé sulfuric acid/100 gallons (9.1 ml of 66° Bé sulfuric acid/100 liters) of bath. These same additions are also equal to 0.02 oz/gallon by weight of 66° Bé sulfuric acid.
6. If the plating range is narrow, but no iridescence is noted, the sulfate content is too high for the chromic acid concentration. Add 0.13 grams per 267 ml (0.485 g/l) of barium carbonate and stir for a few minutes. Each such addition is equivalent to 6.5 ounces of barium carbonate/100 gallons (48.75 grams of barium carbonate/100 liters) of chrome bath.

Notes on the Sulfate Ratio Method

1. The above test is based on the assumption that the chromic acid content is correct. If a hydrometer test or analysis shows it to be low, chromic acid should be added to the tank before testing the Hull Cell.
2. It is important that a representative sample of the bath, taken either after thorough stirring or with a sampling tube, be used for testing,
3. If three or more additions of barium carbonate are required, be sure that the solution sample in the Hull Cell is thoroughly stirred to ensure complete reaction.
4. If gassing at the cathode is intermittent or not steady, the sulfate content is very high and several additions of barium carbonate may be required for the first correction.
5. Some installations require a higher than normal sulfate content to avoid white streaks that result from rainbows being subsequently plated. In this case, adjust the sulfate slightly high to the point at which no rainbow is observed on the panel even if the plating range is somewhat narrow.
6. The Hull Cell test method will adjust to the best operating chromium deposit, but other factors such as poor rinsing or passive nickel will not show a normal range of chromium plating in production and such factors cannot be duplicated in the Hull Cell.

ALKALINE TIN

The Alkaline Stannate Tin bath lends itself quite well to control by plating tests. It must be operated with considerable care to avoid certain conditions that are usually corrected without much difficulty.

For plating tests, a tin anode and a steel cathode are used at a total current of 2 amperes for 5-10 minutes at 175° F (79° C) or a temperature recommended by the supplier. It is desirable to heat the tin-plating bath to about 190° F (83° C) before putting it in the Hull Cell. The solution sample should be light yellow or straw colored. If it is very dark in color, stannous tin is probably present and should be oxidized with a small amount of hydrogen peroxide.

Interpretation - Alkaline Stannate Tin

Optimum Composition -- Smooth white deposits from 0.2-5.0 Amp/dm² (2-50 Amps/ft²). Moderate variations in sodium stannate content are not perceptible on the Hull Cell cathode.

High Caustic Soda -- Spongy deposits.

Low Caustic Soda Content -- Poor conductivity; anodes do not form a yellow film.

Stannous Tin -- Dark, rough deposits.

Low Tin Content -- Very low cathode efficiency.

High Tin Content -- No noticeable effect on the cathode.

High or Low Sodium Acetate -- Little effect on cathode, except possibly slightly smoother cathode.

It is important that the anodes either be continuously filmed or that they have a yellow-green appearance. Under such conditions, tin dissolves as stannic (Sn⁺⁴) whereas, if not "filmed," the objectionable stannous tin (Sn⁺²) is formed.

BRIGHT SULFURIC ACID TIN

The Hull Cell is a valuable tool for control, preventive maintenance, and troubleshooting of Bright Sulfuric Acid Tin baths. Generally, a one-ampere panel is used for barrel baths; a two-ampere panel for rack baths; and a 3-5 ampere panel for high-speed strip and wire plating baths. The plating time is 5 minutes. The bath analysis should be performed prior to Hull Cell testing and the bath chemistry adjusted to vendor recommendations. Steel cathode panels are used for routine investigation. Polished brass panels will facilitate identification of problems related to pitting.

Interpretation

Optimum Composition - A two-ampere panel will produce a smooth, white, bright deposit over the entire panel except for the extreme low current density end of the panel. This area will normally be less bright to dull gray.

High Tin Content - Dull low current density areas, poor throw. Anode polarization rapidly forms and a spongy black film develops. The bath appears to need more brightener.

Low Tin Content - Excessive gassing in the mid-to-high current density areas; formation of a white precipitate in the bottom of the Hull Cell (Sn⁺⁴); loss of efficiency, pitting.

High Acid - Anodes polarize and a spongy film develops on the anode. This is similar to the problem of high metal.

Low Acid - Dullness in the low current density area, poor throwing power. Anodes remain full bright; in extreme cases the anode will appear badly eroded and tin fines are visible in the Hull Cell.

Brighteners - Follow vendor recommendation as to the addition rate.

High Brighteners - Excessive foaming, yellowish cast to the deposit; panel takes on a yellow hue upon standing.

Low Brighteners - General dullness throughout the entire current density range; dull to skip plate in the low current density area of the panel; dull high current density area deposits.

Impurities - Bright Sulfuric Acid Tin Baths

Chloride - Dullness in the low current density area. When contamination level is higher, the high current density area will also be dull.

MISCELLANEOUS SYSTEMS

Numerous other plating processes (e.g. lead, black nickel, chromium, gold, platinum, silver, indium and alloy systems) lend themselves to control using a Hull Cell test. Information on details of running and interpreting Hull Cell tests may be obtained from either the suppliers of these processes or determined by the operator.

In addition to solution control, the Hull Cell may be used to determine "covering power" or the lowest current density at which a deposit is produced. This application is similar to the "cavity" scale, but the Hull Cell offers the advantages of simplicity and numerical measurement of covering power. For this purpose, it is usually convenient to plate for a given length of time; e.g., one minute, at a total cathode current of only 0.2 amperes. This gives a current density range on the panel of about 10-0.1 Amps/ft² (1.0-0.01 Amps/dm²) and is an accurate visual indicator of the minimum covering current density, as well as illustrating the effect of certain addition agents in either improving or decreasing covering power. Important factors in such investigations are the kind of base metal used and its preparation, both of which are related to the hydrogen over-voltage and deposition potential of each metal. An example of this is the influence of surface roughness upon covering power. In general, an etched or otherwise roughened base metal will exhibit different covering power than a similar polished surface. It is, therefore, essential that care be taken in selecting a uniform treatment of the base metal when determining covering power at low current densities.

ELECTROLYTIC PURIFICATION OF PLATING BATHS

It is frequently necessary to electrolyze plating solutions to remove metallic impurities. This can be accomplished in the Hull Cell by electrolyzing a bath sample at a low current density with the anode and cathode parallel; i.e., the cathode panel adjacent to the longest side of the Hull Cell, with the anode opposite. Agitation may be used, if desired. The amount of electrolysis required to give a good test plate in the regular manner can then be calculated for the plating tank.

As an example, 5 Amps/ft² (0.5 Amps/dm²) in the tank:

$$\frac{(3-15/16" \times 2" \times 5 \text{ Amps/ft}^2)}{(144 \text{ in}^2/\text{ft}^2)} = 0.27 \text{ amperes in the Hull Cell}$$

If a 20 minutes electrolysis period removes the impurity satisfactorily, the total electrolysis is 20 x 0.27 = 5.4 ampere-minutes. Therefore, since 3,785 ml equals one gallon, 5.4 ampere-minutes for 267 ml =

$$\frac{3,785 \times 5.4}{267 \times 60} = 1.27 \text{ ampere-hours per gallon (0.33 ampere-hours per liter) of plating bath}$$

PROPRIETARY PROCESSES

When using the Hull Cell to control proprietary plating baths, it is advisable to contact the supplier of the process for their recommendations. These recommendations may involve a change in the current or time of the Hull Cell test in order to better illustrate the variables to be controlled. Some processes also use special addition agents that have a pronounced effect on the appearance of a Hull Cell panel.

TELEPHONE NUMBERS

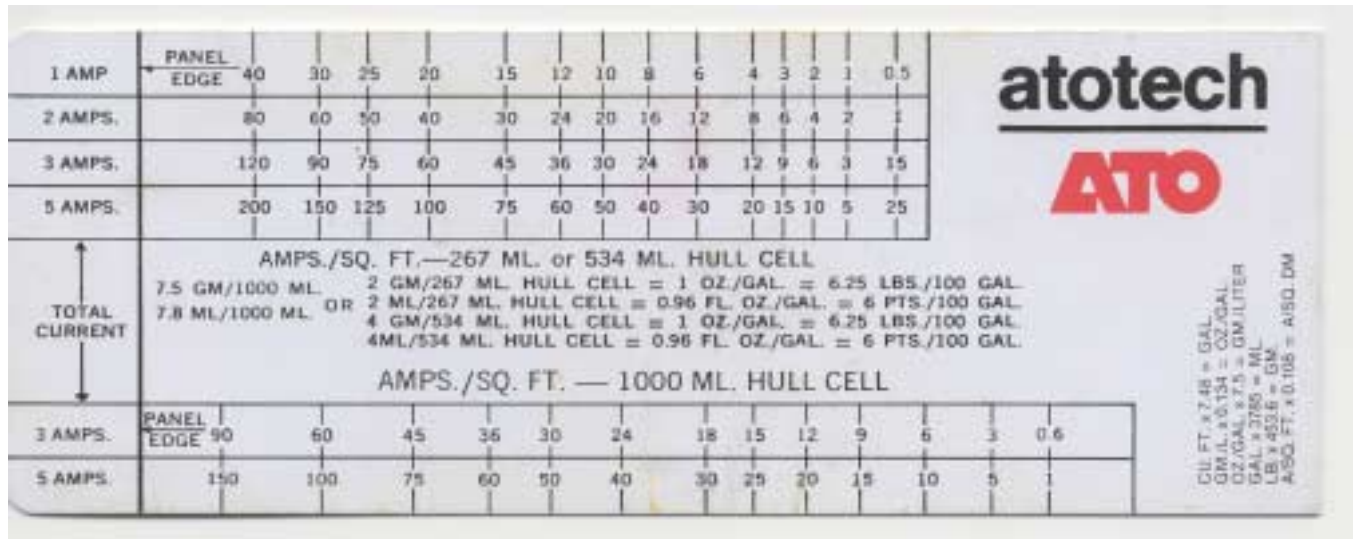
General Information: (803) 817-3500

TO PLACE AN ORDER: 1-800-PLATING

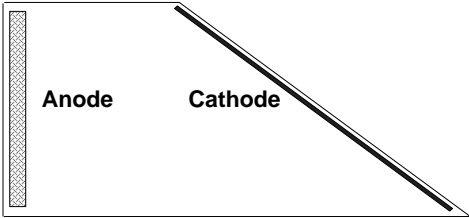
APPENDIX**Hull Cell Articles**

1. **The Anode's Side of the Story** - written by John B. Winters (once Technical Director of R. O. Hull Company - later founder of Incar, Inc.)
2. **All About the Hull Cell - Throwing & Covering Power** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
3. **All About the Hull Cell - Types of Cathode Panels** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
4. **All About the Hull Cell - A Versatile Plater's Tool** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
5. **All About the Hull Cell - Chromium Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
6. **All About the Hull Cell - Nickel Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
7. **All About the Hull Cell - Bright Acid Copper Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
8. **All About the Hull Cell - Cyanide Copper Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
9. **All About the Hull Cell - Alkaline Non-Cyanide Zinc Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
10. **All About the Hull Cell - Zinc Cyanide Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
11. **All About the Hull Cell - Acid Zinc Plating** - written by Marilyn K. Sanicky (now retired Manager, Engineering Services, McGean-Rohco, Inc.)
12. **The Hull Cell** - written by H. J. Sedusky and J. B. Mohler, Research Scientists of The Cleveland Graphite Bronze Co.

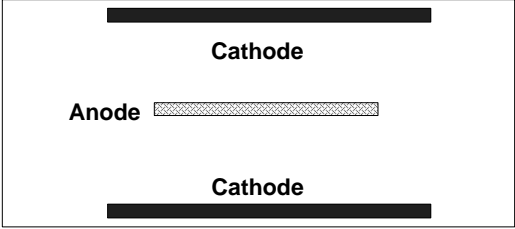
Hull Cell Ruler



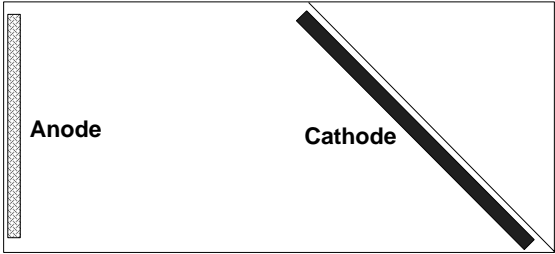
Types of Test Cells



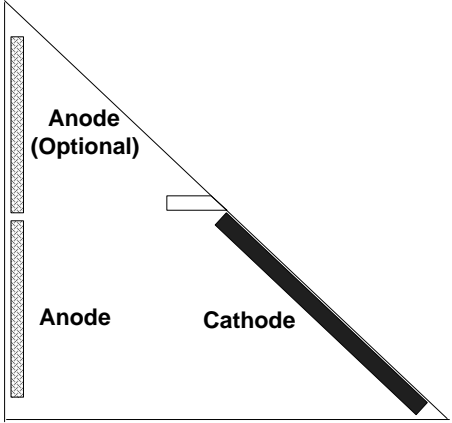
267 ml Hull Cell



Duplicell



1,000 ml Hull Cell



534 ml Hull Cell