McGean-Rohco, Inc.
ROHCO DIVISION

DIRECTIONS FOR HULL CELL PLATING TESTS

The Hull Cell (U.S. Patent 2,149,344) is a miniature plating unit designed to produce a plated deposit that records the character of electroplate obtained at all current densities within the operating range. The character of deposit so made is dependent upon the condition of the plating bath with respect to the primary components, addition agents and impurities. The Hull Cell enables the experienced operator to determine the following facts regarding plating baths:

1. The approximate limits of bright current density range. This is accomplished by comparison of bright plated areas on the panel with current densities given in the chart. Thus, if the bright or operable range is between 3.2 cm (1-1/4 inches) and 6.4 cm (2-1/2 inches) as measured from the left side of the plate, and the total current applied is 3 amps., the corresponding respective current densities from a Hull Cell ruler or chart lie between 7.6 amps/sq. dm. (75 amps./sq. ft.) and 2.7 amps/sq.dm. (25 amps/sq. ft.). 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 poor areas of deposit, but some intermediate current density such as 5.4 amps/sq.dm (50 amps/sq.ft.) should work best.

2. The approximate concentrations of the 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, usually the Hull Cell provides the only satisfactory means for controlling the addition of these highly important materials, provided they exercise a visible effect upon deposits.

4. Metallic or organic impurities. Foreign metals or other harmful impurities in a plating bath exercise a definite effect on the appearance of the Hull Cell deposit, and their presence or absence can be established.

5. The Hull Cell is also an indispensable instrument for experimental plating investigations such as: varying chemical composition; "covering power" or the lowest current density at which a deposit is produced; average cathode efficiency; average metal distribution or throwing power and effects of pH, temperature and decomposition products. The clear lucite Hull Cell enables the operator to observe the plating on the back of the panel to determine relative covering power at very low current densities.

METHOD OF TEST

Before making a Hull Cell plating test, the following points must be observed.

1. Bring the plating bath to be tested to operating level in the plating tank.

2. Either stir the bath thoroughly or use a McGean-Rohco Sampling Tube extending to the bottom of the tank, going over the tank uniformly from one end to the other.

3 Be sure that the sample to be tested is brought to and kept at the proper operating temperature during the test. The best method for testing samples at high temperature is by use of the Model WT or HT Hull Cell, in which are incorporated provisions for a heating element with thermostat control.

4. Use a clean Hull Cell and clean cathode. If more than one kind of plating is to be tested regularly, one cell should be used exclusively for each type of bath to avoid contamination of one bath by the other.

5. Since Hull Cell plating tests are not to be regarded as eliminating the necessity for occasional chemical analysis, such analysis 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. The zinc plated steel cathode panels provided with the set must be stripped of zinc by dipping in a solution of half hydrochloric acid and half water and cleaned with a wet, clean cloth or wet paper towel, just before use. Remember the Hull Cell is an actual plating tank and improperly prepared panels will not respond satisfactorily in the cell, just as in commercial practice.

7. Plating times in the Hull Cell should be timed exactly for duplication of results. These times are not all the same and are specified in the section which follows for the different solutions. A conventional timer can be supplied as an accessory to the Hull Cell Set.

8. The proper volume of sample of plating bath 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. Two grams addition to 267 ml., 4 grams addition to the 534 ml. or 7.5 grams addition to 1000 ml. Hull Cell is equal to one ounce per gallon or 7.5 g/l in the plating tank. To test a bath sample hot, use the Model WT or HT Hull Cell. Never put a lucite Hull Cell on a hot plate.

9. 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.

10. Steel cathodes have a semi-bright and uniform surface. Cathodes should be used once and filed for future reference and not stripped for reuse, as this will change the condition of the surface. Experience has shown that poor or non-uniform steel surfaces are very misleading in interpretation of results. Replacement cathodes are available upon order from McGean-Rohco that duplicate the original zinc plated cathode panels provided with the set. Polished brass panels are also available for copper, nickel and chrome plating tests.

11. 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.

12. Conversion Factors: gms/liter x .134 = oz./gal.

gms/liter x 0.1 = Kg/100 liter
oz./gal. x 6.25 = lb./100 gal.
oz./gal. x 7.5 = gms./liter

SPECIFIC BATHS

By far the best means of using the Hull Cell plating test efficiently is first to determine and record the effects of every variation in each type of plating bath used in production. Thus, if a bright nickel bath is used, each constituent should be taken in turn and effects noted on the cathode deposit, including nickel content, sulfate content, chloride content, brightening agents and the probable metal impurities such as copper, lead, zinc, etc. In conducting such tests, it will be found very advantageous to make up dilute solutions of addition agents so that unit volumes added to the Hull Cell volume of 267 ml. 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 are equivalent to one (1.0) ounce per gallon or 7.5 g/l to the plating tank. Liquid chemicals such as brighteners or addition agents are normally specified or controlled on the basis of liquid (fluid) ounces per gallon or cc/liter.

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

It is emphasized that the value of the Hull Cell test to any operator is proportional to the extent to which it is used and to the experience that the operator has gained in using it. It would be impossible to cover all the innumerable variations of existing baths in detail, but the following generalizations serve as a guide as to what may be expected in testing the different types of baths.

A. BRIGHT NICKEL BATHS...

Bright nickel baths are probably the most difficult to control in order to maintain sufficient luster of deposit so that chromium can be applied subsequently without intermediate buffing. Some brightening agents can be determined by analysis, in which case, Hull Cell tests serve as a check upon the operating condition of the bath. Some brightening agents cannot be checked analytically. In these cases, the Hull Cell becomes an invaluable tool in controlling the addition agent content. Testing of bright nickel demands a uniform quality of steel cathode panel in order to check the ability of the bath to build up brightness, and our cathode panels are recommended for this purpose.

Before Hull Cell tests the bath should be analyzed for Nickel, Sulfate, Chloride, Boric Acid and pH.

A plating test should be made of the bath as sampled then the salt requirements, as determined by analysis, should be added and the pH adjusted. Additional Hull Cell tests should then be made to determine impurities and adjustments of brighteners.

Generally the current used for the 267 ml. or 534 ml. Hull Cell is 3 amperes. For low current density problems a one ampere panel is recommended. Use five amperes for the 1000 ml. Hull Cell.

The Model WT or HT Hull Cell should be used for testing heated baths.

Temperature should be brought to and kept the same as the production baths.

Plating time - - 5 minutes.

Maximum number of tests on one sample -- three, (five in the 534 ml. Hull Cell) unless pH is checked and corrected.

Agitation of solution, if necessary, may be provided by regular movement of a glass stirring rod over the face of the cathode, either manually or mechanically by the use of the McGean-Rohco Hull Cell Agitator. Air agitation can also be provided by use of the Model WT or HT Hull Cell with a built in air line. Hull Cell tests may not always indicate the slight pitting tendencies of baths.

PANEL APPEARANCE

Optimum Composition -- Brilliant, uniform, non-pitted deposits from 0.5-12.5 amp/sq.dm. (5 to 125 amps/sq.ft.)

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 area at high current densities.

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

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

High Anti-pit -- Smoky, irregular deposit.

Low Anti-pit -- Pitting of deposit, particularly noticeable at high current density. To check definitely, bend lower .6 cm (1/4") edge of plate so as to be horizontal and repeat test; examining the horizontal edge for pits if boric acid 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, poor leveling.

Organic Contamination -- Brittle, hazy deposit usually over 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 Temperature of Bath -- Dull or hazy deposit.

Low Temperature of Bath -- Dull or burned deposit at high current density.

Impurities -- Dark at low current densities.

Copper or Zinc -- See "Electrolytic Purification" (Page 21).
Chromium -- Black at high current densities, skip plating in low current densities.
Iron -- Slight burning at high current densities, roughness.

It is obvious from the above descriptions that in many cases a specific problem could have a variety of different causes. Since it would not be economical or logical for the electroplater to treat all the possible causes in his tank, experience has shown that tests can be made on small samples of the problem solution, using a Hull Cell, to determine the exact cause(s) and/or corrections to a specific problem.

B. ROCHELLE COPPER CYANIDE BATHS...

The Rochelle copper bath requires some experience to interpret Hull Cell cathodes properly, because normal deposits are smooth and merely semi-bright under optimum conditions. The bath serves two purposes -- one, for a flash coating, in which variations in bath composition may be tolerated, and the other for deposit thicknesses up to 10 microns (0.0004") for protective coatings, for which the bath composition is more critical.

A total current of two amperes should be used for 5 minutes with a bath temperature of 57° C. (135° F.), or other temperature used in practice. Steel cathodes are recommended; anode should be pure copper. Do not use phosphorized copper. The best means of heating solutions is by use of the Model WT or HT Hull Cell.

PANEL APPEARANCE

Optimum Composition -- Smooth, fairly uniform deposit from 0.5-4.5 amp/sq.dm., (5 to 45 amps/sq.ft.)

Optimum Composition -- (same as above but using an agitated solution) -- semi-bright 0.3-6.0 amp/sq.dm. (3 to 60 amps/sq.ft.)

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

High Overall Concentration -- Same as recommended composition.

Low Free Cyanide -- Somewhat dull deposit, not as uniform and smooth as recommended composition -- solution slightly blue in color.

Slightly High Free Cyanide -- Somewhat lower efficiency than recommended composition but somewhat brighter deposit.

Very High Free Cyanide -- 15.0 g/l or above (2.0 oz./gal.) -- Low efficiency; burnt deposit at high current density.

Low Rochelle Salt -- Dull deposit similar to low free cyanide, but solution not blue.

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

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

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

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

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

Impurities:

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. May be corrected by small additions 0.075 g/l (0.01 oz./gal.)sodium hydrosulfite added to bath as a powder. (0.02 gram/267 ml. in Hull Cell) Additions may be made in these amounts until bath is corrected. By all means avoid excessive additions of sodium hydrosulfite to prevent rough deposits. Commercial chrome control agents may also be used per suppliers' recommendation.

C. HIGH SPEED CYANIDE COPPER...

The High Speed Copper bath lends itself very readily 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 amperes should be used for five minutes with the solution at the operating temperature. The Model WT or 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 flashed well with copper from a low efficiency cyanide copper or Rochelle copper before use. A pure copper anode should be used. Do not use phosphorized copper.

To reveal the bright plate range, the solution in front of the cathode must be agitated. Agitation may be done either by slow movement of a stirring rod during all of the plating time, or by use of the McGean-Rohco Hull Cell agitator.

Panel Appearance

Optimum Composition -- Bright range from 0.5 - 6.0 amp/sq.dm. (5 to 10 amps/sq.ft.). densities 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 in Hull Cell. May be difficult to clean before nickel or to buff.

Low Wetting Agent -- Lack uniformity at medium and low current density range, as well as tendency toward 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 dull and slightly grainy at high current densities.

Impurities:

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

Zinc (over 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 also a tendency toward mottled and non-uniform deposits in medium current density range.

D. BRIGHT ACID COPPER BATHS...

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

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

PANEL APPEARANCE

Optimum Composition -- Full bright panel. If a scratch pattern panel is employed - 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, less conductivity.

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

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

HIgh Chloride -- Loss of leveling, dull to hazy low current density deposits.

Copper Content -- Plus or minus 25% variation 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 cause loss of efficiency and dullness in the low current density areas of the panel. Check suppliers' data sheets for interpretation and balancing of brightener additives.

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

Chromium -- blotchy deposits, haze and blistering.

Organics - The acid copper bath is most sensitive to any and all foreign organics. They cause pitting, brittle deposits and hazes because of codeposition or entrapment of the organic compounds.

F. BRIGHT CYANIDE ZINC ... CONVENTIONAL AND MID-BATHS

Hull Cell tests are very valuable for control of bright cyanide zinc baths since, with experience, the bath balance may be determined as well as addition agents 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 may be applied to baths containing McGean-Rohco zinc brightener and other proprietary cyanide zinc processes.

PANEL APPEARANCE

Optimum Composition — Uniform, bright surface.

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 - over 48.75 g/l (6.5 oz./gal.) -- High bright current density range. Dullness in low current density area.

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

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

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

Impurities: Shown by blistered or dark deposits that stain readily.

Copper -- Copper darkens the plate in 1/4% by volume nitric acid dip.

Lead -- Lead dulls the deposit but does not darken it in 1/4% by volume nitric acid dip.

Cadmium -- In small amounts does not dull the deposit directly, but darkens in 1/4% by volume nitric acid dip.

F. BRIGHT ALKALINE NON-CYANIDE ZINC BATHS...

Hull Cell tests for control of bright zinc baths from alkaline systems 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 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. For barrel baths 0.5 to one ampere panels are run. For rack baths 2 or 3 ampere panels are run. These instructions apply for all proprietary processes not just McGean-Rohco systems. Plating time - - 0.5 ampere panels - - 10 minutes; all other ampere settings - 5 minutes. Note: Plating times and amperage in Hull Cell testing can be varied dependent on conditions being tested or checked for.

PANEL APPEARANCE

Optimum Composition -- Uniform, bright surface.

High Zinc Content -- High efficiency and brightness in the high current density end of the panel and a resultant decrease in efficiency, throw and brightness in 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 amperes; bath efficiency is poor. Metal content may decrease.

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

Brightening Agent(s) -- Best controlled by observation of the production parts. Follow vendor's recommended addition rates. Low brightener is usually evident 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:

Organics -- Blistered dull or dark deposits that stain readily.

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

Copper -- Plate deposit darkens in low current density after postplate dip in 1/4% by volume nitric acid.

Lead -- Dull deposit that neither darkens nor brightens with a post dip in 1/4% by volume nitric acid.

Cadmium -- Darkening of the deposits in 1/4% by volume nitric acid post dip and a cloudy band in the mid-current density area.

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

G. BRIGHT ACID CHLORIDE ZINC BATHS...

The Hull Cell is a very useful tool for control of chloride zinc baths. Because of the high efficiency of this type process, changes from recommended chemistry are often masked. It is, therefore, important to adjust the bath chemistry to the recommended operating range before beginning Hull Cell testing.

Conditions of pH, temperature and agitation of the solution are more 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. Steel cathode panels are suggested. Vigorous paddle agitation is necessary to obtain the proper interpretation of conditions in production air agitated systems if an air agitated Hull Cell is not available.

Plating time -- 5 minutes.

PANEL APPEARANCE

Optimum Composition -- Full bright panel with less than 0.6 dm. (1/4") of burning on the high current density edge of the panel.

Low Zinc Content -- Burning on 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 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" sample of bath. An addition of brightener that gives a measurable reduction in the rough or burned width 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 case the low current density area may show a skip plate and high current density blistering.

Impurities:

Iron -- Yellowing deposit; blue to black staining in the high current density end of the panel after post dipping in either dilute 1/4% by volume 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 1/4% by volume nitric acid or clear chromate solution.

Cadmium -- Overall dullness, black stain in the low current density areas of the panel after 1/4% by volume 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. Progressive degrees of chromium contamination are skip plate in the low current density areas and blistering in the high current density areas.

H. BRIGHT CYANIDE CADMIUM BATHS...

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 to point the way in which the bath may be modified to give the best results. The details given below apply to McGean-Rohco 20 XL and McGean-Rohco Super XL cadmium baths, but the same principles may be applied to the other bright baths.

The use of the Hull Cell is the simplest and most direct means for determining how much 20 XL or Super XL to add to baths. First conduct an "As Is" test panel on sample of the bath, then adjust sample to the proper cadmium and cyanide concentrations. Make incremental additions of 0.2 fl.oz./gals (2 ml. of 20% vol.) of 20XL to the Hull Cell to obtain best bright range or optimum results.

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

PANEL APPEARANCE

Optimum Composition -- Bright plate from 0.3-6.0 amp/sq.dm. (3 to 60 amp/sq.ft.) with new 20XL or Super XL baths, up to 12.0 amps/sq.dm. (120 amps/sq.ft.) with used baths.

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

Low Cadmium - 15.0 g/l (below 2.0 oz./gal.) - bright low current density range, low cathode efficiency, burnt high current density range.

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

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

High Caustic Soda - 26.26 g/l (above 3.5 oz/gal.) - narrows bright current density range. Burn or dull HCD.

Low Caustic Soda - excessive anode polarization; poor conductivity.

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

Low Carbonate - 15 g/l (below 2 oz./gal.) - very slightly duller deposit than normal.

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

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

Impurities:

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

Tin - dull streaks above 2.5 amp/sq.dm. (25 amps/sq.ft.).

Chromium - blisters, skip deposit under 2.5 amp/sq.dm (25 amps/sq.ft.). See "Impurities" section of Rochelle Copper.

I. 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 bivalent 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.

Description is given for the brass solution of the conventional type, 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 35°C. (95°F.). For flash brass over bright nickel test plate time may be shortened.

If pH is measured, the most accurate method is by a pH meter, although pH papers may be used satisfactorily. Satisfactory composition of bath gives a bright yellow or greenish yellow plate from 0.1- 4.0 amp/sq.dm. (1 to 40 amps/sq.ft.) on the Hull Cell panel.

The simplest method of bath control is observation of the color of the brass deposit, in the absence of chemical analysis and pH measurement. If the brass deposit is of 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 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. Make an "As Is" test panel, noting color and plating range. If the color is good, but the width of 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 7.5 g/l (1.0 oz./gm.) sodium bicarbonate to one portion and 3.7 g/l (0.5 oz./gm.) 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 on 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 thickness of deposit up to about 3.2 microns (.00013"). 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.

Ratio CuCN/Zn (CN)	Optimum pH (Electrometric)	Color
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

The 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 almost ideal. Sodium carbonate should be present, and new baths should have 22.5-37.5 g/l (3-5 oz./gal.) 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 be 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 with respect to zinc, so that usually a lower percentage zinc is deposited.

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

Only experience in making such tests will make clear the terms "pink/white," etc. applied to the commercial deposits, but by following the above plan of brass plating solution diagnosis it is possible to match any required color deposit.

J. 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, there is available a lucite Duplicell, in which two panels may be simultaneously prepared with a uniform nickel plate.

METHOD FOR SULFATE RATIO

Reagents Required

1. 0.94N Sulfuric Acid (26.5 cc 66° Be Sulfuric Acid/liter of D.I. water).

2. Barium Carbonate.

PROCEDURE

1. Using your regular nickel bath, plate two steel cathodes simultaneously in the lucite Duplicell so that the cathode panels are adjacent to the long sides, with a standard Hull Cell nickel anode suspended between and on a copper rod. Plate for three minutes with nickel using a current of 2-1/2 amperes. Bright nickels give the widest plating range in chrome and a gallon of known good nickel bath should be put into a closed bottle for this use exclusively.

2. For control of hard chrome, the procedure is the same as for decorative chrome, with nickel plated cathodes and with the chrome bath at the operating temperature in production.

3. Rinse one of the nickel plated panels, transfer to the chromium bath sample in the 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 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

Use Rectifier Models B-267 or B-535 for current; do not use a single phase rectifier without filtered output.

4. If the chromic acid to sulfate ratio is optimum and the bath is normal with respect to trivalent chromium, the panel will be covered with chromium to within 75-80 mm (3/4 to 1") from 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 is somewhat low. If the chrome deposit is spotty, the sulfate is very low. Add 1 cc of 0.94N Sulfuric Acid solution to the 267 ml Hull Cell or 3.75 cc to the 1000 ml Hull Cell and repeat in these increments until the optimum plating range is attained. With a little experience, the proper addition can be made with one or two tests. Each 1 cc/267 ml or 3.75 cc/1000 ml Hull Cell addition is equivalent to 9.1 cc 66° Be Sulfuric Acid/100 liters of bath (34.5 cc 66° Be Sulfuric Acid/100 gallons of bath). These same additions are also equal to 0.02 oz./gal. by weight 66° Be 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 gm/267 ml. (0.485 g/l) Barium Carbonate and stir for a few minutes. Each addition of 0.13 gm/267 ml. (0.485 g/l) Barium Carbonate is equivalent to 48.75 gms. of Barium Carbonate/100 liters of chrome bath. (6-1/2 ounces per 100 gallons of chrome bath.)

NOTES ON PROCEDURE

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. Use our special CHROMETER, a hydrometer for direct chromic acid readings.

2. It is important that a representative sample of the bath be used for test, taken either after thorough stirring or with a sampling tube.

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 $BaCO_3$ may be added for first correction.

5. Some installations require a higher than normal sulfate content to avoid white streaks which result from rainbows being subsequently plated. In this case, adjust 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 can-not be duplicated in the Hull Cell.

K. ALKALINE TIN BATHS...

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 which, however, are usually corrected without much difficulty.

For plating tests a steel cathode is used with a total current of 2 amperes for 5 to 10 minutes at 79° C. (175° F.) or temperature recommended by supplier and a tin anode. It is desirable to heat the tin plating bath to about 83° C. (190°F.) 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 ions are probably present and should be oxidized with a small amount of hydrogen peroxide.

PANEL APPEARANCE

Optimum Composition -- Smooth white deposits from 0.2-5.0 amp/sq.dm. (2 to 50 amps/sq.ft.). 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 acquire a yellow film.

Stannous Tin -- Dark, rough deposits.

Low Tin Content -- Very low cathode efficiency.

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

Sodium Acetate - high or low - little effect on cathode, except possibly slightly smoother cathode with acetate.

Attention is directed to the necessity for continuously "filmed" anodes or anodes having a yellow-green appearance. Under such conditions, tin dissolves as stannic tin (Sn^{+4}) whereas, if not "filmed," objectionable stannous tin (Sn^{+2}) compounds are formed.

L. BRIGHT SULFURIC ACID TIN BATHS

The Hull Cell is a valuable assist for control, preventive maintenance, and troubleshooting of sulfuric acid tin processes. 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 baths. The bath analysis should be performed prior to Hull Cell testing and 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.

Plating time -- 5 minutes.

PANEL APPEARANCE

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 grey.

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 spongy film develops on the anode. 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:

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

M. MISCELLANEOUS PLATING BATHS...

Numerous other plating processes lend themselves to Hull Cell test control, and the effects of each variable in each process gives definite information on simplified control. Such processes as lead, black nickel and chrome, gold, platinum, silver, indium and alloy plating systems are examples of its applicability. Information on details of Hull Cell tests may be obtained from the originators of such processes or determined by the operator for the particular needs of each process or operation.

N. DETERMINATION OF COVERING POWER

In addition to solution control, the Hull Cell may be used in a very interesting manner 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, with a total current on the cathode of only 0.2 amperes. This gives a current density range from about 1.0 to 0.01 amps/sq.dm. (10 to 0.1 amps/sq.ft.) which conveys visibly on the panel an accurate indication of the minimum covering current density, as well as illustrating the remarkable effect of certain addition agents in either improving or decreasing covering power. Important factors in such investigations are the kind of base metal and the means of its preparation, both of which are allied 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 showing different covering power than a similar polished cathode. It is therefore essential that care be exercised in selecting a uniform treatment of the base metal for determining covering power at low current densities.

O. ELECTROLYTIC PURIFICATION OF BATHS...

It is frequently necessary to electrolyze plating baths to remove metallic impurities. *The manner in which this is accomplished in the Hull Cell is to electrolyze the bath sample at 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 translated to the plating tank.

As an example, 0.5 amps/sq.dm. (5 amps./sq.ft.) in the tank =
0.27 amperes through the Hull Cell

$$\left(\frac{10 \text{ cm} \times 2 \text{ cm} \times .5}{929 \text{ cm.sq.}} \quad \frac{3\text{-}15/16" \times 2" \times 5)}{(144 \text{ sq. in.})}\right.$$

If 20 minutes electrolysis removes the impurity satisfactorily, the total electrolysis is 20 x 0.27 = 5.4 ampere-minutes. Therefore, since 3785 ml. equals one gallon, 5.4 ampere-minutes for 267 ml. =

$$\frac{3785 \times 5.4}{267 \times 60} = 1.27 \text{ ampere-hours per gallon of plating bath (0.33 ampere-hours per liter)}$$

* Sedusky and Mohler, January 1947 -- "Metal Finishing"

P. PROPRIETARY PROCESS...

When using Hull Cell Control on proprietary plating baths, it is usually advisable to contact the manufacturer of the particular process for their recommendations. These recommendations may suggest a change in the amperage or time of the Hull Cell test in order to better illustrate the functions to be controlled. Some processes also use special addition agents, which have a pronounced effect on the appearance of a Hull Cell panel.

Current Density in Amps/Sq. Ft.

(Move decimal point one place to the left for Amps/Sq. Decimeter)

	PANEL EDGE													
1 AMP	40	30	25	20	15	12	10	8	6	4	3	2	1	0.5
2 AMPS.	80	60	50	40	30	24	20	16	12	8	6	4	2	1
3 AMPS.	120	90	75	60	45	36	30	24	18	12	9	6	3	15
5 AMPS.	200	150	125	100	75	60	50	40	30	20	15	10	5	25

TOTAL CURRENT

AMPS./SQ. FT.—267 ML. or 534 ML. HULL CELL

7.5 GM/1000 ML.
7.8 ML/1000 ML. OR

2 GM/267 ML. HULL CELL = 1 OZ./GAL. = 6.25 LBS./100 GAL.
2 ML/267 ML. HULL CELL = 0.96 FL. OZ./GAL. = 6 PTS./100 GAL.
4 GM/534 ML. HULL CELL = 1 OZ./GAL. = 6.25 LBS./100 GAL.
4ML/534 ML. HULL CELL = 0.96 FL. OZ./GAL. = 6 PTS./100 GAL.

AMPS./SQ. FT. — 1000 ML. HULL CELL

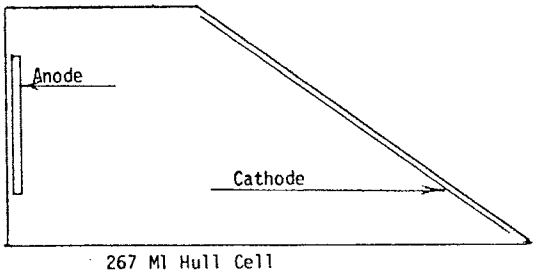
	PANEL EDGE												
3 AMPS.	90	60	45	36	30	24	18	15	12	9	6	3	0.6
5 AMPS.	150	100	75	60	50	40	30	25	20	15	10	5	1

Rohco DIVISION
McGean-Rohco, Inc.

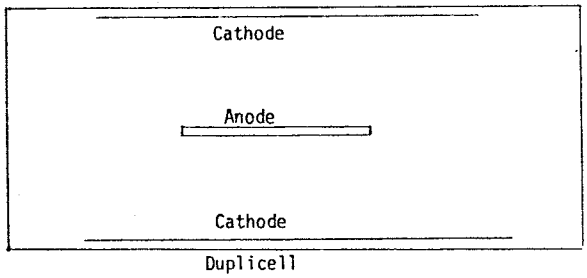
CU. FT. x 7.48 = GAL.
GM./L. x 0.134 = OZ./GAL.
OZ./GAL. x 7.5 = GM./LITER
GAL. x 3785 = ML.
LB. x 453.6 = GM.
A/SQ. FT. x 0.108 = A/SQ. DM

1000 Ml Hull Cell

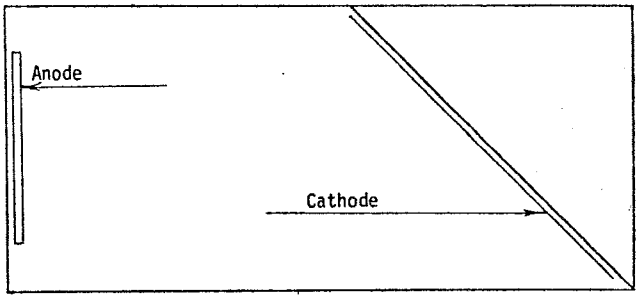
Methods of Testing (top views)



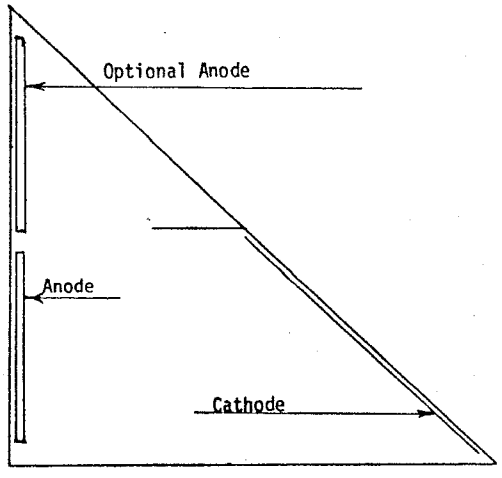
267 Ml Hull Cell



Duplicell



1000 Ml Hull Cell



534 Ml Hull Cell

PD-8312-7-83 (Rev. 8-86)