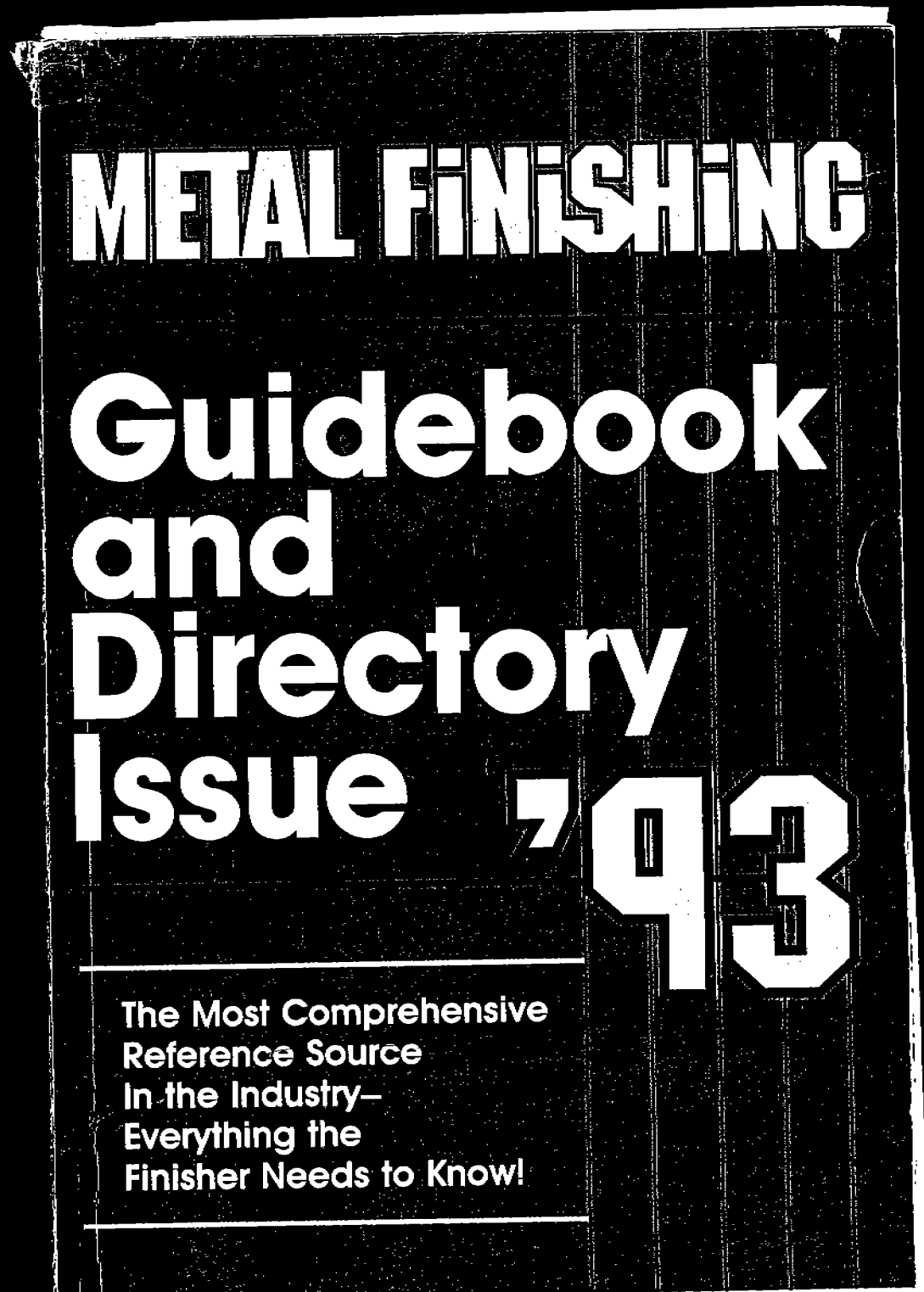
AP-42 Section 12.20
Reference 4
Report Sect. 2
Reference 4→18



Note: This is a reference cited in *AP 42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

METAL FINISHING

THE INDUSTRY'S RECOGNIZED INTERNATIONAL TECHNICAL AUTHORITY SINCE 1903

61st Guidebook and Directory Issue
Published as a 13th issue by *Metal Finishing* magazine

JANUARY 1993
VOLUME 91, NUMBER 1A

EDITORIAL STAFF

Editor: Michael Murphy
Managing Editor: Darlene Berger
Editorial Assistant: Patti Ann Frost
Art Director/Production Manager: Theresa Gaynor

BUSINESS STAFF

Publisher: Eugene B. Nadel
Regional Sales Managers: C. William Niederauer, CBC, and Lawrence A. Post
Circulation Manager: Lawrence E. Hoffer
Assistant Circulation Manager: Amy L. Goodman

ABP
Association of Business Publishers

The Audit Bureau

Metal Finishing (ISSN 0026-0576) is published monthly except semimonthly in January and April, by Elsevier Science Publishing Co. Inc., 655 Avenue of the Americas, New York, N.Y. 10010. Subscription rate per year, including a copy of the *Metal Finishing Guidebook and Directory Issue* and the *Organic Finishing Guidebook and Directory Issue:* $37.00 in the U.S.; Canada and Mexico add $20.00 for surface delivery; all others add $65.00 for surface delivery, $155.00 for air mail. Single copies of *Metal Finishing* (except the *Guidebooks*): $4.50 in the U.S.; outside the U.S., add $8.00 for postage. Second class postage paid at New York, N.Y. and at additional mailing offices.

Change of Address: Postmaster—send address changes to *Metal Finishing*, Elsevier Science Publishing Co. Inc., 655 Avenue of the Americas, New York, N.Y. 10010; 212/633-3749; fax, 212/633-3990; 45 days advance notice is required. Please include both new and old address.

Copyright 1993 by Elsevier Science Publishing Co. Inc. Permission for reprinting selected portions will usually be granted on written application to the publisher. Articles on pertinent subjects are invited. For further information contact the Editor at 3 University Plaza, Hackensack, N.J. 07601. Publication does not necessarily imply endorsement.

Form to finish, McGean-Rohco has the processes you need.

Northwest® Surface Treatment Products
Tri-Max™ liquid cleaners, soak and spray cleaners, buffing compound removers, rust removers, electrocleaners, dry acid salts, blackening compounds, polishing and deburring processes, quenching compounds, rack and parts strippers, tarnish preventives and more.

Northwest® Formulated Products
Norcut™ straight oils, Norsol® soluble oils, Kool-A-Brade® synthetic coolants and other high-caliber products.

Interlox® Phosphate Systems
Phosphating compounds for iron, zinc and manganese. Water-reducible rust-proofing oils and Kolor-N-Kote™ paints.

Decorative Plating
CuFlex® copper, Rellecta nickel, Besplate® nickel, Econo-Chrome chrome and more.

Functional Plating
Roglow® and Robright® cyanide systems, Ecolozinc® and Ekolasid™ non-cyanide systems, Rodip® chromate conversion coating and more.

Zinc Alloy Plating
Reflectalloy® zinc nickel, alkaline zinc nickel, acid zinc nickel and alkaline zinc iron plating processes.

Electroless Plating
Rohco® Armor electroless nickel systems include processes for plastics, metal, composite alloys and others.

PC Plating
Besbon® high-speed through-hole copper processes, tin and tin/lead plating systems.

Gravure System Products
CuFlex® machining, cleaning, striking, copper and chrome plating products.

Nail Coating Products
New Roplast™ water-reducible, anti-withdrawal compounds.

Mechanical Plating Processes
Tru-Plate® products for high quality zinc, copper, tin and alloy surfaces.

Waste Treatment Systems
Kleer-Aid® line of coagulants, emulsion breakers, depuratives and other products.

Test Equipment
Hull Cell™ products of all sizes in lucite, polyethylene and porcelain; jiggle cells; hanging cells; Gomall cells; Haring cells; Heal Guard™ cells; cathode panels and other accessories.

SPC Systems
Custom-designed, computer-integrated systems for monitoring, record keeping and process control.

A World Market Supplier
Argentina • Australia • Canada • Colombia • England • France • Hong Kong • Israel • Japan • Korea • Mexico • New Zealand • Pakistan • Puerto Rico • Singapore • South Africa • Spain • Sweden • Taiwan • Thailand • United States • Germany

McGean-Rohco, Inc.
ROHCO DIVISION
2910 Harvard Avenue, Cleveland, OH 44105-3010
Telephone 216 441-4900, Fax 216 441-1377, Telex 3729244

ELECTROPLATING SOLUTIONS

BRASS PLATING

by Henry Strow

Oxyphen Products Co., Oakville, Conn.

Brass is an alloy of copper and zinc and is the most widely used alloy electroplate. Although all of the alloys of copper and zinc can be electroplated, this discussion will concern only the alloys with over 60% copper.

The largest amount of brass plating is for decorative use, but there are important engineering uses such as the plating of steel wire cord for steel-belted radial tires to secure rubber adhesion. For bright decorative work, most is done by flash plating brass over bright nickel or other suitable bright plate. Heavier brass plating is required where buffing or brushing is required, or where the work is to be colored or antiqued, usually with subsequent brushing or highlighting.

The brass alloy most often plated is a yellow color and contains 70 to 80% copper, with the balance zinc. This is a ductile, stable alloy with only about one shade of color variation over the entire range.

This brass alloy is plated with a solution makeup as follows:

Copper cyanide	4.2	oz/gal	(32	g/L)
Zinc cyanide	1.3	"	10	"
Sodium cyanide	6.5	"	50	"
Sodium carbonate (soda ash)	1	"	7.5	"
Sodium bicarbonate	1.5	"	10	"
Ammonia	1 to 2 quarts per 100 gal (2.5 to 5 ml/L)			

This will give an analysis as follows:

Copper (as metal)	3.0	oz/gal	(22	g/L)
Zinc (as metal)	0.7	"	5	"
Sodium cyanide	3.0	"	22	"

(Use analysis as for total sodium cyanide in cyanide zinc solutions)

pH	10.0 to 10.2
Temp. of operation	75 to 95 °F (25 to 35 °C)

This solution is a general purpose solution. For flash plating the composition should be about 65% the strength of the standard formula. The more dilute solutions will give a wider uniform plating range but will not provide enough conductivity for barrel plating. The standard formula given is only typical. If the same ratios of components are maintained, it may be used stronger or weaker as individual circumstances demand.

The major ingredients of the solution and their functions and control are as follows:

Electroplating Engineering Handbook
by L.J. Durney
790 pages $97.95

This standard handbook for electroplating engineers consists of two parts, as in earlier editions. The first part provides general processing data such as metal preparation, testing and troubleshooting. The second part comprises engineering and fundamentals and practice. The handbook is a worthwhile addition to the finisher's library.

Send Orders to:

METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service,
call (201) 487-3700 or
FAX your order to
(201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

BRASS & BRONZE PLATING ANODES

- **Flat tops, rectangulars & ovals, special shapes.**
- **Standard or special compositions.**

Also Cadmium, Copper (Electrolytic, Phosphorized), Copper-Tin, Lead (Pure & Antimonial), Nickel, Tin, Tin-Lead/Solder, Tin-Zinc, Zinc. Standard & Special Compositions & Shapes.

Belmont METALS INC
312 Belmont Ave. • Brooklyn, N.Y. 11207
718-342-4900 • FAX: 718-342-0175

Zinc Plating
by H. Geduld 360 pages $100.00

This book contains 15 chapters including a history, cleaning procedures, equipment and plant layout, cyanide, zincate and acid baths, post-plate treatments, troubleshooting, special operations such as mechanical and strip and wire continuous processing, control of solutions and waste treatment. It is a practical volume written for the practitioner and chemist.

Send Orders to:
METAL FINISHING
Three University Plaza, Hackensack, NJ 07601
For faster service, call (201) 487-3700 or
FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

Copper is present as the cyanide complex. Its concentration can be varied over a wide range. The copper content of the solution is the major factor in determining the efficiency of the plating. For practical purposes the upper limit of copper is determined by the cost of the dragout and is generally about 6 oz/gal (45 g/L) as metal. Lower concentrations of copper give somewhat lower efficiency, but the throwing power of the solution and the upper usable current density improve. Lowest practical limit for stable operation is about 1.5 oz/gal (10 g/L) as metal.

Zinc content is best held at about one third of the copper content, chiefly to avoid unstable operation. This ratio has no influence on the alloy deposited or its color. Color and alloy are controlled by the cyanide to zinc ratio.

Sodium cyanide is a multipurpose ingredient. The sodium cyanide content controls the anode solution. The ratio of sodium cyanide to zinc controls the alloy (and color) deposited. Too high a cyanide content lowers the efficiency of the plating and will give poor coverage in recesses.

The important ratio in brass plating is the ratio of the sodium cyanide to zinc. Since zinc is present in the solution in an equilibrium between the cyanide and the zincate content, the "free cyanide" content of a brass solution is a misleading term. For example, free cyanide is never used in a cyanide zinc plating solution. Low ratios of sodium cyanide to zinc give higher zinc contents, and higher sodium cyanide ratios will give higher copper contents. With quite high ratios of sodium cyanide to zinc, rich low brass (85/15) or even architectural bronze (90/10 alloy) are produced. The lowest ratios attainable are limited by the solubility of zinc. The analysis of sodium cyanide in brass plating is confusing. Unless a known reproducible method is used, results can be meaningless and a correct ratio is not possible to obtain.

Ammonia is an important ingredient. Its function is to increase the zinc content of the deposit, extending the range of uniform plating and brightening the plate. The normal amount of an original addition is from 1 quart to 1 gallon of aqueous ammonia per 100 gallons of solution (2.5 to 10 ml/L). The amount necessary is dependent on the temperature of operation. Temperatures above 100°F (38°C) require even more than the above amount of ammonia. The brass solution generates some ammonia during operation and at temperatures below 90°F (33°C) ammonia additions will be small. The addition of ammonia does not change the pH of the solution. Very large amounts of ammonia will give a banded plate with white, purple and orange bands at various current densities.

Carbonate is both an ingredient and an impurity. Small amounts, up to 4 oz/gal (15 g/L), are required to buffer the pH of the solution. The carbonate exists in an equilibrium between the carbonate and bicarbonate and is a strong buffer in the pH range of operation. Carbonate is also generated in the operation of the solution and can build up to quite high levels without interfering with the plating. Normally it will achieve an equilibrium between dragout and generation so that removal by freezing out is seldom necessary.

pH of the solution is not critical. Normal range is from 9.8 to 10.3. The solution is well buffered in that range. pH values below 9.8 may give problems with zinc solubility and may increase attack on steel anode containers. High pH values (usually over 10.7) may give banded plate and redness at low current densities. pH is raised by additions of caustic soda and lowered by additions of sodium bicarbonate.

Temperature of operation can be varied over a wide range although it should be controlled within a 5°F range in any specific application. Plating can be done at 70–80°F (21–27°C) but the efficiency of plating is much higher at 90°F (32°C).

Metallic impurities are discussed later, as anode impurities, since this is the primary source of impurities. One impurity that is frequently dragged in to brass plating solutions used in flash plating is nickel. This forms such a strong complex that it rarely causes trouble and then only at extremely high current densities.

Properly operated, the brass plating solution will maintain color and alloy over a wide range of current densities. When the range of uniform color is narrow, it is usually because the solution is out of balance. Additions must be made to restore balance. If the balance is correct, the cause is impurities in the solution. Organic impurities such as soap, wetting agents and emulsified dirts can cause brown or off-color dull plates. Filtration, especially through activated carbon, will remove these impurities. Metallic impurities may be plated out at low current densities. Obviously, if the anodes are impure, dummy plating will not remove impurities unless the impure anodes are replaced by anodes of acceptable composition.

Higher copper alloys such as so-called red brass (rich, low, or 85/15) alloy or architectural bronze (90/10 alloy) can be plated. The major change is to operate with a higher cyanide to zinc ratio. The solutions have lower efficiency than conventional yellow brass. Partially to compensate for this they are operated at temperatures of 100–120°F (33 to 52°C) and with higher copper content. A typical formula for makeup of this solution is as follows:

Copper cyanide	6	oz/gal	(45	g/L)	
Zinc cyanide	1	"	7.5	"	
Sodium cyanide	10	"	75	"	
Sodium carbonate	1	"	7.5	"	
Sodium bicarbonate	1.5	"	10	"	
Ammonia	1/2 to 1 pint per 100 gal (60–120 ml/100L)				

Color control from this solution is more difficult when operating yellow brass solutions since the alloy must be held within closer limits (plus or minus 1%).

Ammonia must be added with care as larger amounts will yield yellow plate at low current densities. Higher cyanide to zinc ratios give redder color and vice versa. A two-tone deposit (yellow and red on the same piece) indicates low cyanide.

Anodes should be approximately of the same composition as the alloy being plated. For general yellow brass plating, 70 Cu/30 Zn anodes are recommended. Cast or rolled anodes are satisfactory. Common shapes are balls, slugs or flat top shapes which will fit the anode baskets used. Bar or slab anodes are also satisfactory. Steel baskets are subject to corrosion under some conditions, putting iron into solution as ferrocyanides. The ferrocyanide precipitates with the zinc in the solution, giving a white to gray precipitate. This should be filtered out or otherwise removed.

Purity of the anodes is important. Lead is a common impurity and must be kept below 0.02%. Lead in very low concentrations causes red plate in recesses. Tin should also be kept below 0.03%. Other metallic impurities are not as critical nor as apt to be found.

Brass plating has many of the characteristics of cyanide zinc plating. It is slow to plate on cast and malleable iron. It is an excellent plate over zincated aluminum. On zinc castings the brass will diffuse rapidly into the zinc so that a substantial thickness of deposit is necessary.

No special cleaning or preparation is necessary on most base metals for brass plating. Equipment required is that conventionally used for all cyanide plating solutions. Unlined steel tanks should not be made anodic and lined tanks are recommended. Barrel plating may be done at 6 to 14V. Still tanks require 2 to 6V with current sufficient to provide about 20 A/ft² (2.2 A/dm²).

HIGH SPEED BRASS PLATING

While conventional brass plating fills most of the needs, higher speed solutions are often necessary where heavier thicknesses are required and for uses such as wire and strip plating where times are measured in seconds. Two types of high speed solutions are used.

The first of these is a conventional solution which is operated at temperatures of 130°F (45°C) to 165°F (75°C). Concentrations are the same as conventional brass but may be up to 50% higher in all components. The higher speed is due to the greater efficiency and higher current densities possible (up to 60 A/ft²) At the lower end of the temperature range color may be maintained by ammonia additions with fairly large additions made at frequent intervals. Additions may be made as often as hourly. Addition agents are available which are stable at the higher temperatures and which require only infrequent additions. Monoethanolamine is recommended in the literature at approximately ½% by volume.

The second is high speed brass solutions which were introduced along with the high speed cyanide copper solutions around 1938. These were highly alkaline, fairly concentrated, and of good efficiency.

A typical formula is:

Copper cyanide	10	oz/gal	(75 g/L)
Sodium cyanide	16.6	"	(125 ")
Zinc cyanide	0.7	"	(5 ")
Caustic soda (sodium hydroxide)	6.0	"	(45 ")
Temperature			160°F (70°C)
Current density			10 to 80 A/ft²

Addition agents are necessary to produce uniform color and to give wide plating range. These solutions are suitable for both barrel and still plating. No special equipment is necessary except that barrels should be able to withstand the high temperatures. Barrel solutions are generally operated at slightly lower temperatures than still tanks.

Impurities in the high speed solutions have the same effect as in the conventional solutions and are controlled in the same way. Special variations of the highly alkaline solutions are used for strip plating using higher temperatures and concentrations.

The high alkali high speed brass may also be used to produce the higher copper (gold colored) alloys by using potassium cyanide rather than sodium cyanide and operating at lower temperatures.

Modern Electroplating

by F. Lowenheim

801 pages $95.00

This is the third edition of this valuable textbook. Numerous authorities have contributed summaries on the principles of plating and metal finishing, control, maintenance, deposit properties and troubleshooting. A worthwhile reference.

Send Orders to: METAL FINISHING, Three University Plaza, Hackensack, NJ 07601

For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

CADMIUM PLATING

by Hugh Morrow

Cadmium Council Inc., Greenwich, Conn.

Most cadmium plating is carried out in alkaline cyanide baths prepared by dissolving cadmium oxide (CdO) in a sodium cyanide (NaCN) solution. Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) are formed by reactions within and are part of this bath. Cadmium balls suspended in steel wire cages serve as the plating anodes. Typical bath compositions suitable for various plating methods and workpieces are summarized in Table I.

The characteristics of an alkaline cyanide cadmium plating bath are determined by the ratio of the total sodium cyanide to cadmium metal content. Maintenance of the recommended ratio is important to the operating characteristics of the bath. Sodium hydroxide is formed by reaction with CdO and is also added in amounts of about 1.0 oz/gal to improve conductivity of the solutions for barrel plating. It may also be used to counteract solution drag-in. Sodium carbonate is formed by decomposition of NaCN, reaction with carbon dioxide (CO_2) in the air, and by poor anode efficiency.

All of these alkaline cyanide cadmium plating baths employ addition agents to impart a uniform, fine grained deposit. However, excessive amounts of grain refiners are discouraged, and their use is not recommended for cadmium plating on cast iron.

The choice of a plating bath depends on the size and configuration of the workpiece being plated. Large numbers of small parts are most conveniently barrel plated with solutions of a lower NaCN-to-Cd ratio, while larger parts with intricate and recessed surfaces must be coated by still plating techniques of high throwing power. Automatic plating is normally used for intermediate size products which are arranged on racks and then automatically sequenced through a plating procedure.

Other considerations in bath selection include plating efficiency, plating speed, deposit uniformity and hydrogen evolution. For instance, to obtain uniform plate thickness, a current density of 20 to 40 ASF is recommended, but higher values are used for high speed, high efficiency plating. In such a case, however, bath agitation and cooling are required.

Table I. Alkaline Cyanide Cadmium Plating Baths

Total NaCN-to-Cd Ratio.	*Concentration, oz/gal*				
	Cd	*CdO*	*NaCN*	*NaOH*	*Na_2CO_3*
4.0	2.6	3.0	10.4	1.9	4–10
4.1	2.6	3.0	10.7	8.0	4–6
4.5	4.8	5.5	21.6	3.4	4–6
5.0	2.7	3.0	13.5	1.9	4–8
7.2	2.6	3.0	18.2	1.9	4–6

Preparation of the Plating Bath:

Bath preparation is most conveniently carried out in a spare tank of approximately the same volume as the production plating tank. Fill the tank roughly 70% full of water, heat to 90°F, and dissolve the sodium cyanide. For barrel plating, the 1.0 oz/gal of NaOH should be added at this time. Carefully add the CdO while stirring the solution to insure that the CdO completely dissolves.

After all salts have been dissolved, add 1.5 to 2 lbs of purification grade zinc dust per 100 gallons of solution and stir thoroughly for 30 minutes. Let the solution stand for four hours, then filter it into the production plating tank, leaving about 5% of the solution and sediment at the bottom of the plating bath make-up tank.

Install approximately one cadmium anode per linear foot of conductor bar, and electrolyze at 0.25 to 0.50 V for 24 to 48 hours. Add the grain refiner agent depending on the surface appearance desired, and plate for about two days at a current density of 10 ASF to normalize the solution.

Operating Conditions:

Still Plating:

A cathode current density of 5 to 70 ASF may be used, but the normal ranges are 15 to 25 ASF for nonagitated baths and 30 to 50 ASF for agitated baths. Either the cathode rod or the solution may be agitated. The maximum anode current density should be about 20 ASF.

When steel wire cages are used to hold the cadmium anode balls, excess anode area must be provided. Up to 50% of the total anode area may consist of case-hardened steel. Bath temperature should be 75 to 90°F, but preferably held at 80 to 85°F.

The cadmium metal content should be held at the desired value between 2.6 and 4.6 oz/gal as determined by the plating process required (e.g., high throwing power or high speed-high efficiency).

The free-cyanide content is normally 8 to 10 oz/gal. At higher temperatures, however, a higher free-cyanide level is necessary to insure uniform results.

The sodium carbonate concentration should be limited to 8 oz/gal or to lower values for high metal content baths, since the presence of both high cadmium metal and high sodium carbonate contents tends to polarize the anodes, limit the usable current density range, and produce dark and streaky deposits.

To obtain the maximum throwing power for still plating, use a bath containing 2.2 oz/gal Cd, total NaCN of 17 oz/gal (Cd-to-NaCN ratio of 7.7), and operated at 10 ASF.

Barrel Plating:

Small barrels may be operated at 6 to 8V. For barrels larger than 14" diameter by 30" long, the voltage must be 10 to 12V. The other operating conditions are similar to those for still plating.

Small lightweight parts are normally plated by barrel plating at low current densities (5 to 7 ASF) depending on the metal concentration and bath temperature. Under these conditions, 0.2 mil of cadmium will be barrel plated in 20 to 30 minutes.

Brighteners:

Organic or metallic compounds are often added to alkaline cyanide cadmium plating baths to influence the formation of the electrodeposited cadmium crystals and thus the brightness of the coating. They are largely proprietary and, among the organics, include:

Aldehydes	Furfural	Molasses
Coumarin	Gelatin	Sugar
Dextrin	Milk	Some Sulfonic Acids

Metallic brighteners include nickel, cobalt, molybdenum and selenium compounds.

Best results are achieved by a moderate use of both types. Excessive amounts of the organic brighteners are less harmful in that they ultimately hydrolyze and become harmless. Metallic brighteners should never be used unless technical facilities and competent personnel are available. Baths which are used excessively and which contain large amounts of organic brighteners must be filtered frequently or continuously.

NON-CYANIDE PLATING BATHS

In recent years, the need for pollution control of cyanide solutions and for cadmium plating solutions which generate minimal hydrogen evolution has led to development of several non-cyanide cadmium plating baths. These solutions are a neutral sulfate, an acid fluoborate, or an acid sulfate.

The compositions and operating conditions of each of these baths, along with those of one of the typical alkaline cyanide solutions, are summarized in Table II. Brighteners are generally added to these baths as required, and the cadmium anodes are normally of 99.95% purity.

Of the four plating baths outined in Table II, the acid fluoborate bath is capable of high cathode efficiency at high current density but does not, along with the other non-cyanide baths, have the excellent throwing power of the alkaline cyanide bath. Because of their higher cathode efficiency, the non-cyanide baths are often preferred for the cadmium plating of quenched and tempered high strength steels since less hydrogen is generated at the cathode, and any danger of hydrogen embrittlement is much less.

In any case, all cadmium plated high strength parts are usually based at 375°F within four hours of plating to drive off any hydrogen present. The baking times vary from 30 minutes to 23 hours, depending on the specification, and are a function of both the base steel strength level and the maximum section thickness of the plated part.

Table II. Typical Cadmium Electroplating Baths

Bath Component (oz/gal) or Operating Condition	*Alkaline Cyanide*	*Neutral Sulfate*	*Acid Fluoborate*	*Acid Sulfate*
Ammonium chloride	—	1.5–3.0	—	—
Ammonium fluoborate	—	—	8.0	—
Ammonium sulfate	—	10.0–15.0	—	—
Boric acid	—	—	3.6	—
Cadmium	2.7	0.5–1.5	12.6	—
Cadmium fluoborate	—	—	32.2	—
Cadmium oxide	3.0	—	—	1.0–1.5
Sodium carbonate	4.0–8.0	—	—	—
Sodium cyanide	13.5	—	—	—
Sodium hydroxide	1.9	—	—	—
Sulfuric acid	—	—	—	4.5–5.0
Current density, ASF	5–90	2–15	30–60	10–60
Temperature, °F	60–100	60–100	70–100	60–90

DECORATIVE CHROMIUM PLATING

by Donald L. Snyder

M & T Harshaw, Cleveland

Electrodeposition of chromium is the principal means of imparting the physical and chemical properties of chromium to the surface of less expensive and easier to form materials such as steel and plastics. The most desirable properties of chromium as a metal coating are its inherent protective and decorative characteristics. The deposit's high reflectively is retained in service because of chromium's excellent tarnish, corrosion, wear and scratch resistance.

Chromium is almost exclusively plated over a nickel electrodeposit which can easily be plated over substrates such as plastics, steel, aluminum, copper alloys, and zinc die castings. Nickel is preferred because it protects the substrate from corrosion, helps give chromium a white color, and is protected from surface oxidation by the chromium. Stainless steel is the only substrate that is frequently plated directly with chromium, but a nickel preplate before chromium is also used. Multiple or single layers of nickel and copper can precede the nickel/chromium deposits depending upon the intended use of the part. Decorative chromium deposits typically are plated in the 2 to 20 millionths of an inch range. Thicker deposits tend to be duller and contain visible cracks.

The traditional chromium deposit is produced from an electroplating electrolyte containing hexavalent chromium ions and has a pleasing bluish-white decorative appearance. About 1975, a chromium electrolyte containing the less toxic and less hazardous trivalent chromium ion began replacing many decorative hexavalent chromium electroplating installations. Depending upon the process, trivalent chromium electrolytes can either produce a metallic white deposit almost identical in appearance to the bluish-white hexavalent chromium deposits or a deep looking pewter or stainless steel appearing deposit. In almost all chromium plating applications, both hexavalent and trivalent chromium processes are interchangeable with each other; however, one or the other process might offer unique advantages.

CHEMISTRY FOR HEXAVALENT CHROMIUM

Hexavalent chromium electrolytes require a source of chromium and one or more catalysts in order to plate. The formulation of the traditional process, called the conventional bath, contains hexavalent chromium and sulfate as the only catalyst. Proprietary additives can be added to the conventional hexavalent chromium plating bath formulation to enhance particular plating operations or the deposit's properties. In most cases, these proprietary processes are called mixed-catalyst baths since the additives contain at least one additional catalyst in addition to sulfate.

Mixed-catalyst baths are used when their special properties are required but they are more expensive to operate than conventional processes. They typically plate at faster speeds, have better coverage, have wider bright ranges, and are more tolerant to impurities. They also are less sensitive to current interruptions and can be plated over more passive surfaces.

The basic formulation of both types of hexavalent chromium processes are very similar. They consist of chromic trioxide (CrO_3) which when combined with water forms chromic acid (H_2CrO_4), and the sulfate ion (SO_4) added in the form of sulfuric acid or a sulfate salt. Even though chemically incorrect, in most literature solid chromatic trioxide is commonly referred to as its hydrated form, chromic acid.

A number of theories have been proposed to explain the mechanism of hexavalent chromium electroplating. Basically, they all resemble the following multiple reactions.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \rightarrow CrO_4^{-2} + 2H^+ \quad (1)$$

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \rightarrow Cr_2O_7^{-2} + 2H^+ + H_2O \quad (2)$$

ction:

$$Cr_2O_7^{-2} + 14H^+ + 12(e) \xrightarrow{CAT} 2Cr^o + 7H_2O \quad (3)$$

tion has an efficiency of about 20% or less. CAT is a required catalyst, e.g. (e) refers to an electron.

:

$$2H^+ + 2(e) \rightarrow H_2 + \text{mist} \quad (4)$$

tion consumes 80% or more of the available power.

$$Cr_2O_7^{-2} + 14H^+ + 6(e) \rightarrow 2Cr^{+3} + 7H_2O \quad (5)$$

$$2Cr^{+3} + 3O_2 - 6(e) \xrightarrow{PbO_2} 2CrO_3 \quad (6)$$

tion takes place at the lead anode, PbO_2.

nventional formulations consist of about 250 g/L (33 oz/gal) chromic trioxide, d", with about 2.5 g/L (0.33 oz/gal) sulfate. Concentrated conventional baths t 400 g/L (53 oz/gal) chromic trioxide and 4.0 g/L (0.53 oz/gal) sulfate. In ever, concentrations in between these are used.

te formulation is extensively used to give good coverage, moderate nickel ation, and consistent current efficiency. It also has a lower cost to originally ates faster, and produces less waste to treat. The concentrated formulation gives ge and greater resistance to impurities and requires lower operating voltages; s more expensive to operate because of its higher chromium concentration and additional chromium to be waste treated.

cal point in all bath formulations is the requirement for close control of the ight ratio in order to produce consistent plating results. Ratios of between 80:1 typical with a ratio around 100:1 being most common for conventional processes. esults in relatively poor throwing and covering power and an increased limiting ty. Higher ratios result in slow deposition rates, produce dull deposits, have vering power, and decreased limiting current density.

ition of a fluoride catalyst necessitates an adjustment in the CrO_3/SO_4 weight of 170:1 to 210:1 are required with 190:1 being most typical. The chromium . for both the dilute and concentrated mixed-catalyst formulations are the same tional baths, however, the sulfate concentration is lowered.

most plating baths in which the metal, M, is present in solution as a cation, mium metal is present as an anion complex, $Cr_2O_7^{=}$, which very likely undergoes plexing with ions such as the sulfate catalyst to permit chromium deposition. ilicofluoride ions are extensively used today in mixed-catalyst formulations, proprietary self-regulating baths. The solubility constants of sparingly soluble talysts are utilized to control the catalysts' ratio in self-regulating baths because catalyst will dissolve. For this reason, less frequent catalyst analysis is required. routine analyses and chemical control of the catalysts are needed in nonself-regulations since they must be added to the bath as they are depleted.

ic acid concentrations may be maintained by making frequent specific gravity ns using a hydrometer. Occasionally, more accurate chromium analyses should d by an analytical method specific for chromium. Chromium is consumed and of the bath. It is replenished by additions of chromic acid.

concentrations should be determined frequently by measuring the volume of the pitated with barium. Occasionally, gravimetric analyses should be conducted to quick, less accurate, centrifuge method. Sulfate concentrations may be raised

by adding sulfuric acid. To add 0.05 g/L H_2SO_4, add 0.0272 ml/L concentrated H_2SO_4. Sulfate is both dragged into and out of the tank. To lower the concentration of sulfate by 0.05 g/L of H_2SO_4, add 0.01 g/L barium carbonate. Sulfate is an impurity in other chemicals such as chromic acid. For this reason, sulfate should be controlled carefully and any sulfate present as impurities should be accounted for.

CHEMISTRY—TRIVALENT CHROMIUM

The literature contains far less information on the chemistry of trivalent chromium processes than for hexavalent. This is the result of the relative newness of the commercially successful processes, the proprietorships of the processes, and the wider differences in the chemistries used. Basically, the significant reactions in the trivalent chromium processes are very simple.

Deposition Reaction:

$$Cr^{+3} + 3(e) \rightarrow Cr^0 \quad (7)$$

Side Reaction:

$$Cr^{+3} \rightarrow Cr^{+6} + 3(e) \quad (8)$$

This takes place at the anode under some conditions.

The electrolytes for trivalent chromium plating solutions differ in chemistry, but they all contain a source of trivalent chromium which is typically added as the sulfate or chloride salt. They also contain a stabilizing material that combines with the chromium to permit it to plate in the desired form. Salts are also added to increase conductivity in the solution. Wetting agents are used to help in the deposition reaction and to reduce the surface tension of the solution.

The method used to eliminate the side reaction distinguishes the single cell from the double cell process. The single cell process has built into the bath chemistry and anodes a mechanism to stop this reaction from occurring. A secondary mechanism converts hexavalent to trivalent if any does appear in the solution. Normal addition of additives to the bath is all that is necessary to eliminate hexavalent chromium. The anodes are placed below solution level to eliminate misting.

The double cell process stops the side reaction by isolating the chromium containing solution from the anode by putting each anode into a box with its own chromium-free electrolyte. The anode electrolyte is changed frequently to dispose of the chromium that might get into the box. Mist suppressants are added to the anode electrolyte to reduce misting. The chromium electrolyte is frequently treated for the removal of hexavalent chromium.

Control of trivalent chromium plating processes is typically easier than for hexavalent chromium processes. The literature says that an operator should "think nickel plating not chromium plating" when controlling a trivalent chromium process. The troubleshooting guide for trivalent chromium processes are a few lines long compared to several pages for hexavalent chromium. The additives are added based upon amp-hours, specific gravity and pH. In addition, chemical analysis on a monthly basis appears to be sufficient for control. The single cell process has a test paper, used in a manner similar to pH paper, that measures total metallic impurities making chemical analysis of metallic impurities unnecessary.

OPERATIONS

The typical operating conditions for trivalent and hexavalent chromium electroplating processes are shown in Table I.

Equipment:

Tank linings, for both types of processes, must be made from suitable synthetic material such as PVC or plastisol. Hexavalent chromium uses lead-7% tin anodes which are consumed

Table I. Chromium Plating Typical Operating Conditions

	Trivalent Chromium	*Hexavalent Chromium*
Chromium, g/L	5 to 25	100 to 200
pH	2.3-4.0	Less than 1
Temperature, °F	70-120	90-120
Cathode current density, A/ft^2	40-150	175-300
Agitation	Mild air	Optional
Rectifier voltage	4-15	4-12
Anode-cathode ratio	2:1	1:1-3:1
Anode material		
Single-cell	Carbon	Lead-7% tin
Double-cell	Lead-7% tin	
Chromium concentration, g/L		
Single-cell	4-20	150-300
Double-cell	5-10	
Maximum thickness, mil		
Single-cell		
Room temperature	about 0.05	5 or more
High temperature	1 or more	
Double-cell	about 0.01	
Plating rate, mil per min		
Single-cell (constant)		
Room temperature	0.005-0.007	0.005-0.007
High temperature	0.007-0.010	
Double-cell (average)	0.004 or less	

during plating. Heating and cooling coils can be made from the same lead alloy or synthetic materials.

The single cell trivalent process uses insoluble graphite anodes that do not need to be changed with use. The double cell process requires the same soluble anodes as used for hexavalent chromium. Titanium or Teflon spaghetti coils are used for heating and cooling in both trivalent processes.

In most cases, a plating line adequately designed for one process can be used for another after thorough cleaning. For trivalent chromium processes, lead and hexavalent chromium must be completely removed since they both act as poisons.

The current carrying capacity of the plating racks must be designed for the highest amperage they will carry. They must also be designed so that the parts on the racks will utilize the bath's plating benefits and minimize the bath's negative plating characteristics. The plating amps for hexavalent chromium processes are at least twice those used for trivalent processes so the racks must be heavier to carry the current. In general, racks designed for hexavalent chromium processes can be used in trivalent processes, but the reverse is not true.

Since trivalent chromium processes will not "burn" and they have greater covering and throwing powers than hexavalent processes (see Table II), the parts can be placed closer together on the racks and high current density areas can face the anodes. This increases productivity and makes shielding and robbing of the part's high current density areas unnecessary as is required for hexavalent chromium processes. Auxiliary anodes are sometimes necessary with hexavalent processes to obtain coverage in the recesses, but typically unnecessary in trivalent processes except for deep recesses.

Trivalent chromium processes do not require scrubbers and, if the room is adequately ventilated, tank ventilation is typically not used. This is due to the almost complete elimination of misting and odor with trivalent chromium processes, the low chromium concentration,

Table II. Trivalent and Hexavalent Chromium Comparison

	Trivalent Chromium	*Hexavalent Chromium*
Throwing power	Good	Poor
Covering power	Good	Poor
Current interruptions	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Intolerant
Deposit structure (micro-discontinuous)		
Single cell	Microporous and microcracked	Special processes required
Double cell	Microporous	
Ease of burning	Very hard	Easy
Ease of rinsing	Easy	Moderate
Color buffing requirement	Never	Occasional
Filtering requirement		
Single cell	Only after purification	Never
Double cell	Daily with carbon	
Conditioning/dummying		
Single cell	Never	Start up each day
Double cell	Start up and routinely	
Passivity of nonplated surfaces	Needs post dip	"Chromate" surfaces
Color of deposit		
Single cell		
Ambient temperature	Pewter or Stainless steel	Blue-white
Elevated temperature	Metallic white	
Double cell		
Elevated temperature	Metallic white	
Waste treatment	Easy	Moderate
Relative safety	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Heavy
Odor	Almost eliminated	Strong and dangerous

and the greatly reduced toxicity and corrosion properties of trivalent as compared to hexavalent chromium. Trivalent chromium solution drains and rinses easily thus greatly reducing the amount of chromium drag-out. If any solution does dry on the part, it is less hazardous since the chromium is in the trivalent state. It also does not stain the part.

Anodes:

In hexavalent chromium plating, insoluble lead or lead-7% tin anodes are used since chromium is replenished by the addition of chromic acid. The single cell trivalent chromium process uses insoluble carbon anodes while the double cell process uses lead or lead alloy anodes. The lead anodes dissolve during use and must be isolated from the plating solution by a box covered by an ion selective membrane.

WASTE TREATMENT

The best "waste treatment" method is not to drag out any plating solution from the tank and, if it is, return as much as possible back to the tank. Due to hexavalent chromium's poor draining characteristic and its misting, a lot of solution is unavoidably removed from the tank. Atmospheric evaporators and ion exchange are examples of what is being used to return dragged-out hexavalent chromium solution back to the plating tank to save chemical and waste treatment costs. Plating solution that cannot be recovered must be waste treated.

Atmospheric evaporators are extensively used to return trivalent chromium back to its plating tank. If trivalent chromium has to be waste treated, its cost is approximately one-tenth that of treating hexavalent chromium. Trivalent chromium solutions never have to be discarded because of normal metallic contamination. The single cell trivalent chromium processes can be treated in one hour for metallic contamination by a chemical purifier which is part of the process. Metals can also be removed by long term low current dummying. The double cell process uses only the long term dummying procedure. Hexavalent chromium processes are essentially insensitive to organic contamination since the hexavalent chromium destroys most organics while itself being converted to trivalent chromium. The single cell process is relatively insensitive to organic impurities but can be carbon treated if required. The double cell process is treated routinely with carbon and peroxide to remove organic impurities.

CORROSION PROTECTION

Chromium plays an important part in the protection provided by nickel/chromium systems. In fact, heavier chromium deposits have a greater proportional effect on the corrosion resistance than increased thickness of nickel. Decorative hexavalent chromium deposits are usually not plated to thicknesses greater than about 25 millionths of an inch. Ten millionths or less is typical. Over 25 millionths, random cracking occurs that is visible to the eye, detracting from the appearance and corrosion resistance.

The single cell trivalent chromium process can produce a deposit with well over one-half mil of chromium without loss of appearance and an increase in corrosion resistance is reported. The double cell trivalent chromium process is limited in most plating operations to a maximum thickness of about 10 to 15 millionths of an inch.

Thick "crack-free" hexavalent chromium processes have been developed that do not produce visible cracks when plated, but if the deposit is flexed, large cracks develop detracting from the appearance and corrosion resistance. In practice, this technology is not very useful for decorative chromium plating because the large cracks will eventually form in service.

Microdiscontinuous chromium deposits, chromium layers that have microscopic pores or cracks, enhance the corrosion resistance of nickel/chromium deposits. With ordinary hexavalent chromium deposits, failure of the deposit is often due to deep pits developing as a result of the corrosion starting at random cracks or pores in the chromium surface. As these cracks or pores are relatively widely spaced, the current which is developed by the chromium/nickel couple is concentrated at a few points and deep pits are formed which in time penetrate through to the basis metal. With microdiscontinuous chromium, there is a very large number of initially invisible cracks or pores in the chromium. This spreads out the same amount of total nickel corrosion over thousands of sights instead of just a few retarding the corrosion penetration down to the substrate. A typical plating standard would call for a minimum of 60,000 pores per square inch or 700 cracks per linear inch. All trivalent chromium deposits are microdiscontinuous as plated. Hexavalent chromium deposits must undergo special treatments to produce microdiscontinuous chromium deposits.

DECORATIVE BLACK CHROMIUM

Thin black chromium deposits are used for functional and decorative applications. Important functional applications include solar energy collectors for heat production and anti-glare surfaces. Decorative functions include furniture, plumbing fixtures, optical equipment, boat equipment, and builders' hardware. The decorative jet black finish enhances users' appeal for the product and so its popularity depends upon the customers' changing desire for black finishes.

Black chromium deposits offer a surface with properties similar to regular chromium deposits. In addition, black chromium deposits have a greater degree of microporosity which helps absorb oil and paint. This property improves its corrosion resistance, wearability, and appearance.

Table III. Decorative Black Chromium Formulations

	Bath A	*Bath B*	*Bath C*
Chromic acid, g/L	250	340	250
Fluosilicic acid, g/L	—	0.34	0.25
Acetic acid, g/L	216	—	—
Barium acetate, g/L	7.6	11	—
Temperature, °F	100	70	90
Current density, A/Ft^2	40-90	200	150-450

Most black chromium processes are proprietary because of the difficulty of obtaining consistent plating characteristics and deposit properties. In many applications, plating black chromium over regular chromium is recommended. For all decorative and most functional black chromium deposits, the typical thickness is around 10 millionths of an inch. Three general formulations are given in Table III. Low carbon steel anodes can be used with plating times of up to 10 minutes. Most formulations will only produce a maximum deposit thickness and then stop plating due to the nonconductive nature of the deposit. To produce black deposits, barium salts are typically added to remove any traces of sulfate. Only hexavalent chromium formulations are presently available although experimental trivalent chromium formulations are being investigated.

BULK CHROMIUM PLATING

Plating racks are typically used to hold parts, transfer parts to and from the plating solution, and carry the direct current to the part. Very small parts such as eyelets, screws, nuts, and bolts cannot be economically placed individually on racks so they are plated in bulk in barrels or trays; however, even under the best of plating conditions, the reject rate can be very high. This is due to incomplete coverage and black/gray deposits mostly due to poor cathode contact and current interruption.

Both hexavalent and trivalent chromium processes are being used for bulk plating of parts. Hexavalent chromium has been used primarily and special formulations have been developed which can produce near 100% coverage if precise control is used. Table IV contains typical barrel hexavalent chromium formulations. Since current interruptions are not avoidable in barrels and trays, stable complexed fluoride containing solutions are normally used.

It is extremely important that the bright nickel used prior to chromium be fresh and not passive. This is typically accomplished by plating a minimum of 0.1 mils of nickel in the same barrel and, with a few rinses in between, transferring the parts directly into the chromium tank. Since the parts are not held by a rack, poor or no contact with cathode leads is common. Contact must depend upon gravity while being dampened by the solution, to hold the part against the cathode contact points.

To increase the likelihood of good contact and satisfactory plating, platers use low current density, low temperatures, and specially designed barrels and trays. Cathode contact points in barrels are constructed from wire mesh, solid steel liners, button contact points less

Table IV. Hexavalent Chromium Barrel Formulations

	Bath A	*Bath B*
Chromic acid, g/L	525	340
Sulfate, g/L	1	0.98
Fluosilicate, g/L	7	6
Temperature, °F	90 to 105	Room to 95
Voltage	6 to 18	6 to 18
Time of plating (Minutes to produce 10 millionths)	8	10

than an inch apart, or steel bars that tumble the parts as they move. Large barrels with small loads also help to increase the frequency of contact and reduce temperature build up inside the confined space of the barrel. In general, the highest practical current density possible, without burning, should be used.

Screw or spiral design plating equipment are also used. The parts are put into the barrel at one end and transferred through the barrel for plating inside the threads of the screw. This permits a continuous flow of plated parts. Vibratory agitation and centrifugal force barrels are also available. In all cases, the barrels must be constructed so that the hydrogen gas generated during plating can escape from the barrel rather than being trapped and potentially exploding. Tray plating requires that parts be layered onto a metallic screen and vibrated or tumbled during plating.

Trivalent chromium solutions have recently been used for barrel and tray plating of chromium. Since current interruptions do not hurt the deposit in trivalent chromium processes and burning is never a problem, this technology will probably be much more popular in the future. The same type of barrels and trays used in hexavalent chromium can be used for trivalent processes. Also, standard unmodified nickel barrels have been used. The problems that have to be overcome are temperature build up in the confined barrel and localized metallic contamination. Nonplated nickel and many other metals will slowly dissolve in trivalent chromium solutions. If the solution agitation is not good enough, the dissolved metallic contamination will stay close to the part giving a localized high metallic contamination condition. Only proprietary trivalent chromium formlulations are available due to the formulations being patented and the newness of trivalent chromium barrel plating.

Chromium Plating

by R. Weiner and A. Walmsley

239 pages $90.00

A thorough and well-written book on both decorative and engineering (hard) chromium plating. It will be of interest to anyone engaged in production chromium plating and also to students, researchers and design engineers. Anyone contemplating the installation of chromium plating facilities will find it of special value.

Send Orders to:
METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service, call (201) 487-3700
or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

FUNCTIONAL CHROMIUM PLATING

by Kenneth R. Newby

M & T Harshaw, Somerset, N.J.

Functional or hard chromium plating is produced from chromic acid (CrO_3) solutions which contain one or more catalytic anions. The chromium metal electrodeposited is extremely hard and corrosion resistant. It has a low coefficient of friction and imparts exceptional wear characteristics to parts on which it is plated. This process is generally used to give deposit thicknesses of greater than 0.1 mil (2.5 μm) and up to 20 mils (500 μm) or more. The major uses are to provide coatings with superior wear, abrasion and/or corrosion resistance. Functional chromium is also used to rebuild or salvage worn parts such as rolls and roll journals, molding dies and other tools, cylinder liners, crankshafts, and mismachined items.

CHEMISTRY

The same hexavalent chromic acid solution could be used for both decorative and functional chromium plating; however, in order to achieve the best possible results in either of these applications differing chemistries and operating conditions should be employed. Those best utilized in decorative applications where nickel activation and superior chromium coverage are of paramount importance are described elsewhere. (See separate article on Decorative Chromium Plating). For functional plating where plating speed and deposit characteristics such as hardness and wear are needed, the chemistries and techniques described below are appropriate.

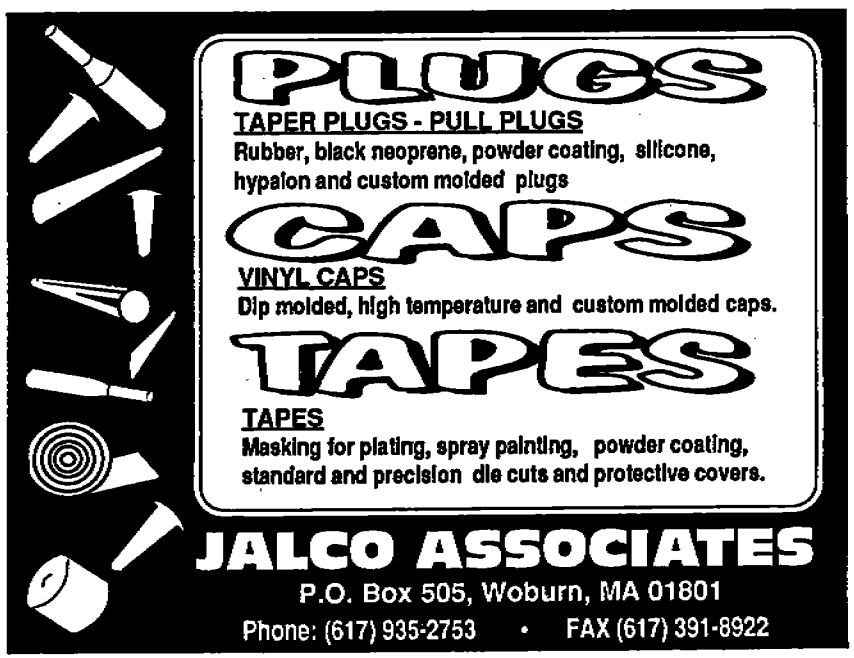
For functional chromium plating three basic formulations are used. All three use chromium trioxide (CrO_3) as the chromium source. When these are dissolved in water, chromic acid (H_2CrO_4) is formed. The sulfate ion ($SO_4^=$) is also necessary and is usually introduced as sulfuric acid or as a salt such as sodium sulfate. In the conventional chemistry, which was developed in the 1920s, these are the only constituents. The chromic acid is present in concentrations of 20-60 oz/gal.

The sulfate concentration is critical and is always held in a ratio relative to the chromic acid concentration. A CrO_3/SO_4 ratio of 100/1 is the most common. At lower ratios such as 80/1 smoother deposits are obtained but both throwing power and covering power are reduced. At ratios of up to 130/1 the opposite characteristics are found. At even higher ratios dull deposits and slower plating rates are obtained. Several proprietary baths are available which automatically control the ratio.

The fluoride or mixed catalyst plating baths were commercialized in the 1950s. In these chemistries a higher plating efficiency, typically 20-25% versus 7-15% for conventional, and a harder, more wear resistant deposit is obtained. In this chemistry chromic acid many range from 20-50 oz/gal with 28-33 oz/gal being the most common. The chromic acid to sulfate ratio is normally 150-250/1 range for mixed catalyst baths. The fluoride is commonly added as the $SiF_6^=$ ion in an amount of 0.25-0.4 oz/gal (2-3 g/L). This chemistry provides better activation for plating on bright nickel and is less susceptible to problems with current breaks than is the conventional chemistry.

One limitation of a fluoride containing bath is that exposed steel areas will be chemically etched by the bath during warm up and plating times. Therefore, in order to protect areas not to be plated or areas in low current density regions where coverage is poor, it is necessary to mask the surface. This chemistry also tends to build up iron contamination levels more rapidly than other nonfluoride baths.

A new fluoride-free chromium chemistry with the plating speed and physical deposit characteristics similar to a mixed catalyst bath came onto the marketplace in 1986. The operating conditions for this proprietary bath are 33 oz/gal chromic acid, 0.33 oz/gal sulfate, 130-140°F, and an efficiency of 20-26%. The chromic acid and catalyst levels are maintained



by the proprietary addition agents. This bath, being fluoride-free, will not attack exposed nonplated steel areas like mixed catalyst baths. It is possible to convert conventional baths to the fluoride-free or to the mixed catalyst systems; however, these two high speed baths cannot be converted from one to the other. Table I summarizes the recommended chemistries of each of these three systems in oz/gal.

Table I. Examples of Chromium Plating Solutions

Chemical	*Conventional*	*Mixed Catalyst*	*Fluoride-free Proprietary*
CrO_3	33	32	33
$SO_4^=$	0.33	0.16	0.33
$SiF_6^=$	—	0.3	—
Proprietary catalyst	—	—	yes

OPERATING CONDITIONS

Typical operating conditions for functional chromium plating are given in Table II.

Table II. Operating Conditions

	Conventional	*Mixed Catalyst*	*Fluoride-free Proprietary*
Temperature, °F	120-140	130-140	130-140
Cathode current density, A/in^2	0.25-2.5	1-4	1-6
Solution agitation	Optional	Optional	Optional
Anode-cathode ratio	1:1-3:1	1:1-3:1	1:1-2:1
Anode material	Lead-tin (7%) alloy or lead-antimony (6%)	Lead-tin (7%) alloy	Lead-tin (7%) alloy

At higher temperatures, smoother deposits with less burning or nodulation will be obtained. Frequently either shields or thieves must be used to prevent severe build-up in the high current density regions. The use of conforming anodes that are shaped so that the anode to cathode distances are the same at all points on a part is an excellent method for obtaining a uniform deposit thickness.

Defects in hard chromium plating usually fall into either adhesion or deposit roughness classes. While a detailed treatment of either of those subjects is beyond this article, both problems have frequent causes. Adhesion failures are usually caused by poor cleaning or by an inadequate reverse chromic acid etch for non-Ni or Cr bearing substrates. In the case of nickel, care must be taken to keep the substrate cathodic in order to prevent passivation. In plating chromium onto chromium the part is first made anodic (1 A/in^2 for about 1-2 minutes) and then to initiate plating the voltage must be slowly ramped up from the lowest rectifier settings possible.

The second type of general defect is that of rough or pitted deposits. If the plating bath chemistry is properly adjusted and the defects are over the entire substrate then the most likely cause is one of poor base metal preparation. Chromium deposition at best will mirror the substrate and most frequently will magnify any pits, scratches, or nodules present on the substrate. If roughness is only in the high current density regions then the use of shields and/or thieves may solve the problem. Also, if throwing power is not of concern, the chromic acid to sulfate ratio can be lowered to 80-90/1. The other alternative is to lower the overall current density.

Plating cathode current efficiencies and plating speeds are given in Tables III and IV.

Table III. Cathode Current Efficiency (in Percent)

Current Density A/in^2	*Conventional Bath* 130°F	140°F	*High Speed Baths** 130°F	140°F
1.0	10.9	10.8	15.0	14.2
1.5	12.4	12.0	18.5	17.9
2.0	14.0	13.6	21.4	20.6
3.0	16.3	14.9	24.0	23.4
4.0	18.1	17.0	26.0	25.3
5.0	19.4	18.2	26.8	26.2
6.0	20.7	19.3	27.5	27.0

*Mixed catalyst or fluoride-free

Table IV. Plating Speed (In Thousandths of an Inch per Hour)

Current Density A/in^2	*Conventional Bath* 130°F	140°F	*High Speed Baths** 130°F	140°F
1.0	0.30	0.30	0.42	0.39
1.5	0.52	0.50	0.77	0.75
2.0	0.78	0.76	1.2	1.1
3.0	1.4	1.2	2.0	1.9
4.0	2.0	1.9	2.9	2.8
5.0	2.7	2.5	3.7	3.6
6.0	3.5	3.2	4.6	4.5

*Mixed catalyst or fluoride-free

POWER SUPPLY

Chromium plating differs from other plating systems in that the dc current must be freer of "current breaks" or "current ripple". This is especially important at the low output end where ripple can lead to poor adhesion for chromium being deposited onto chromium. The various types of rectifiers have undergone changes over the years, so it is necessary to choose one which is specifically for chromium plating as compared to zinc, copper or nickel where ripple has little importance.

A general rule is that ac ripple should be less than 10% under load, preferably less than 5%, and that no negative spikes (as observed on an oscilloscope, for instance) are produced over the voltage and current range to be used in plating. Occasionally, one phase may go out; while in other plating baths this may not produce defective work, in chromium plating solutions a dull and frequently rough plate would be obtained immediately, along with a reduction in thickness. The mixed catalyst baths are less sensitive to ac ripple problems than the conventional sulfate bath.

ANODES

In chromium plating, an insoluble anode is used since chromium is replenished by the addition of chromic acid. Iron anodes have been used, but are not generally suitable because they add iron to the bath and allow the build-up of trivalent chromium. Platinum has had limited success but also allows the build-up of trivalent chromium in solution. The universally used material is lead or lead alloy, especially 7% tin, which oxidizes the trivalent back to hexavalent chromium during electrolysis.

The reaction at the anode is dominated by the formation and release of oxygen, but a side reaction is the oxidation of trivalent chromium when it is present. During nonplating

periods, yellow lead chromate forms on the surface of the lead. Anodes occasionally may be cleaned by electrolyzing outside the plating tank, by soaking in special cleaning solutions, or by scrubbing. Usually the anodes can be activated by electrolysis before each use. The important thing to watch is that the resistance on the anodes does not rise as they age due to scale build-up.

The ability of the lead anode to keep the trivalent chromium at about 0.5 oz/gal or less is dependent on keeping the lead anode active (brown, black color) and the ratio of anode to cathode area above 1:1 and preferably above 1.5:1. As the ratio is lowered to less than 1:1, the tendency for trivalent chromium to accumulate in the bath increases sharply. If the amount rises above about 1 oz/gal problems become significant. Above 2 oz/gal, the problems get progressively worse until the bath becomes unsatisfactory for use. These problems include burning or rough chromium deposits at high current densities, possibly a brown film at low densities, and a tremendous decrease in bath conductivity so that only low currents are obtained at full tank voltages.

If the type of plating requires that the lead anode area be less than the cathode area, then auxiliary electrolysis may be required to reoxidize the trivalent chromium. This may be done in the same tank if time (e.g., overnight) or space are available, or it may be done in a separate tank. The anode area may be 20 to 30 times the cathode area (e.g., a small cathode with regular tank anodes evenly spaced) to increase the rate of oxidation. Solution agitation is also beneficial.

Care and control of anodes rank with control of solution chemistry and operating conditions for successful chromium plating.

FIXTURING AND RACK DESIGN

For both decorative and functional chromium plating, careful attention is required for fixturing and rack design. The techniques for decorative plating, with its very thin deposit, are very different than those for functional plating, with its much thicker deposit. In functional chromium (hard chrome), a major objective is to obtain very nearly the same chromium thickness over significant areas of a part. In order to engineer racks and fixtures, the designer must consider:

1. Current distribution, i.e., to obtain complete coverage, prevent high current density burning and obtain as uniform chromium thickness as possible over the part.
2. Solution flow, i.e., be sure that all plated areas are supplied with sufficient solution of uniform concentration to prevent corners or recessed areas from depleting the chromium from solution.
3. Parts positioning, i.e., to insure recessed areas do not form traps for gas bubbles which prevent coverage in that area and "cupping" of solution does not occur, which results in excessive drag-in of impurities into the plating bath and drag-out of chromic acid.

In the choice of racking methods, the following must be considered:

1. Number of identical parts to be plated per unit time.
2. Function of the chromium, thickness, area to be plated, and engineering application.
3. Capabilities of the shop to perform finishing operations on the part.
4. Tolerances which must be met by the plater.
5. Shielding or masking areas which are not to be chromium plated.

The racks are usually coated with plastic which is electrically nonconductive and resistant to chromic acid.

STOP OFFS

Many applications require that specified areas of a part not be plated. These are covered with resists or "stop offs" to prevent local plating. A number of available "stop off" materials are described in the following section.

Tapes:

There are two classes of tapes. First, there are conductive tapes which accept plated metal and prevent excessive build-up where plating is undesirable. These are made of lead,

PLATING SOLUTION PURIFICATION
SLUDGE WASTE REDUCTION
ELECTRO WINNING METAL RECOVERY
Our new Porous Pot Technology can do all of the above and more. Very low cost and extremely effective.
HIGH SPEED CHROME PLATING METHOD
TRAINING COURSE
The Reversible Rack 2 Bus Bar System produces hard and bright deposits up to .030 per hour on a diameter. This is done in the old 100 to 1chrome, sulfate solution. A 382 page training manual, 11 hour video, 7-1/2 hour audio tape course. New price is $250.00 Post Paid. NTSC or PAL-Beta or VHS- English or Spanish version. Call or write:
HARD CHROME PLATING CONSULTANTS INC.
BOX 44082G, CLEVELAND, OH 44144
216/631-9090 FAX 216/631-9060

REPUBLIC LEAD ANODES
Whatever your lead or tin anode needs are, let us, with our 68 years experience help you with them.
Over 20 styles of standard and conforming anodes to choose from.
Exclusive "Homogeneous Bonding" process assures positive electrical contact between hook and anode, throughout the life of the anode.
Eighty distributors nationwide to serve you. Call for the name of the distributor in your area.
"Sixty-Eight Years of Proven Quality"
REPUBLIC ANODE FABRICATORS, INC.
Phone 216/641-2575 • Fax 216/641-5408
P.O. Box 605070 • Cleveland, OH 44105

Deposition Technologies for Films and Coatings
by R.F. Bunshah
585 pages $79.00
Eleven specialists pooled their efforts to produce this excellent compilation based on a course on deposition methods. Subjects range from plasma discharge to the various types of vacuum coating, such as evaporation, sputtering and ion plating. Deposition from aqueous baths is also considered.
Send Orders to:
METAL FINISHING
Three University Plaza, Hackensack, NJ 07601
For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705
All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $3.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

Hot Dip Strippable Plating Mask Kit
Clean, sharp, distinct stop off lines. Kit with 1 quart pot and 5 lbs. of Thermo-Cote N-4 strippable coating. Cools fast to give you perfect mask. Non-Contaminating. Peel off and remelt for reuse. Write for details and prices.
Thermo-Cote® INC
295 VREELAND AVE. P.O. BOX 247
PATERSON, NJ 07543
TEL.:(201)345-6206

aluminum or copper surfaces which are bonded to an adhesive material. The tapes are quite flexible and can be cut and trimmed with a razor blade; however, during long periods in the tank, the adhesive may fail and lifting of tape at edges may occur. This results in spillover of plating under the tape. Also, the combination of tape adhesive, chromic acid, time and temperature seems to result in a tenacious residue left on the part when the tape is removed. In many cases, however, lead tape is the most convenient and satisfactory method of stopping off.

A second type of tape used is nonconductive. There are many tapes available in combinations of plastics and adhesives. Some tapes such as those made of polyesters (e.g., Mylar) are rigid, while some polyvinyl chloride (PVC) based tapes are stretchable and can be made to conform to the shape of the part.

Conductive tapes are used where one wants to plate the surface being masked in order to obtain more uniform chromium thickness on the area actually being plated. The tape acts as a current robber. Insulating tapes are usually less expensive than conductive tapes. Also there are as many occasions where one wants to insulate an adjoining nonplated surface as there are for plating such a surface. For example, when plating an outside diameter up to a shoulder, one wants to insulate the shoulder.

Lacquers:

There are a number of chromic acid resistant lacquers available. They can be applied by spraying, dipping or painting. They are an insulating material, the same as nonconducting tape. The chief advantage of lacquer stop offs is the selective way in which they can be painted or sprayed where needed.

Wax:

Waxes are insulating coatings almost always applied by dipping the part completely in the wax and then trimming the wax to expose the areas to be plated. There is a special technology and skill required for practical use of wax which is best learned from the wax manufacturers and suppliers. One particular point: by judicious trimming of the wax, the skillful operator can create a shield which prevents excessive build-up at edges.

Shields and Robbers:

Because of the high current densities used in chromium plating, "thieves" or "robbers" and shields are used more than in other plating procedures. The purpose of the electrical robber is to prevent burning or excess build-up of plate on corners and edges. Typically, a robber is a length of steel wire or rod which is attached electrically to the part being plated and is placed (on the basis of experience) at an appropriate distance from the edge which is to be protected. The robber is so named because it receives the plate which otherwise would have built up on the edge of the workpiece, producing an undesirable result.

A shield is an insulating material which is used to alter the distribution of the electric field between the anodes and cathodes (parts). It can be shown mathematically that a shield should be positioned one-half as far away as the thief or robber from the surface it is protecting. The practical plater should be familiar with both techniques, as both have advantages and neither is satisfactory in all applications.

SPECIALTY CHROMIUM BATHS

Trivalent Chromium:

Although chromium was historically first plated out of trivalent baths, it has only been in recent years that commercial decorative systems have been developed. (These baths are described under Decorative Chromium.) Since the present trivalent chemistries can only plate thicknesses of a few tenths of a mil, they cannot at present be utilized for applications requiring functional or hard chromium type of thicknesses or properties.

Black Chromium:

This process has received a moderate amount of attention over the last 15 years due to its usefulness as an energy absorbing surface in solar collectors. Black chromium has a high absorption (alpha) for solar energy and a low emissivity (epsilon), that is, low reradiation back to the outside. Comparison values for several materials are given in Table V.

Table V. Solar Properties for Several Surface Materials

Coating Sample	*Absorptivity*	*Emissivity*	
Black chrome	0.868	0.088	9.8
Black nickel #1	0.877	0.066	13.3
Black nickel #2	0.867	0.109	8.0
Nextel black paint	0.967	0.967	1.0

Because of outstanding durability and resistance to high temperatures, black chromium is favored over other finishes. With improved techniques, black chromium can provide consistent and reproducible absorption values of 0.90 to 0.95 and can maintain low emittance levels of 0.10 (250°F). Thermal stability up to 400°C (752°F) has been demonstrated.

In addition to solar energy applications, black chromium is used as a black electroplated finish on decorative parts and parts requiring low reflectivity. Black chromium can be obtained from a number of published formulations some of which are given in the section on Decorative Chromium Plating.

Porous Chromium:

During World War II, "porous chromium" plate came into prominence through its use on piston rings and cylinder bores of aircraft and diesel engines. It is applied on original equipment and for salvage of worn cylinders. Porous chromium plate may be described as a regular hard chromium plate about 0.004" or more thick, made especially resistant to scoring, seizing or galling in wear resistant applications, or given better lubricating qualities, by virtue of its having an "interrupted" surface made up of a series or collection of indentations and prominences which are produced by various methods. Porous chromium has been found of value wherever borderline lubrication conditions are encountered, or where "breaking-in" to assure proper seating of working parts is necessary.

Three principal types of porous chromium plate are used. One is referred to as the "mechanical" type, which is produced by hard chromium plating over a roughened, cut or engraved basis metal. The other two, produced by chemical or electrochemical etching of the chromium deposit, are referred to as the "pit" and "channel" types. A fourth type, which is also used, consists of etching pits into the surface of the finished chromium deposit through holes in a plastic mask.

With the etching methods, the porosity is produced by etching the chromium deposit which has been suitably predisposed to the desired type porosity by proper correlation of plating conditions, bath composition (specifically CrO_3/SO_4 ratio) and plating temperature as shown in Table VI.

Table VI. Porous Chromium Plating

Type of Porosity	*Concentration CrO_3, g/L*	*Ratio*	*Temperature, °F*	*Current Density, A/in²*
Pit	250	100:1	122	3-4
Channel	250	115:1	140	3-4

The newer self-regulating, high speed baths are also used for both types of porosity and offer advantages in ease of control, speed of plating, and hardness of deposit. The deposits, whether predisposed to the pit or channel type, may be etched by any of several methods of chemically etching or dissolving chromium. The one most generally used has been anodic treatment in a chromic acid solution. The extent of etching is important, but may vary considerably depending on the result to be accomplished; i.e., whether the etching is for porosity development alone or also for reducing plate thickness for dimensional requirements.

While chromium must be plated to close tolerances regardless of the type of porosity, it always requires a final finishing operation such as honing, lapping, grinding or polishing. This operation removes about 0.001", or less, with the mechanical type or channel type porosity, to give a smooth solid surface of chromium with "plateaus" of suitable size. In the case of pit type porosity, the honing or finishing removes a greater thickness in the form of a loose crust of etched chromium to leave a chromium surface interspersed with pits, the extent and number of pits depending on the amount of etching and honing. In some applications, aircraft cylinders, for example, the porous chromium plate must be specially cleaned after honing to remove fine particles of chromium or honing debris left in the pits or grooves from the finishing operation. Such final cleaning is usually done by vapor blasting.

ENVIRONMENTAL CONCERNS

Air Handling:

Copious quantities of hydrogen are evolved at the cathode and of oxygen at the anode during chromium plating. As these gases break the surface of the bath they carry with them the bath constituents, especially chromic acid, as a mist. This mist must be entirely collected by a good tank ventilation system coupled to a well maintained good quality scrubber. Heavy fines can be levied by OSHA for chromic acid mists escaping from the tank into the workplace and by the EPA for mists leaving the building.

The use of stable surface active agents as fume suppressants is an easy way to reduce the environmental and workplace safety hazards associated with misting. These agents act principally by lowering surface tension to reduce the size of evolved gas bubbles. Commercial practice does not support the concern that fume suppressants may cause an increased tendency for pitting. As most fume suppressants will generate some level of foam on the solution surface, it is important that this foam layer be free from accumulated grease or oily residues which could attach to a part lowered into the solution and result in pitting.

Impurity Removal From a Plating Bath:

The slow but persistent build-up of cationic impurities such as iron, copper, zinc and aluminum in a chromium bath has historically been the life limiting step for a solution. As these impurity levels exceed 1-2 oz/gal (including trivalent chromium) poorer quality deposits will result. The solution conductivity will also be reduced, eventually limiting the current which can be passed by a given rectifier voltage. Until recent years the only solution to this dilemma was to dump all or a portion of a bath and remake with new chemistry. Presently, two alternatives to dumping are available—ion exchange and electrodialysis. Ion exchange techniques are probably best used as a batch treatment. This is due to the necessity to first dilute the bath chemistry approximately 50%, then cation exchange it (all active constituents of nonself-regulating hard chrome baths are anions), and then evaporate off water until the original concentration is reestablished. Electrodialysis is a technique probably best suited to continuously maintaining a low impurity level. It works, frequently in the tank itself, by having the cationic impurities move under the influence of potential and concentration gradient through a cation selective membrane. On the other side they are removed either by plating out on a cathode or by being precipitated as a hydroxide. As more and more shops are moving toward a closed loop water system these impurity removal technologies will become increasingly important to functional chromium platers.

COPPER PLATING

by Anthony Sato and Romualdas Barauskas

LeaRonal Inc., Freeport, N.Y.

COPPER CYANIDE BATHS

Copper cyanide plating, with its accompanying health hazard and waste disposal problems (also shared with other cyanide plating baths), is still essential in many plating operations as a strike and, to a decreasing extent, for thick deposits. In dealing with the chemistry of the copper cyanide bath, distinction must be made between total cyanide and free cyanide. Cuprous cyanide must be complexed with either potassium or sodium cyanide to form soluble copper compounds in aqueous solutions. The major complexed form is considered to be either potassium copper cyanide, $K_2Cu(CN)_3$, or sodium copper cyanide, $Na_2Cu(CN)_3$. The sum of that required for the complexation of copper cyanide plus the amount of cyanide required for the proper functioning of the bath (free cyanide) is the total cyanide. The total cyanide required by weight is given in the following equation:

Total potassium cyanide = Copper cyanide required × 1.45 + Free potassium cyanide required

Total sodium cyanide = Copper cyanide required × 1.1 + Free sodium cyanide required

As an example:

A plating bath needs 2.0 g/L of copper cyanide and 0.5 g/L of free potassium cyanide. How much potassium cyanide is required for the bath?

Total potassium cyanide = 2.0 × 1.45 + 0.5 = 3.4 g/L

The following plating bath formulations are suitable for the majority of uses in cyanide copper plating and are easy to control. These formulations can be modified by the plater after reading the operating parameters and notes on maintenance and control. It is recommended, whenever possible, to use the potassium formulations for extended plating range and a greater tolerance to deviation from recommended operating parameters.

Anodes for all baths should be high purity copper that is oxide-free. They can be bagged copper slabs or bagged steel baskets containing copper nuggets. Plain steel anodes may be mixed with the copper to control copper cyanide content if copper content in the plating bath tends to increase with use. Anode/cathode ratio should be 1:1 to 2:1.

General Purpose Strike:

The general-purpose strike is used for improved adhesion, activation of passive substrates, or as an insurance step in the cleaning cycle. When used for zinc die castings,

the hydroxide concentration should be kept at a maximum of 3.75 g/L (0.5 oz/gal). Deposits are usually in the range of 0.5 to 2.0 μm (0.02 to 0.08 mil) in thickness.

	Potassium	*Sodium*
Copper cyanide	30.0 g/L (4.0 oz/gal)	30.0 g/L (4.0 oz/gal)
Total potassium cyanide	58.5 g/L (7.8 oz/gal)	—
Total sodium cyanide	—	48.0 g/L (6.4 oz/gal)
Potassium hydroxide	3.75–7.5 g/L (0.5–1.0 oz/gal)	
Sodium hydroxide		3.75–7.5 g/L (0.5–1.0 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 g/L (2.0 oz/gal)
Rochelle salt	30.0 g/L (4.0 oz/gal)	30.0 g/L (4.0 oz/gal)
Free potassium cyanide by analysis	11.25–15.0 g/L (1.5–2.0 oz/gal)	—
Free sodium cyanide by analysis	—	11.25–15.0 g/L (1.5–2.0 oz/gal)
Temperature	24–66 °C (75–140 °F)	
Current density	0.5–4 A/dm² (5–40 ASF)	
Time	30 seconds to 2 minutes or until fully covered	
Cathode efficiency	30 to 60%	
Recommended agitation	None or mechanical	

Strike Plate Bath:

The strike-plate bath is the one most used for the plating of zincated aluminum. It is also used for zinc die castings and other metals that are subject to attack by subsequent plating baths or finishing operations that require more than a strike deposit for protection. This formulation eliminates the need for two baths—a strike followed by a plate in a high efficiency bath. Deposits range from 3.0 to 5.0 μm (0.12 to 0.20 mil) in thickness for the parameters given in the formulation.

	Potassium	*Sodium*
Copper cyanide	42.0 g/L (5.6 oz/gal)	42.0 g/L (5.6 oz/gal)
Total potassium cyanide	66.6 g/L (8.9 oz/gal)	—
Total sodium cyanide	—	51.9 g/L (6.9 oz/gal)
Potassium carbonate	30.0 g/L (4.0 oz/gal)	—
Sodium carbonate	—	30.0 g/L (4.0 oz/gal)
Rochelle salt	60.0 g/L (8.0 oz/gal)	60.0 g/L (8.0 oz/gal)
Free potassium cyanide by analysis	5.7 g/L (0.8 oz/gal)	
Free sodium cyanide by analysis	—	5.7 g/L (0.8 oz/gal)
pH	10.2–10.5	
Temperature	40–55 °C (100–130 °F)	
Current density and time	Initial (strike) 2.5–3.0 A/dm² (25.0 to 30.0 ASF) 2 minutes Final (plate) 1.0–1.5 A/dm² (10.0–15.0 ASF) 3–5 minutes	
Cathode efficiency	30–50%	
Recommended agitation	None or mechanical	

Use diluted tartaric acid or acetic acid to lower the pH; hydroxide to raise it.

High Efficiency Bath:

The high efficiency bath is used when a rapid build-up of a significant copper thickness is required. The copper cyanide can be as high as 120.0 g/L (16.0 oz/gal) for applications such as wire plating. Although the brightness and grain refinement of the deposit can be improved by the use of periodic reverse current or current interruption, the best results are obtained by using suitable additives.

	Potassium	*Sodium*
Copper cyanide	60.0 g/L (8.0 oz/gal)	75 g/L (10.0 oz/gal)
Total potassium cyanide	102.0 g/L (13.6 oz/gal)	—
Total sodium cyanide	—	97.5 g/L (13.0 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 (2.0 oz/gal)
Potassium hydroxide	15.0 g/L (2.0 oz/gal)	—
Sodium hydroxide	—	15.0 g/L (2.0 oz/gal)
Rochelle salt	45.0 g/L (6.0 oz/gal)	45.0 g/L (6.0 oz/gal)
Free potassium cyanide by analysis	15.0 g/L (2.0 oz/gal)	—
Free sodium cyanide by analysis	—	15.0 g/L (2.0 oz/gal)
Temperature	60 to 71 °C (140–160 °F)	
Current density	up to 80 ASF	
Cathode efficiency	90 to 99%	
Recommended agitation	Mechanical, solution or air	

Barrel Plating:

The strike bath, high efficiency bath, or both in combination, can be used for barrel plating. Typical compositions for barrel plating are as follows:

	Potassium	*Sodium*
Copper cyanide	45.0–60.0 g/L (6.0–8.0 oz/gal)	45.0–60.0 g/L (6.0–8.0 oz/gal)
Total potassium cyanide	80.3–109.5 g/L (10.7–14.0 oz/gal)	—
Total sodium cyanide	—	64.5–88.5 g/L (8.6–11.8 oz/gal)
Potassium carbonate	15.0 g/L (2.0 oz/gal)	—
Sodium carbonate	—	15.0 g/L (2.0 oz/gal)
Potassium hydroxide	7.5–22.5 g/L (1.0–3.0 oz/gal)	—
Sodium hydroxide	—	7.5–22.5 g/L (1.0–3.0 oz/gal)
Rochelle salt	45 g/L (6.0 oz/gal)	45 g/L (6.0 oz/gal)
Free potassium cyanide by analysis	15.0–22.5 g/L (2.0–3.0 oz/gal)	—
Free sodium cyanide by analysis	—	15.0–22.5 g/L (2.0–3.0 oz/gal)
Temperature	60–71 °C (140°–160 °F)	—

Bath Preparation:

Dissolve potassium or sodium cyanide in cold water. In a separate container mix copper cyanide with water to form a thin slurry and slowly add to the potassium or sodium cyanide solution while mixing. The dissolving reaction is exothermic and the solution should not be allowed to overheat, as this may decompose some of the free cyanide. Add the rest of the required materials after dissolving the copper cyanide. Carbon treatment of the bath before use is recommended. All salts should be sulfur-free to prevent dull, red deposits in low current density plating areas.

Maintenance and Control:

Constituents:

It is recommended that all constituents in the formulation be controlled to within 10% of their nominal values, especially the free cyanide. The copper cyanide concentration controls the allowable plating current density in combination with agitation. The free cyanide concentration controls efficiency, plating range, throwing power and anode polarization. The hydroxide concentration controls conductivity and throwing power. Carbonates buffer the solution and reduce anode polarization. Although high carbonate concentration of 90.0 to 120.0 g/L (12.0 to 16.0 oz/gal) decreases the plating range, it is added to new baths to stabilize their initial operation. Rochelle salt enhances anode corrosion and provides some grain refinement. Potassium formulations have a broader plating range than sodium formulations.

Temperature:

Temperature above 71 °C (160 °F) in the high efficiency and barrel formulations promotes the breakdown of cyanide and the rapid build-up of carbonates.

Agitation:

Mechanical and/or solution agitation is recommended. Use air agitation only when required since air agitation promotes carbonate build-up.

Contamination:

Organic contamination causes non-uniform, dull, rough or pitted deposits. In severe cases of organic contamination, the anodes may polarize. Carbon treatment will remove organic contamination. A copper strike should not be considered to be a cleaner and should be carbon treated periodically to prevent organic contamination from spreading to other plating baths. Hexavalent chromium contamination causes skip plate in the low current density plating area, blisters and non-uniform deposits.

The best method for eliminating the problem of chromium contamination is to eliminate the source. Hexavalent chromium in the bath can be reduced to trivalent by using proprietary reducing agents. Zinc contamination causes non-uniform or brass-colored deposits and can be removed by dummying the bath at 0.2 to 0.4 A/dm² (2 to 4 ASF). Sulfur and its compounds cause dull, red deposits in the low current density plating areas and usually appears from new baths because of impure cyanides or leaching from tank linings. Small amounts of a zinc salt, such as zinc cyanide, will eliminate sulfur red from the deposits. Most other common types of metallic contamination cause deposit roughness and can usually be removed by dummying and filtration.

Carbonate:

Excessive sodium carbonate can be removed by freezing out at a low temperature because of its limited solubility below −3 °C (26 °F). Both potassium and sodium carbonate can be removed by precipitation with calcium oxide, calcium hydroxide or calcium sulfate.

COPPER PYROPHOSPHATE PLATING BATHS

Copper pyrophosphate plating baths require more control and maintenance than cyanide baths, however, the solutions are relatively non-toxic. The main uses of copper pyrophosphate baths have been electroforming, plating on plastics and printed circuits.

The chemistry involved in copper pyrophosphate plating is the formation of the potassium copper pyrophosphate complex $[K_6Cu(P_2O_7)_2 \cdot 6H_2O]$ from copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$) and potassium pyrophosphate ($K_4P_2O_7$). The ratio of pyrophosphate ($P_2O_7^{-4}$) to copper (Cu^{+2}) in the compound is 5.48 to 1. Any pyrophosphate in excess of this ratio is called "free" or "excess" pyrophosphate. Free or excess pyrophosphate is essential for the operation of the bath in providing conductivity and anode corrosion. This is done by running a pyrophosphate to copper (P_2O_7/Cu) ratio of 7 to 8:1 in the plating bath. A strike bath may have a higher ratio. Potassium pyrophosphate baths are recommended over sodium formulations for better conductivity and higher solubility of the potassium copper complex.

Anodes for all baths should be high purity copper that is oxide-free. Anodes can be copper slabs or copper nuggets in titanium baskets. Anode bags are not recommended. Anode to cathode ratio should be 2:1. Copper pyrophosphate baths tend to build orthophosphate (HPO_4^{-2}) concentration by the hydrolysis of pyrophosphate. Small amounts of orthophosphate are not harmful. However, higher concentrations in excess of 100.0 g/L (13.3 oz/gal) may cause banded deposits with decreased plating range and conductivity in the standard plating baths.

In the printed circuit bath, the orthophosphate concentration should not be allowed to exceed 40.0 to 60.0 g/L (5.5 to 8.0 oz/gal) because, beyond this point, there is a decrease in the throwing power of the solution and ductility of the deposit. Orthophosphate concentration is lowered by dilution or replacement of the bath. The anode and cathode efficiencies of copper pyrophosphate baths are essentially 100%. Maximum agitation is required for the best results. When using air agitation, the volume of air required should be 1 to 1.5 times the surface area to be plated. Ultrasonic agitation may also be used.

Strike:

Copper pyrophosphate plating baths can form immersion coatings, similar to acid coppers, on steel and zinc die castings and cause poor adhesion. A cyanide- or pyro-copper strike is used for steel, and a cyanide strike for zinc is recommended. The pyro-copper strike is a diluted version of the plating bath which can have a P_2O_7/Cu ratio of 10:1 or higher. A typical formulation would be:

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	25.0–30.0 g/L (3.3–4.0 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	95.7–176.0 g/L (12.8–23.5 oz/gal)
Potassium nitrate	1.5–3.0 g/L (0.2–0.4 oz/gal)
Concentrated ammonium hydroxide	½ to 1 ml/L
pH	8.0 to 8.5
Temperature	22 to 30 °C (72 to 86 °F)
Current density	0.6–1.5 A/dm² (6.0–15.0 ASF)
Agitation	Mechanical and air
Filtration	Continuous

Operating parameters by analysis are:

Copper metal	9.0–10.7 g/L (1.2–1.4 oz/gal)
Pyrophosphate	63.0–107.0 g/L (8.4–14.2 oz/gal)
P_2O_7/Cu ratio	7 to 10:1

Typical Pyrophosphate Bath:

The following copper pyrophosphate plating bath formulation can be used for all plating applications except printed circuits. Current interruption or periodic reverse current can further refine the grain structure.

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	52.5–84.0 g/L (7.0–11.2 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	201.1–349.1 g/L (26.8–46.5 oz/gal)
Potassium nitrate	3.0–6.0 g/L
Concentrated ammonium hydroxide	3.75–11.0 ml/L
pH	8.0–8.7
Temperature	43° to 60°C (110° to 140°F)
Current density	1.0–8.0 A/dm² (10.0–80.0 ASF)
Agitation	Mechanical and air
Filtration	Continuous

Operating parameters by analysis are:

Copper metal	18.8–30.0 g/L (2.5–4.0 oz/gal)
Pyrophosphate	131.6–225.0 g/L (17.5–30.0 oz/gal)
P_2O_7/Cu ratio	7.0–7.5:1

Printed Circuit Bath:

The use of non-proprietary or proprietary additives that improve the throwing power and ductility of deposit is recommended for printed circuit application.

Copper pyrophosphate ($Cu_2P_2O_7 \cdot 3H_2O$)	57.8–73.3 g/L (7.7–9.8 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	231.0–316.5 g/L (30.8–42.2 oz/gal)
Potassium nitrate	8.2–15.8 g/L (1.1–2.1 oz/gal)
Concentrated ammonium hydroxide	2.7–7.5 ml/L (0.3–0.75% by volume)
Addition agent	As required
pH	8.0–8.4
Temperature	49 to 54°C (120 to 130°F)
Current density	2.5–6.0 A/dm² (25.0–60.0 ASF)
Agitation	Mechanical and air

Operating parameters by analysis are:

Copper metal	20.7–26.2 g/L (2.75–3.5 oz/gal)
Pyrophosphate	150.0–204.4 g/L (20.0–27.2 oz/gal)
P_2O_7/Cu ratio	7.2 to 7.8:1

Copper pyrophosphate baths are sensitive to contamination, especially organic contamination, and are made from purified liquid concentrates.

Maintenance and Control:

Constituents:

Ammonia aids in anode corrosion and acts as a grain refiner. Ammonia is replenished daily because of evaporation loss. Nitrate increases the high current density plating range and is a cathode depolarizer. The pH is controlled by using pyrophosphoric acid or potassium hydroxide as required.

Temperature:

Operating the baths above 60°C (140°F) causes the rapid hydrolysis of pyrophosphate to orthophosphate.

Agitation:

Copper pyrophosphate baths need vigorous agitation for a normal operating current density plating range. The most common form used is air agitation by itself or in combination with mechanical agitation. Ultrasonic and solution jet agitation can also be used.

Contaminants:

Copper pyrophosphate baths are sensitive to organic contamination such as oil or breakdown products of organic addition agents. Organic, cyanide and lead contamination can cause dull, non-uniform deposits with a narrow plating range. Carbon treatment will remove organic contamination and treating with hydrogen peroxide or potassium permanganate before carbon treatment will remove cyanide and severe organic contamination. Lead can be removed by dummying.

Orthophosphate:

In addition to high temperature, localized overheating or too low a pH can cause the rapid build-up of orthophosphate.

Handbook of Printed Circuit Manufacturing

by R.H. Clark

615 pages $75.00

This book is a primary, comprehensive reference for those engaged in the manufacture and sale of printed circuits. Each major operation such as screen printing and pattern plating is covered in a separate chapter. Basic definitions are supplied, enabling the book to serve for the training of personnel.

METAL FINISHING,
Three University Plaza, Hackensack, NJ 07601

For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

CP CHEMICALS

MAJOR PRODUCER OF QUALITY

COPPER CHEMICALS

- Copper Cyanide
- Potassium-Copper Cyanide
- Sodium-Copper Cyanide
- Copper Sulphate
- Potassium-Copper Pyrophosphate
- Copper Carbonate
- Copper Oxychloride
- Copper Acetate
- Copper Pyrophosphate

Call us for a total listing of the chemicals, solutions and compounds we produce for the metal finishing industry.

CP Chemicals, Inc.

1 Parker Plaza, Fort Lee, NJ 07024
1-201-944-6020

COPPER SULFATE BATHS

Copper sulfate baths are economical to prepare, operate and waste treat. They are used in printed circuits, electronics, rotogravure, electroforming, decorative, and plating on plastics applications.

The chemistry of the solution is simple, with copper sulfate and sulfuric acid forming the ionized species in solution. The baths are highly conductive. Previous problems with throwing power have been overcome with the advent of the modern high throw formulations and additives. Steel parts must be cyanide copper or nickel plated in strike formulations to prevent immersion coatings and poor adhesion. Zinc die castings and other acid sensitive metals must have sufficient deposit to prevent attack by the sulfuric acid. The baths are operated at room temperature. Anodes should be phosphorized (0.02 to 0.08% by wt phosphorous), oxide-free, high purity rolled copper. Copper anode nuggets in titanium baskets can be used. Anodes should be bagged. The anode to cathode ratio should be 2:1. Anode and cathode efficiencies are essentially 100%. Since copper sulfate plating has become of major importance to the industry, a troubleshooting guide is given in this section.

Standard Acid Copper Plating:

The following are the standard formulations for copper sulfate baths. Air agitation with or without mechanical agitation, is recommended.

General Formulation:		
Copper sulfate	26–33 oz/gal	(195–248 g/L)
Sulfuric acid	4–10 oz/gal	(30–75 g/L)
Chloride	50–120 PPM	
Current density	20–100 ASF	
Semibright plating (Clifton-Phillips):		
Copper sulfate	33 oz/gal	(248 g/L)
Sulfuric acid	1.5 oz/gal	(11 g/L)
Chloride	50–120 PPM	
Thiourea	0.0001 oz/gal	(0.00075 g/L)
Wetting agent	0.027 oz/gal	(0.2 g/L)
Bright plating (Beaver):		
Copper sulfate	28 oz/gal	(210 g/L)
Sulfuric acid	8 oz/gal	(60 g/L)
Chloride	50–120 PPM	
Thiourea	0.0013 oz/gal	(0.01 g/L)
Dextrin	0.0013 oz/gal	(0.01 g/L)
Bright plating (Clifton-Phillips):		
Copper sulfate	26.5 oz/gal	(199 g/L)
Sulfuric acid	4 oz/gal	(30 g/L)
Chloride	50–120 PPM	
Thiourea	0.005 oz/gal	(0.0375 g/L)
Molasses	0.1 oz/gal	(0.75 g/L)

High Throw Bath:

The following formulation is used in printed circuit, barrel plating and other applications, where high throwing power is required.

Copper sulfate	8.0–12.0 oz/gal (60.0–90.0 g/L)
Sulfuric acid	23.0–29.0 oz/gal (172–217 g/L)
Chloride	50–100 PPM*
Proprietary additive	Per vendor recommendations

*10 cc of reagent grade concentrated hydrochloric acid per 100 gallons is equivalent to 12 PPM.

Bath Preparation:

Baths can be made by dissolving copper sulfate in water and then adding sulfuric acid. Carbon treatment is recommended. Baths can be made without carbon treatment using purified liquid copper sulfate.

Maintenance and Control:

Constituents:

Copper sulfate is the source of copper ions in solution. Since the anode and cathode efficiencies are normally close to 100%, the anodes replenish the copper ions so that the copper concentration remains fairly stable in solution. The sulfuric acid increases the conductivity of the solution and reduces the anode and cathode polarization. It prevents precipitation of basic salts and improves throwing power. In high throw formulations the weight ratio of copper metal to sulfuric acid should be maintained at approximately 1:10. Copper sulfate is reduced in concentration in high throw formulations to prevent common ion precipitation effects as the sulfuric acid is increased. Sulfuric acid concentrations above 11% by volume begin to reduce cathode efficiency. Chloride ion, in bright and high throw baths, reduces anode polarization and eliminates striated deposits in the high current density areas.

Temperature:

These baths are operated at room temperature for the majority of applications. If temperature is too low, cathode efficiency and plating range will be reduced. Baths used where bright deposits are not required may be operated at temperatures as high as 50°C (120°F) to increase the plating range in electroforming, printed circuit or rotogravure applications.

Agitation:

Air, mechanical, solution jet or rotating work agitation can be used. The more vigorous the agitation, the broader the allowable plating current density.

Contaminants:

Organic contaminants are the ones most commonly dealt with in acid copper plating. Major sources are decomposition products of brighteners, tank liners, unleached anode bags, stop-offs, resists and impure salts or acid. Contaminants will adversely affect the appearance and the physical properties of the deposit.

A green coloration of the bath indicates significant organic contamination. Organic impurities are removed by treatment with activated carbon. In cases of severe contamination, hydrogen peroxide, or even potassium permanganate, may be necessary to break down the organics so that the carbon can effectively remove them. Cellulose filter aids should not be used.

Some common metallic contaminants and their effects are as follows:

Antimony (10–80 g/L): rough, brittle deposits. Gelatin or tannin added to the bath will inhibit its codeposition.
Arsenic (20–100 PPM): same as antimony.
Bismuth: same as antimony.
Cadmium (>500 PPM): can cause an immersion deposit and polarization of the anode during idle time. Can tie up chloride ions.
Iron (>1000 PPM): reduces bath conductivity and throwing power.
Nickel (>1000 PPM): same as iron.
Selenium (>10 PPM): anode polarization, roughness.
Tellurium (>10 PPM): same as selenium.
Tin (500–1500 PPM): immersion deposits and polarization of anodes during idle time.
Zinc (>500 PPM): same as cadmium.

Troubleshooting Guide:

Problem	*Cause*	*Corrective Action*
High current density burning	Low copper	Analyze and adjust
	Low temperature	Heat bath
	Insufficient agitation	Lower current, unless agitation can be improved
	Organic contamination	Carbon treat
	Low chloride (bright baths)	Analyze and adjust
Loss of brightness (in bright formulations)	Low additive	Determine addition by hull cell
	Organic contaminants	Carbon treat
	Low chloride	Analyze and adjust
	High temperature	Cool the bath
	Low copper	Analyze and adjust
Rough deposit	Particles in solution	Filter bath
	Torn anode bags	Replace torn bag
	Improper anodes (bright baths)	Use phosphorized copper anodes for bright baths.
	Low chloride (bright baths)	Analyze and adjust
Pitting	Organic contamination	Carbon treat
	Anode slough	Bag anodes
	Low chloride (bright baths)	Analyze and adjust
Low current	Organic contamination	Carbon treat
	Low sulfuric acid	Analyze and adjust
	Low additive	Determine addition by Hull cell
	High chloride	Precipitate with silver nitrate and filter
	Current density too low	Increase current
	High temperature	Cool bath
Anode polarization	Tin, gold contamination	Dummy with a copper foil (no current)
	Low temperature	Heat bath
	Improper anodes	Bright baths require phosphorized anodes
	High chloride	Precipitate with silver nitrate and filter
	High sulfuric acid	Analyze and dilute bath
	Low copper sulfate	Analyze and adjust

COPPER FLUOBORATE BATH

This bath allows the use of higher current densities and increased plating speed since copper fluoborate is extremely soluble and large amounts can be dissolved in water. The main drawback is its corrosivity, consequently, construction materials are normally limited to: hard rubber, polypropylene, PVC, and carbon/karbate. In all other aspects, the copper fluoborate bath is similar to copper sulfate plating.

	High Concentration	*Low Concentration*
Copper fluoborate	60 oz/gal (450 g/L)	30 oz/gal (225 g/L)
Fluoboric acid	5.4 oz/gal (40.5 g/L)	2 oz/gal (15 g/L)
pH (colorimetric)	0.2–0.6	1.0–1.7
Temperature	65–150°F	65–150°F
Baume	37.5–39.5°	21–22°
Current density	125–350 ASF	75–125 ASF

The anodes should be OFHC copper. Anode bags should be made of Dynel or polypropylene. Normally, the bath is made up with copper fluoborate concentrate (1.54 gm/cc or 50.84° Be) which contains 92.0 oz/gal cupric fluoborate (26.9% by weight copper metal), 1.4 oz/gal fluoboric acid and 2 oz/gal boric acid (to prevent the formation of free fluoride due to fluoborate hydrolysis). The fluoboric acid (1.37 gm/cc on 39.16° Be) typically contains 90 oz/gal of fluoboric acid and 0.9 oz/gal of boric acid.

Contaminants:

Organic contaminants can affect the deposit appearance/uniformity and mechanical properties, especially ductility. These can be removed by carbon treatment. Cellulose filter aids, free of silica can be used. These baths are often carbon filtered continuously. Lead is the only common metallic contaminant which causes problems and it can be precipitated with sulfuric acid.

Additives:

Normally no organic additives are used. Molasses can harden deposits and minimize edge effects. Some of the same additives (e.g. acetyl cyanamide) used for copper sulfate baths can also be used with the fluoborate formulations.

Printed Circuits Handbook

by C.F. Coombs

914 pages $64.95

This how-to-book is a must for the practitioner's technical shelves and is required reading for anyone involved with the everyday problems arising in printed circuit manufacture. All aspects of the fabrication process are considered.

Send Orders to:
METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service, call (201) 487-3700
or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

GOLD PLATING

by Alfred M. Weisberg

Technic Inc., Providence, R.I.

All types of gold and gold alloy electroplates are applied for many different applications by many different industries. However, there are eight general classes that may be listed that will include much of present day gold plating.

Class A— Decorative 24K gold flash (2 to 4 millionths), rack and barrel.

Class B— Decorative gold alloy flash (2 to 4 millionths), rack and barrel.

Class C— Decorative gold alloy heavy (20 to over 400 millionths), rack. These deposits may be either C-1 karat color or C-2 karat assay.

Class D— Industrial/electronic high purity soft gold (20 to 200 millionths), rack, barrel and selective.

Class E— Industrial/electronic hard bright heavy 99.5% gold (20 to 200 millionths), rack, barrel, and selective.

Class F— Industrial/electronic gold alloy heavy (20 to over 400 millionths), rack and selective.

Class G— Refinishing, repair and general, pure and bright alloy (5 to 40 millionths), rack and selective brush.

Class H— Miscellaneous, including electroforming of gold and gold alloys, statuary and architectural, etc.

To further simplify an enormous and diverse subject, gold and gold alloy plating solutions may be considered to belong to five general groups:

1. Alkaline gold cyanide, for gold and gold alloy plating. Class A, B, C, D, occasionally F and G, and H.
2. Neutral gold cyanide, for high purity gold plating. Class D and G.
3. Acid gold cyanide, for bright hard gold and gold alloy plating. Occasionally Class B, C, E, F and G.
4. Non-cyanide, generally sulfite, for gold and gold alloy plating. Occasionally Class A, B, C, D, F, G and H.
5. Miscellaneous.

There are literally hundreds of formulations within these five classes of gold plating solutions.

Physical, engineering or aesthetic considerations will determine which of these groups should be considered for a particular job, but economics will usually be the determining factor in selecting a specific formulation and plating method. The price of gold per troy ounce is only one aspect of the economics that must be considered in deciding between rack, barrel, brush, continuous or selective plating. For any individual applications, it is necessary to balance and optimize:

1. The cost of the bath. The volume necessary for a particular method and the gold concentration.
2. The speed of plating. This determines the size of the equipment and the bath and the cost for a given desired production.
3. The cost of drag-out loss. This will depend on the gold concentration used, the shape of the part, if it is rack, barrel, continuous or selective plating, and must include the probable recovery of dragged-out gold by electrolytic or ion exchange recovery.
4. The cost of control and maintenance. Some high speed and high efficiency baths require almost constant attendance and analysis.
5. The cost of the longevity of the bath. High speed and especially high purity

TECHNIC PLATINUM CLAD ANODES

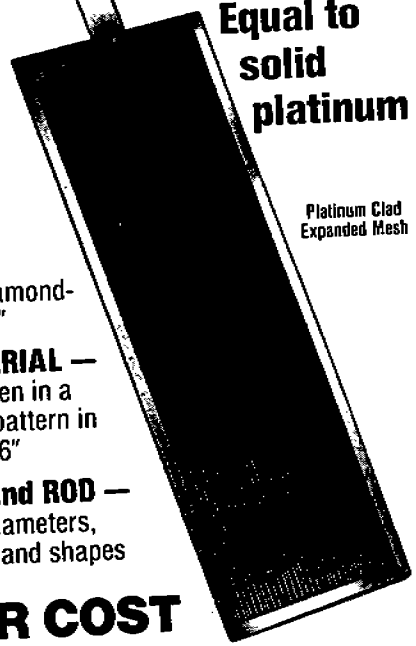
LONG LIFE

Anode Materials Cross Sections (500X)

Platinum Clad Columbium (Niobium)

Platinum Electroplated Titanium

Equal to solid platinum

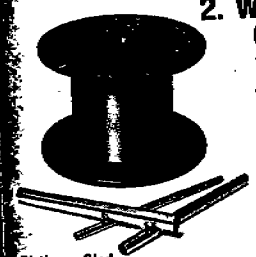


Platinum Clad Expanded Mesh

1. EXPANDED MESH — 1/16" diamond-shaped holes in widths up to 6"

2. WOVEN MATERIAL — Clad wire woven in a 10 x 10 mesh pattern in widths up to 36"

3. WIRE and ROD — Many diameters, lengths and shapes



Platinum Clad Wire and Rods

LOWER COST

- Permanent metallurgical bond
- Perfect for precious metal electroplating and accountability
- Longer life than electroplated anodes
- Excellent for high voltage applications
- Ideal for cathodic protection

TECHNIC INC EQUIPMENT DIVISION

CRANSTON, RI 401-781-6100 • ANAHEIM, CA 714-632-0200
SAN JOSE, CA 408-287-3732 • ILLINOIS 708-396-1221
TEXAS 214-790-8500 • KOREA • HONG KONG
SINGAPORE • EUROPE • CANADA • JAPAN • ASIA

401-728-7081 • 55 Maryland Ave., Pawtucket, RI 02860 • Fax 401-722-1720

baths with good drag-out recovery must be changed periodically to maintain purity. This results in a certain loss on changeover.

6. Cost of money (interest) to keep the bath.
7. The initial cost of the equipment.
8. The overhead cost of the equipment (whether it is operating or not operating), that is, the interest cost per hour or per day.

Sometimes a simple manual rack or barrel method will be cost effective and at other times, a high speed fully automated plant is justified.

Gold is, today, a freely traded commodity with a different price everyday. In order to plate successfully, it is necessary to watch and control costs.

DECORATIVE GOLD PLATING
Class A, B, C and sometimes G

Much, but not all, decorative plating is applied to jewelry, watch attachments, and other items of personal use and adornment. The thicknesses of gold or gold alloy are usually 0.000002–5" and the time of plating is 5 to 30 seconds. The recommended trade practice rules for the jewelry industry require that this deposit be called gold flash or gold wash. (In order to be called gold electroplate, it is necessary to have a minimum of 0.000007".) These deposits are usually applied over a bright nickel underplate and are bright as plated. They do not require any brightening agents or grain refining agents. There are hundreds of different colors and hues but the Class A and B baths shown in Table I will give a representative sample of colors.

All of the "coloring" baths in Table I should use 316 stainless steel anodes. The ratio of anode to cathode area is best at 1:1 or 3:1. Very high ratios, when the tank is used as an anode, tend to give an uneven color, and thickness of deposit and the end pieces will frequently burn. No agitation should be used to ensure a uniform color. Sliding or tapping on the cathode bar will increase the deposition of gold and make each color richer but will quickly deplete gold and unbalance the bath. Gold and alloying metals should be added periodically, based on ampere-hour meter readings. The baths, with the exception of the white, green and rose solutions, should operate at approximately 6% cathode current efficiency. Every 11 ampere-hours of operation, five grams of gold should be added, together with the proper amount of alloy.

All operating conditions should be controlled as closely as possible. Any variation of the conditions will affect the cathode current efficiency of either the gold or the alloy, or both. Changes in the amount of the metals deposited will change the color of the deposit. Other factors that will alter the color of the deposit are:

1. The surface finish of the basis metal will change the apparent color of the deposit. This is particularly noticeable when a single item has both bright and textured areas. Plated in the same bath, they will appear to be two different colors.
2. The color of the basis metal alters the color of the gold deposit by adding its color to the gold until the deposit is sufficiently thick to obscure the base. Most gold alloy deposits, if properly applied, will obscure the base after 2½ millionths of an inch have been applied. Proprietary additives will allow the gold to obscure the base with as little as 1½ millionths to allow richer colors with the use of less gold.
3. Current density. Too low a current density tends to favor the deposition of gold and causes the alloy to become richer. Too high a current density at first favors the alloy and pales out the color. Further raising the current density causes the development of pink or orange or red tones.
4. Free cyanide. Solutions containing copper are very sensitive to changes in the free-cyanide content. Low cyanide causes an increase in the pink or red shades and high cyanide significantly increases the yellow by holding back the copper.
5. Temperature. The effect is similar to current density. Low temperatures favor

IT'S BACK FROM THE GRAVE AND AFTER YOUR ENTIRE COMPANY.

Choose your precious metal refiner carefully. Or the refining media and precious metal bearing hazardous wastes your company generates could come back to haunt you.

Advanced Chemical Company knows that in today's environmentally conscious world, a precious metal refiner must do more than just refine precious metals. So we're skilled in manifesting, labeling, waste treatment and E.P.A. regulations. We also provide licensed hazardous waste transportation and an environmentally safe facility.

Call Advanced Chemical Company. We'll guarantee that your settlement check will be the end of your refining transaction. And we'll put your "cradle to grave" concerns to rest.

AC
ADVANCED CHEMICAL COMPANY

105 Bellows Street, Warwick, RI
Telephone (401) 785-3434
(800) 553-3568
Fax (401) 941-9210

Available From VMC

PLATINUM CLAD

NIOBIUM ANODES

Expanded Mesh Solid Strip

VMC now manufactures and markets a complete line of Platinum Clad Niobium Anodes. Our Clad Metal Anodes offer a smooth, uniform, non-porous layer of platinum metallurgically bonded to a niobium substrate. The cladding process affords a "densely packed" platinum anode surface with a superior performance in both high speed and high current density applications. Meanwhile, the niobium substrate, with its chemically resistant and advanced conductivity properties, complements the superior platinum clad composite. Therefore, making the **VMC ANODE** the right choice for both precious and base metal plating baths.

Permits increased production.

Applications include **precious metal** and **base metal** plating as well as **electrolytic recovery, anodizing, electroforming**, also some **fluoride** applications, and **electrochemical** process manufacturing.

Optimum Life/ Superior Control

VMC Pt Clad Nb Anodes are cost efficient. Often lasting as much as 4-5 times longer than platinum plated products. That's a potential 250% increase in cost efficiency over plated anodes.

Better current distribution allows for increased control of plating thickness.

Platinum thicknesses of 125μin or 250μin on one or both sides; supplied in strip or expanded mesh. Anodes can be fabricated to customer specifications.

Specify **VMC Pt Clad Nb Anodes** for your new equipment requirements and replacement needs.

For additional information, write or call:

VMC **VINCENT METALS CORPORATION**
84 Canonchet Rd., Hope Valley, RI 02832 • Phone: (401) 539-3053

Table I. Gold and Gold Alloy Flash Baths (Type A & B)

	HAMILTONS								
	24K or English	*Low Cyanide English*	*Yellow*	*Pink*	*Green*	*White #1*	*White #2*	*Green*	*Pink*	*Rose*
Gold as potassium gold cyanide, g/L	1.25-2	1.25-2	1.25-2	1.25-2	1.25-2	0.4	0.325	2	0.82	6
Free potassium cyanide, g/L	7.5	7.5	7.5	2.0	2.0	15	15	7.5	4	4
Dipotassium phosphate, oz/gal	2	2	2	2	2	2	2	2	2	—
g/L	15	15	15	15	15	15	15	15	15	15
Sodium hydroxide, g/L	—	—	—	—	—	—	—	—	—	—
Sodium carbonate, g/L	—	—	—	—	—	—	—	—	—	30
Nickel as potassium nickel cyanide, g/L		0.025-1.4	0.025	0.025	0.025	1.1	—	—	0.2	—
Copper as potassium copper cyanide, g/L	—	—	0.13	1.1	—	—	—	—	2.7	—
Silver as potassium silver cyanide, g/L	—	—	—	—	0.05	—	—	0.25	—	—
Tin, g/L	—	—	—	—	—	—	2.1	—	—	—
Temperature, °F	140-160	140-160	150-160	140-160	140-160	150-160	150-160	130-160	150-160	150-180
Current density, ASF	10-40	10-40	10-35	20-50	10-40	30-60	30-50	10-30	30-40	20-50

the gold yellows and higher temperatures favor the alloy colors. Temperatures over 160°F should be avoided, except in the case of rose golds, because of the rapid breakdown of cyanide and the darkening of the color.

6. pH. It is rarely necessary to adjust the pH of a gold or gold alloy bath. They are usually buffered between 10 and 11. Only pink or rose or red golds are favored by higher readings.

BARREL PLATING
Class A and B

Gold as $KAu(CN)_2$	0.4 g/L
Free cyanide NaCN	30 "
Disodium phosphate	23 "
Temperature	100–120°F
Anodes	Stainless steel 1:1 or better

In typical jewelry barrel plating, about 6 V is necessary. A decorative finish of 0.000002" is deposited in three to four minutes. If the parts are small and densely packed in the barrel, it may be necessary to plate up to eight minutes to get an even coverage.

The above formulation may be altered to achieve various colors. Champagne or light Hamilton colors may be achieved by adding 1.5 to 3 g/L of nickel. Lowering the temperature will also produce a lighter and more uniform color.

ANTIQUE GOLDS
Class A and B

The art of the 19th century platers was to produce a finish that looked as if it had been mercury gilt over silver or copper (Vermeil) and buried or weathered by the elements for a century or so. Each master plater developed an antique finish that was his trademark. The modern basic method to achieve this effect is to:

1. "Burn on" a dark smutty finish.
2. Relieve the highlights on a deeply recessed piece or the flat surface on a filigreed piece by either hand-rubbing with pumice and sodium bicarbonate, wheel-relieving with a cotton buff, tampico brush or a brass or nickel-silver wheel. Other methods are possible.
3. Flash gold or a gold alloy deposit on the imperfectly cleaned highlights.

The more the solutions in Table II are abused, and the more the operator violates good plating practice and good cleanliness, the better and more distinctive the finish will be.

Table II. Antique Baths

	Bright Yellow Highlights Orange Brown Smut	*Green Highlights Green Black Smut*
Gold as $KAu(CN)_2$, g/L	6	2
Silver as potassium silver cyanide, g/L	—	0.3
Sodium hydroxide, g/L	15	—
Sodium carbonate, g/L	30	—
Ammonium carbonate, g/L	—	38
Sodium cyanide, g/L	4	15
Temperature, °F	160–180	70–90
Agitation	none	none
Current density, ASF	30–40	10

GOLD SILVER

to meet all military and commercial specifications

TECHNISPEED® R, G
Ultra High Speed Golds for continuous plating.

OROSENE® 880
For vibratory plating.

OROSENE® GBX
Ultra High Speed Golds for continuous plating.

OROTEMP 24®, 24S, 24T Ultra pure neutral gold. Tight grained, ductile and heat resistant.

TECHNI GOLD 25®, 50, 75 NON-CYANIDE
Ultra bright, alkaline gold. Superior throw, color and corrosion resistance.

TECHNI-GOLD 16K, 18K and OROCLAD
Mirror bright alloy golds.

ELECTROLESS DMAB
Electroless gold.

ELECTROLESS BH

TECHNI-SILVER E, E-2
Ultra bright cyanide baths.

OROSENE 999®, and OROTHERM HT®
Heat resistant 24Kt hard acid bright golds.

OROSENE® 80
High Speed Barrel Plating.

OROTEMP 20, 20RS, 20R Ultra high speed golds. Bright pure gold.

HG BRIGHT GOLD
23Kt. low stress hard bright gold.

OROMERSE® and OROMERSE BR
Immersion/electroless golds.

ELECTRONIC GRADE POTASSIUM GOLD CYANIDE

TECHNI-SILVER Cy(−)LESS
NON-CYANIDE bright silver.

GOLD BRUSH PLATING SOLUTIONS
GOLD STRIPS
GOLD RECOVERY UNITS
RESINS and REFINING
GOLD PLATING EQUIPMENT and CONSOLES 1-200 Gallons
GOLD FAST FINGER PLATERS
Continuous PC Plating

Send for:
- Product Checklist
- Equipment Checklist
- Latest Govt. Gold Specs
- "What Gold To Use"

TECHNIC INC.
GOLD/RHODIUM/SILVER

RHODE ISLAND: 401-781-6100
ILLINOIS: 312-262-2662/TEXAS: 214-780-6500
CALIFORNIA: 408-287-3732/714-632-0200
CANADA: 416-283-7400/514-684-4563
EUROPE/HONG KONG/KOREA

An expensive finish, requiring double-racking, but a beautiful finish, is Russian Antique. This may be produced by relieving the green gold antique in Table II and then flashing over with the 24K or English gold.

Table III. A Selection of Typical Acid Gold Color Baths for Thick Deposits

	22 K Yellow	*24 K Yellow*	*Hamilton 1N*	*Hamilton 2N*	*Hamilton 3N*
Gold, g/L	4–8	4–8	4–8	4–8	4–8
Conducting salts, g/L	120	120	120	120	120
Nickel as nickel metal, g/L	0.2	—	7–10	4–6	1–3
Cobalt as cobalt metal, g/L	1	0.5	—	—	—
pH	4.0–4.5	4.4–4.8	4.0–4.2	4.0–4.2	4.0–4.2
Temperature, °F	90–100	80–90	120–140	100–120	90–100
Current density, ASF	10–20	10–20	10–20	10–20	10–20
Agitation	Required	Required	Required	Required	Required

The old bath antiques of the 1940's and 1950's that did not require double-racking or stringing are no longer practical because of the high price of gold.

HEAVY DECORATIVE GOLD
Class C-1 and C-2

It is necessary to distinguish between the actual karat assay of a gold alloy electroplate and the apparent karat color of the plate. In general, a decorative karat deposit will appear to be a much lower karat than it actually will assay. A 14K color deposit may actually assay 20 to 21 K. The formulas in Table III will deposit karat colors but will actually assay a higher karat. (In computing costs, it is best to assume the deposit is pure gold.)

INDUSTRIAL/ELECTRONIC GOLD PLATING

Gold is electroplated for many different electrical and electronic purposes, however, today the majority of gold plating is applied to three specific classes of components:

Semiconductors
Printed/etched circuits
Contacts/connectors

The requirements for the deposit of each of these components, and the methods of plating that are used, are:

	Purity	*Hardness*	*Surface*	*Rack*	*Barrel*	*Continuous*
Semi-conductors	99.95%	60–80 Knoop	mat	yes	yes	yes
Printed/etched circuits	99.5 – 99.7%	120–180 Knoop	bright	yes	no	yes
Contact/ connectors	99.5 – 99.7%	120–180 Knoop	bright	yes	yes	yes

The gold plating solutions that are actually used by the electronic plater may be conveniently classified by pH range.

The Optima series from Electrode Products includes oxide coatings such as IOA (iridium oxide), COA (combined metal and oxide), and RUA (ruthenium oxide).

Custom, state-of-the-art electrodes and electrocatalytic coatings

For automotive, electronic, & electrochemical applications

- OPTIMA™ anode and cathode coatings (recoatings)
- Substrate materials
- Substrate engineering
- Technical support
- Application development programs

To meet demand by the automotive and electronics industries, Electrode Products recently doubled its precious metal coated OPTIMA anode manufacturing. And for electrochemical applications, we had to quadruple electrode precious metal thermal coating manufacturing!

Why? Our anodes are virtually non-polluting, offer high chemical resistance, and last long, proving superior to nickel, lead, lead alloy, steel, graphite and magnetite. All for a price you can afford!

So if maximum, money-saving anode performance is in style with you, try Electrode Products.

ELECTRODE PRODUCTS, INC.
2 Milltown Court, Union, NJ 07083
Tel: (908) 851-6938
Fax: (908) 851-6906

ELC-174

Alkaline cyanide	pH over 10
Neutral cyanide	pH 6 to 9
Acid cyanide	pH 3½ to 5

(Below a pH of 3½, the gold cyanide is generally unstable and precipitates.)

Non-cyanide (usually sulfite)	pH 9 to 10

The baths that are primarily used by the industry are as follows:

	Alkaline cyanide	*Neutral cyanide*	*Acid cyanide*	*Non-cyanide*
Semiconductors	Class D	Class D	—	—
Printed circuits	—	—	Class E	—
Connectors	Class E	—	Class E	—

Low karat gold alloys, Group 2 or 3 (Class F), have not found much application in the US. The alloying metal generally affects the electrical properties of the gold adversely. As little as 1% of iron will increase the electrical resistance of gold over 1000%, and similar amounts of other metals have less, but still unacceptable, effects on the conductivity of the gold deposit. Even amounts of alloy, much less than 1%, will inhibit or totally prevent good welding or die bonding of semi-conductor chips to a gold surface. Duplex coatings of a low karat gold base overplated with a high karat gold surface, while acceptable in some applications from an electrical point of view, have tended to lose their economic advantages as good engineering and new design has required less total gold.

ALKALINE CYANIDE BATHS
Group 1 (Class D)

Typical baths that are still used are:

	Mat	*Bright*
Gold as potassium gold cyanide, g/L	8–20	8–20
Silver as potassium silver cyanide, g/L	—	0.3–0.6
Dipotassium phosphate, g/L	22–45	—
Potassium cyanide, g/L	15–30	60–100
pH	12	12
Temperature, °F	120–160	60–80
Anodes	stainless steel	stainless steel
Anode/cathode	1:1	1:1 to 5:1
Agitation	moderate-vigorous	none to moderate
Current density (Rack), ASF	3–5	3–8
Current density (Barrel), ASF	1–2	1–2
Current efficiency, %	90–95	90–100
Time to plate 0.0001"	8 min @ 5 ASF	7 min @ 6 ASF
Replenishment	1 oz gold/ 4½ amp-hours	1 oz gold/ 4½ amp-hours

Note: For the mat deposit, the higher the temperature, the better the deposit and the higher the speed of plating; however, temperatures over 150°F result in rapid breakdown of the free cyanide and a build up of cyanide breakdown impurities.

Platers who want to make money these days call on Engelhard's GOLD MIZER™ Program once and for all.

Gold Mizer combines all the advantages offered by Engelhard—breadth of line, advanced technology, responsive service—into a total approach to cutting your costs and improving efficiency.

Among the components of the Gold Mizer Program are:

- Engold™ process for improved metal distribution with current densities up to 2,000 ASF.
- Ultra-Life™ 3000 Series platinized titanium anodes for longer life performance.
- Tech Help 24™ for responsive tech service in 24 hours or less.
- Accuassay™ guarantee for full metal salt content.
- Full-value consignments and refining programs to streamline procurement procedures.
- M&T/Harshaw base metals and cleaners.
- Aurabrite decorative gold processes.
- Rhodium, platinum and palladium processes.

Plus many more. And one call can get them all. For information, see box below. For technical service, use the Tech Help 24 Hotline: 800-345-2608. Engelhard Precious Metals Coatings Group, 1 West Central Avenue, East Newark, NJ 07029.

Wherever you are, Engelhard is nearby.

U.S. East:	U.S. Midwest:	U.S. West:	Canada:
800-524-2887	708-595-8181	800-631-3341	416-727-3191
201-268-7828		714-779-7231	

ENGELHARD
EXCEPTIONAL TECHNOLOGIES

The alkaline cyanide baths are particularly sensitive to organic impurities—both those introduced by drag-in and by the absence of general cleanliness, as well as those caused by cyanide breakdown. In order to maintain a good appearing and structurally sound deposit, it is necessary to carbon treat and filter the solution periodically. The grade of carbon used must be pure enough not to introduce more impurities than it removes. Constant filtration through a filter packed with carbon is accepted practice, but is not as efficient in removing impurities as a batch treatment. If the solution is quite contaminated before treatment, it is important to save the used carbon and the used filter cartridge for refining to recover any gold lost in the treatment.

The best method to carbon treat a solution is to:

1. Heat the solution to 150–160°F.
2. Transfer the hot solution to an auxiliary tank.
3. Add 1/8 to 1/4 oz of carbon per gallon of solution.
4. Mix for no longer than 20 to 30 minutes.
5. Filter the solution by decantation back into the original tank.

No general rule can be given for the frequency of carbon treatment. This will depend upon general cleanliness and housekeeping, as well as the work being processed; however, it will vary from once every two weeks to once every two months. The room temperature bright bath will require much less carbon treatment than the hot cyanide bath.

NEUTRAL CYANIDE SOLUTIONS
Group 2 (Class D)

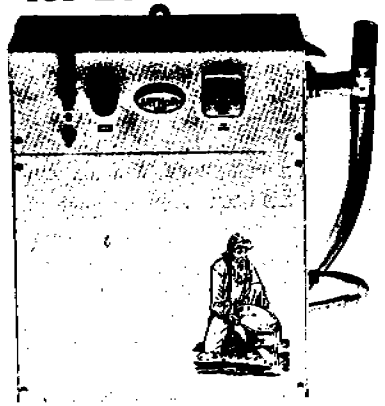
The neutral cyanide baths are primarily used by the semi-conductor industry. Considerable care must be exercised to prevent contamination of the solution as even a few parts per million of undesirable inorganics can cause the deposit to fail in compression or die bonding.

Typical non-proprietary solutions are:

	Rack or Barrel	*High Speed Continuous*
Gold as potassium gold cyanide, g/L	8–20	15–30
Monopotassium phosphate, g/L	80	—
or		
Potassium citrate, g/L	70	90
pH	6.0–8.0	4.5–5.5
Temperature, °F	160	120–160
Agitation	desired	violent
Anodes	Platinum clad columbium	Platinum clad columbium
Current density, ASF	1–3	100–400
Current efficiency, %	90	95–98
Time to plate 0.0001"	12 minutes	10–20 seconds
Replenishment	1 oz gold/ 4½ amp-hrs	1 oz gold/ 4½ amp-hrs

Note: Pulse plating may be used to advantage with the high speed formulation. Most effective is a 10% duty cycle. Proprietary baths add grain refiners that decrease porosity, increase the maximum allowable current density, decrease grain size, and generally improve the appearance of the deposit.

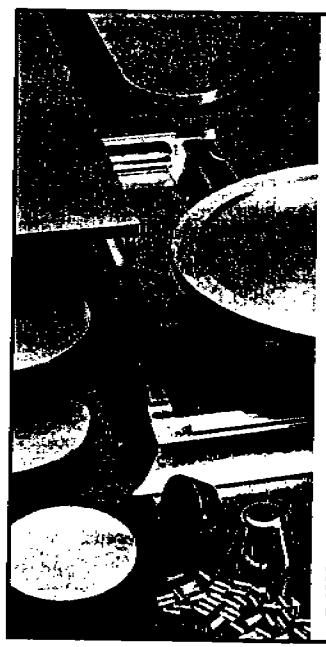
Auromet Precious Metals for the Plating Industry
Gold Solutions and Salts of superior quality; carefully and expertly prepared to give excellent results with economy
24 KARAT • BRIGHT • BARREL • DECORATIVE • HARD PREPLATE • CUSTOM MATCHED • POTASSIUM GOLD CYANIDE SALTS
Platinum and Indium ANODES AND PLATING SOLUTIONS
Silver . . . ANODES . . . BRIGHT SOLUTIONS . . . SILVER CYANIDE • POTASSIUM SILVER CYANIDE
Rhodium and Palladium PLATING SOLUTIONS AND CONCENTRATES
Complete Refining and Assay Service
Our Technical Staff is always available to assist you with your plating problems.
AUROMET CORPORATION
37 Chasner Street • Hempstead, N.Y. 11550 • 718-895-1066 • 516-538-4515
INQUIRE ABOUT OUR IMMERSION SOLUTIONS

Jaynor's Gold Digger:
Makes solid gold for 25¢ an ounce.

No more refining of solutions or burnable resins.
Just send metal. Like all great ideas, the Jaynor Precious Metal Recovery System –the Gold Digger– is simplicity itself. Instead of using bulky resins, the 38-lb TV-sized Gold Digger attaches to your dragout tank and plates the metal out on a cathode panel. The metal is 80% to 90% pure. Start mining solid gold!
Jaynor can design and build a custom Gold Digger to fit your specific needs.
JAYNOR INC. PRECIOUS METAL RECOVERY SYSTEM
Write or Call JAYNOR, INC. P.O. Box 1112
Falls Church, VA 22041 (703)256-2122

ACID CYANIDE PLATING SOLUTIONS
Group 3 (Class E)

	Barrel	*Rack or Barrel*	*High Speed/ Continuous*
	Mat Bath #1	*Bright* Bath #2	
Gold as potassium gold cyanide, g/L	8	8	8–16
Citric acid, g/L	60	60	90
Cobalt as cobalt metal, g/L	—	0.2–0.5	0.75
or			
Nickel as nickel metal, g/L			
pH	3.8–5.0	3.8–4.5	3.8–4.3
Temperature, °F	120–140	70–90	70–120
Anodes	platinum clad	platinum clad or stainless steel	platinum clad
Agitation	desirable	desirable	violent
Current density, ASF	1–5	5–20	100–400
Current efficiency, %		30–40	30–40
Time to plate 0.0001"		10 min @ 10 ASF	15 sec @ 400 ASF
Replenishment		1 oz gold/ 12 amp-hrs	1 oz gold/ 12 amp-hrs

Note: Pulse plating can be applied with the high speed bath, but is not widely used.



Sputtering and Evaporation Materials

Williams Advanced Materials offers a unique combination of products, service and experience.

- High purity precious metals • Fabrication
- Bonding • Analytic Capabilities
- Upgrading/Recycling

Since the development of Physical Vapor Deposition technology, Williams Advanced Materials has been supplying high purity precious metals to the PVD industry.

For more information, contact
Williams Advanced Materials
2978 Main Street, Buffalo, NY 14214
(716) 837-1000 / FAX: (716) 833-2926.

Williams ADVANCED MATERIALS
UNIQUELY QUALIFIED

INDIUM PLATING

by James A. Slattery

Indium Corp. of America, Utica, N.Y.

Indium Cyanide Bath:

Indium is the only trivalent metal that can readily be electrodeposited from a cyanide solution. Solution make-up and operational parameters are summarized in Table I. Indium hydroxide is first prepared by the precipitation of $InCl_3$ using NH_4OH or NaOH. The purified and dried $In(OH)_3$ is then dissolved in an alkaline cyanide solution stabilized with a sugar such as D-glucose, dextrose or sorbitol. The cyanide bath is used in applications demanding extremely high throwing power and adhesion. Deposits are uniform and bright mat in appearance. Since this is a high pH bath it has the disadvantage of requiring the use of insoluble anodes, necessitating replenishment in the form of an indium cyanide concentrate. Its cathode efficiency is initially 90% but upon bath aging decreases from this value to 50 to 75%; thus, periodic determination of the plating rate is required.

Indium Sulfamate Bath:

The indium sulfamate bath was developed to overcome several disadvantages of the cyanide bath.

Table I. Indium Cyanide Plating Bath

Indium as metal	4 Troy oz/gal (33 g/L)
Dextrose	4 " (33 ")
Total cyanide (KCN)	12.77 Av. oz/gal (96 ")
Potassium hydroxide (KOH)	8.5 Av. oz/gal (64 ")
Temperature (static)	Room temperature
Cathode efficiency	50–75%
Anodes	Plain Steel
Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Excellent
Critical temperature (working)	Difficult
Color of solution	None, with or without agitation
Wettability	Clear, pale yellow to dark amber
Tendency to pit	Easy
Control of solution	None
Use	Cyanide and metal by additions
Current	General
pH	15–20 ASF (162–216 A/m²)
	High pH

Replenishment: Since insoluble anodes are used, it is necessary to replace the indium metal content of this alkaline bath. A concentrate, Cy-An-In, can be added directly to the bath. Under normal conditions addition of cyanide will not be required, however, it is best to keep the cyanide concentration at about 100 g/L.

Efficiency: Plating efficiency of the bath will be maintained within a range suitable enough for normal plating until the indium content is reduced. Its plating rate should be checked at regular intervals because, as the bath is depleted, a decrease in rate of deposition is to be expected.

The sulfamate bath has the advantages of using soluble indium anodes and possesses a relatively constant cathode efficiency of 90% which remains stable for the life of the bath. Sulfamate baths are very stable and are considered one of the easiest of all plating baths to both operate and control. They even have a built-in pH indicator in that a milky white precipitate of indium hydroxide becomes evident if the pH should rise above 3.5. It is desirable, however, to closely control pH preferably to 1.5 to 2.0. pH tends to rise on operation and is lowered by the addition of granular sulfamic acid.

The bath possesses a throwing power only slightly less than the cyanide bath; deposits are uniform and bright mat in appearance. Operational parameters are summarized in Table II. One or more still water rinses incorporated after the plating tank will function as drag-out stations. Indium is easily recovered as $In(OH)_3$ by adjusting the pH to above 5 with sodium hydroxide. The indium hydroxide formed is allowed to settle, is collected, and can be shipped to refiners.

Indium Fluoborate Bath:

The fluoborate bath offers the advantages of fine grained deposits, ease of formulation from stable concentrates and low fluctuations in bath composition. pH is controlled by additions of fluoboric acid to the range of 0.5 to 1.5. The bath uses pure indium anodes at 100% anode efficiency. The major drawback of this bath is the low cathode efficiency of 40 to 75% which offsets advantages of plating at higher current densities. A split anode system (indium and platinum) is usually employed to aid in equalizing the variances in the cathode and anode current efficiencies. Table III lists the operational parameters of the indium fluoborate bath.

Table II. Indium Sulfamate Bath

Indium sulfamate	14 oz/gal (105.36 g/L)
Sodium sulfamate	20 " (150 ")
Sulfamic acid	3.5 " (26.4 ")
Sodium chloride	6 " (45.84 ")
Dextrose	1 " (8.0 ")
Triethanolamine	0.3 " (2.29 ")
pH*	1–3.5 (1.5–2 preferred)
Temperature (static)	Room temperature
Cathode efficiency	90%
Anode efficiency	Indium, 100%
Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Easy
Critical temperature (working)	None, with or without agitation
Color of solution	Clear (when new). After use will darken because of organic material breakdown. This has shown no effect on deposit. Filtering of bath can be done through activated carbon to maintain clarity of bath.
Wettability	Fairly easy
Tendency to pit	None
Control of solution	Metal and pH*
Use of solution	General
Current density	Optimum 10–20 ASF (108–216 A/m²). If metal is increased, current density can be increased up to 100 ASF (1080 A/m²)

*The pH of this bath is controlled by the addition of sulfamic acid.

Where else would you go for indium plating baths?

After all, Indium Corporation of America developed the first commercial indium plating bath. Which led us to the alkaline Cy-An-In® indium-cyanide bath and concentrate. And, for an acid bath of nearly comparable throwing power, the indium sulfamate bath.

We also offer indium anodes—cast, rolled or extruded to your specifications, plus these quality chemicals:

indium trifluoride
indium trichloride (anhydrous and solution)
indium nitrate
indium sulfate (anhydrous and solution)
indium sulfide
indium hydroxide
indium fluoborate (solution)
indium oxide
indium tin oxide

When you want the finest indium plating solutions, anodes and chemicals—delivered when you need them, call Indium Corporation of America. Who else?

INDIUM CORPORATION OF AMERICA

Corporate Headquarters: 1676 Lincoln Avenue, Utica, New York 13502
(315) 768-6400 or 800-4 INDIUM • Fax (315) 768-6362 or 800-221-5759
European Headquarters: INDIUM CORPORATION OF EUROPE
7 Grisedale Court, Woburn Road Industrial Estate, Kempston, Bedford MK42 7EE England
(0234) 840255 • Fax (0234) 841498

Table III. Indium Fluoborate Bath

Indium fluoborate	31.5 oz/gal (236 g/L)
Boric acid	2.9–4.0 " (22–30 ")
Ammonium fluoborate	5.3–6.7 " (40–50 ")
pH (colorimetric)	1.0
Temperature (static)	70–90° F (21–32° C)
Cathode efficiency	40–75%
Anode efficiency	Indium, 100%
Throwing power	Good
Quality of plate	Good
Ease of solution analysis	Easy
Critical temperature (working)	70–90°F (21–32° C) with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	None
Control of solution	Metal and pH*
Use	General
Current Density	50–100 ASF (540–1080 A/m²)

*The pH of this bath is controlled by the addition of 42% fluoboric acid. Some insoluble anodes (platinum or graphite) should be used, as the anode and cathode efficiency are not in good relation.

Complexed Chelated Alkaline Baths:

In the attempt to formulate a non-cyanide alkaline bath employing soluble indium anodes, several baths have been proposed using EDTA, nitrilotriacetic acid, tartrates and other chelating agents. Most have limitations in poor cathode efficiency and ease of recovery of spent plating solution and are not in widespread commercial use as compared to the sulfamate bath.

INDIUM
PLATING SOLUTIONS

Plating Baths
- Bright Indium Sulfamate Bath
- Indium Sulfate Bath
- Indium Fluoborate Bath
- Basic Indium Cyanide Bath

Indium Salts
- Indium Trifluoride
- Indium Trichloride
- Indium Hydroxide
- Indium Fluoborate
- Indium Sulfate
- Indium Sulfide
- Indium Oxide
- Indium Nitrate

Plus Indium Anodes in purity from 99 to 99.99999+%

ARCONIUM
SPECIALTY ALLOYS

Your Source for Indium Plating Solutions
400 Harris Avenue, Providence, RI 02909
401-456-0800, Fax 401-421-2419
Toll Free 800-343-0282

IRON PLATING

by Roland H. Williams

Bureau of Engraving, Washington, D.C.

Iron plating is used very rarely today due to the poor metalurgical properties of electrodeposited iron. The best deposits are obtained from the chloride bath and can, if heat-treated above 500°F, be bent and formed a small amount. All other solutions produce a deposit so brittle it cannot be stressed without breaking. The chloride bath, however, presents containment and environmental problems due to high temperature, toxicity, and acidity of the solution.

Iron deposits and the base metal are highly subject to hydrogen embrittlement. Unless some unique property of iron (such as magnetism) is necessary in the deposit, there is almost always a better alternative material. The last known use of iron plating in large volumes was for the plating of iron sleeves in light alloy engine blocks and for the electroforming of large, flat printing plates at the US Bureau of Engraving and Printing. These plates were machined to size on magnetic chucks.

Iron plating solutions are stable and simple to operate. The plating baths used are the chloride, fluoborate, sulfamate, and sulfate. Except for the chloride, these are all essentially slightly acid solutions and have the general characteristics of their nickel counterparts.

SOLUTIONS AND OPERATING CONDITIONS

Chloride Bath:

The most commonly usd is the ferrous chloride-calcium chloride solution. The advantage of this bath is its high conductivity, high permissible current densities or fast plating rates, and relatively strong, ductile, and smooth deposits.

Ferrous chloride, dihydrate	40–60 oz/gal
Calcium chloride	20–25 "
Temperature	190° to 210°F
pH (HCl)	0.2–1.8
Current density, no agitation	20 to 80 amp/ft²
with agitation	to 200 " "

Calcium chloride gives off heat in dissolving so the water used should not be hot to start. The solution is heated to above 150°F, the pH lowered to about 0.8 to 1.0 with hydrochloric acid, then degreased steel wool is added to reduce the ferric ion, and activated carbon to remove harmful organic impurities. The solution is finally filtered into the plating tank, using a siliceous filter aid.

Maximum ductility is obtained at higher temperatures, lowest pH and high current density. Heat treat at 500°F for two hours per ⅛" of thickness. Harder deposits are obtained at 190°F, pH above 1.0 and lower current densities.

Continuous addition of hydrochloric acid is recommended to control pH. High purity iron anodes must be used if ductile deposits are derived because the solution is easily contaminated by carbon and alloying metals found in steels.

Sulfate Baths:

Where plating speed is of no concern and lower operating temperatures are desired, the sulfate plating baths are suitable. The current density at which burning occurs is about one-half that of the chloride solution. The sulfate is also not as soluble as the chloride. On the other hand, the sulfate solution can be operated at appreciably lower temperatures than the chloride solution. For example, whereas the deposit stress becomes excessive below 190° in the chloride solution, the stress of a deposit from a sulfate solution is not excessive as low as 90°F if the current density is limited to 40 amp/ft².

1. *Ferrous Sulfate:*

Ferrous sulfate	32 oz/gal
pH	2.8–3.5
Temperature	90–150°F
Current density, maximum	40 amp/ft² at 90°F
	100 " at 150°F
Surface tension	40 dynes/cm

Cathode agitation is desirable.

2. *Ferrous Ammonium Sulfate:*

Ferrous ammonium sulfate	33–48 oz/gal
pH	2.8–5.0 "
Temperature	75–150°F
Current density	20 amp/ft² at 75°F
	to 100 " at 150°F

Cathode agitation is desirable.

Instead of ferrous ammonium sulfate, the bath can be prepared with 23-34 oz/gal ferrous sulfate ($FeSO_4 7H_2O$) plus 11-16 oz/gal ammonium sulfate.

3. *Mixed Sulfate-Chloride:*

Ferrous sulfate	33 oz/gal
Ferrous chloride	4.8 "
Ammonium chloride	2.7 "
pH	3.5–5.5
Temperature	80–160°F
Current density	20 to 100 amp/ft²

Cathode rod agitation.

Fluoborate Bath:

The fluoborate bath, like other flouborate solutions, received considerable impetus during the 1940's and early 50's. The solution has a high conductivity and good stability. The claim is made of higher current densities that the chloride solution at lower operating temperatures. The bath, in general, is similar to the others. The current efficiency drops with decreasing pH, the deposit is made brittle and stressed by organic contamination, and increased operating temperatures permit higher metal content and higher current densities.

Iron fluoborate	30.3 oz/gal
Metallic iron	7.37 "
Sodium chloride	1.34 "
Baume at 80°F	19–21°
pH (colorimetric)	3.0–3.4
Temperature	135–145°F
Average tank voltage	2–6
Average cathode current density	20–90 amp/ft²
Anode to cathode ratio	1:1

Two-thirds of the required amount of water is placed in the plating tank and the specified amount of sodium chloride is added. When the salt has been completely dissolved, the ferrous fluoborate concentrate is added directly into the tank. Water is then added to bring the volume of the solution up to its required concentration. After this, the solution should be adjusted to the specified operating pH, clarified by treatment with activated carbon in a storage tank and then filtered. The carbon may be built-up on the filter pads and the solution circulated through the filter, but sufficient time must be allowed to remove the solid particles and other contaminants. Electrolysis at 3-5 amp/ft² is also recommended. The bath is then heated to operating temperature and is ready for use.

Sulfamate Bath:

The sulfamate bath is similar to the sulfate but permits higher cathode current density. Iron sulfamate is available as a purified solution concentrate. The general characteristics of the deposit with respect to stress, hardness and permissible current density is similar to those from other iron plating baths. A particular bath and its operating conditions are:

	Range	*Recommended*
Iron as ferrous ion	9–15 oz/gal	10 oz/gal
Ammonium sulfamate	3–6 "	4–5 "
Sodium chloride	3–8 "	5–6 "
pH	2.5–3.3	2.7–3.0
Temperature	110–150°F	120–140°F
Current density	10–100 amp/ft²	50 amp/ft²

Proprietary addition agents are available to reduce the stress and, as in other iron solutions, a wetting agent is recommended to eliminate pitting. In general, precautions against contamination, and the usual purification procedures apply to this solution.

Electroplating and Related Processes

by J.B. Mohler

311 pages $53.50

This is a good introductory volume to the industry. The explanations are clear and the material is uncluttered with verbiage or meaningless illustrations. The reader wastes no time while preparing the groundwork for further study.

Send Orders to: METAL FINISHING, Three University Plaza, Hackensack, NJ 07601

For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

NICKEL PLATING

by George A. DiBari

International Nickel Inc., Saddle Brook, N.J.

Nickel plating for decorative, engineering and electroforming purposes is possible because the properties, including the appearance, of electrodeposited nickel can be controlled and varied over broad ranges.

Decorative nickel coatings are obtained by plating from solutions containing organic addition agents. The coatings are protective, mirror-bright and smooth.

Nickel coatings for engineering purposes are usually prepared from solutions that deposit pure nickel. The property sought in engineering end-uses is generally corrosion resistance, but wear resistance, solderability, magnetic and other properties may be relevant in specific applications.

Electroforming is a specialized use of the electroplating process in which nickel is deposited and subsequently removed from a mandrel to yield an all-nickel component or article. Electroformed nickel tools, such as molds, dies, record stampers, seamless belts and textile printing screens are important commercial products.

The processes used for decorative, engineering and electroforming purposes have a great deal in common, but differ in detail. The details are described below after considering what the various processes have in common.

BASIC CONSIDERATIONS

All nickel plating processes have certain features in common and are limited by natural laws which determine the rate of deposition, the thickness of the coating and its distribution. These laws make it possible to control the process and operate it continuously.

The Process:

Nickel plating is the electrolytic deposition of a layer of nickel upon a substrate. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). Direct current is applied between the anode (positive) and the cathode (negative). Conductivity between the electrodes is provided by an aqueous solution of nickel salts.

When nickel salts are dissolved in water, the nickel is present in solution as divalent, positively charged ions (Ni^{++}). When current flows, divalent nickel ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni°) at the cathode. The reverse occurs at the anode where metallic nickel dissolves to form divalent ions. The electrochemical reaction in simplest terms is:

$$Ni^{++} + 2e^- \rightleftharpoons Ni^\circ$$

Because the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode, the nickel plating process can be operated for long periods of time without interruption.

Estimating Nickel Thickness:

The amount of nickel that is deposited at the cathode is determined by the product of the current (amperes) and the time (hours). Under ideal conditions, 26.8 amperes flowing for one hour will deposit 29.4 grams of nickel (1.095 grams per ampere-hour).

If the area being plated is known, the average thickness of the nickel coating can be estimated. For example, if 29.4 grams of nickel are deposited on one square foot of area, the thickness of the deposit is 0.0014". (Thickness equals the weight of nickel divided by the product of the area and the density of nickel. It is important to use consistent units. The density of nickel is 0.322 lbs/in³).

Because a small percentage of the current is consumed at the cathode in discharging hydrogen ions, the efficiency of nickel deposition is less than 100%. This fact must be taken into account in estimating the weight and the thickness of nickel that will be deposited under practical plating conditions.

Table I is a data sheet on depositing nickel based on 96.5% cathode efficiency. The table relates coating thickness, weight per unit area, current density and time of plating.

Some factors useful in making nickel plating calculations are given in Table II.

Table I. Data Sheet on Depositing Nickel (Based on 96.5% Cathode Efficiency)

Thickness in Inches	*Thickness in Micrometers*	*Oz/ft²*	*G/ft²*	*Amp-hr*	*Minutes for Obtaining Coating at Various Current Densities, A/ft²* 10	20	50	100
0.0001	2.5	0.0721	2.04	1.99	12	6	2.4	1.2
0.0002	5.1	0.144	4.08	3.98	24	12	4.8	2.4
0.0005	12.7	0.360	10.20	9.95	59.6	30	12.2	6.1
0.0008	20.3	0.578	16.32	15.9	95.6	47.8	19.2	9.6
0.0010	25.4	0.721	20.40	19.9	119.2	59.6	23.9	12.0
0.0015	38.1	1.082	30.60	29.8	178.8	89.3	35.7	18.0
0.0020	50.8	1.44	40.80	39.8	238.4	119	47.7	23.9

Table II. Factors Useful in Making Nickel Plating Calculations (Assume 100% Cathode Efficiency)

Multiply	*By*	*To Estimate*
Wt of $NiSO_4 \cdot 7H_2O$	21%	Wt of Ni contained
Wt of $NiSO_4 \cdot 6H_2O$	22%	Wt of Ni contained
Wt of $NiCl_2 \cdot 6H_2O$	25%	Wt of Ni contained
Wt of $NiCl_2 \cdot 6H_2O$	30%	Wt of Cl contained
Wt of nickel carbonate	50%	Wt of Ni contained
Amp-hrs nickel plating	1.095	g nickel deposited
	0.0386	oz nickel deposited
Amp-min/ft²	0.000869	Mils nickel deposited
Mils thickness	19.18	amp-hr/ft²
	1151	amp-min/ft²
	0.0226	g/cm²
	0.742	oz/ft²

Anode efficiency is normally 100%. Because anode efficiency exceeds cathode efficiency by a small percentage, nickel ion concentration and pH will rise as the bath is used.

Drag-out of nickel plating solution may compensate for nickel metal build-up in solution to some extent, but at some point it may be necessary to remove a portion of solution from the plating tank and replace the solution removed with water and other constituents. The pH of the solution is maintained by adding acid.

Metal Distribution:

The relation between current and thickness distribution is an important basic consideration. It is desirable to apply uniform thicknesses of nickel on all significant surfaces to achieve predictable service life and to meet plating specifications which require minimum coating thickness values at specified points on the surface.

The amount of metal that will deposit on the surface of any object being plated will be proportional to the current that reaches the surface. Recessed areas on the surface will receive less current.

The current density and, consequently, the rate of metal deposition in the recessed area will be lower than at points which project from the surface. The electrodeposited coating will be relatively thin at recessed areas, and relatively thick on projecting areas (Fig. 1).

The thickness of the deposit at the cathode and the distribution of the coating can be controlled by proper racking and placement of the parts in solution, and by the use of thieves, shields and auxiliary anodes. Parts can be designed to minimize problems. It may be necessary to deposit more nickel than is specified to meet a minimum thickness requirement on a specific article.

The nickel processes used for decorative, engineering and electroforming purposes thus all have the same electrochemical reaction in common. The weight of nickel deposited at the cathode is controlled by natural laws which make it possible to estimate the thickness of the nickel deposited. These estimates must be adjusted to account for variations in cathode efficiencies for specific processes.

Normally, cathode efficiency values are between 93 and 97% for most nickel processes. The actual thickness at any point on a shaped article depends on current flow. In practice, it is necessary to measure coating thicknesses on actual parts before thickness can be controlled within a specified range.

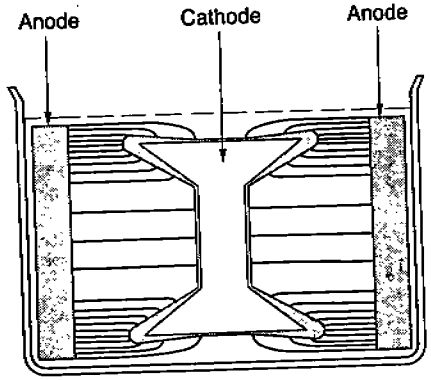


Fig. 1. Current distribution is not uniform over a shaped article. Areas remote from the anode will receive a smaller share of the available current than areas near to the anode.

Trouble-free plating is in the bag...

because out of our handy, easy-pouring, 10 kg bags come the world's purest electrolytic nickel anodes – Falconbridge Crowns, Microcrowns and D-Crowns. The round, smooth shape of these products will save you time as they pour easily and have superb settling properties without bridging. What's more, when they're supplied in our 50 kg or 250 kg drums, they can be scooped, swiftly and efficiently.

Consistent purity and versatile packaging are just two of the many ways that Falconbridge helps keep customers competitive in a tough, ever-changing marketplace.

Our world-wide resources are focussed on providing products and services which will satisfy the highest quality standards.

At Falconbridge, we put your plating needs first. And that's worth considering before you place your next nickel order.

Quality nickel products from Falconbridge

Falconbridge U.S. Incorporated
Twin Towers, Suite 245
9955 Steubenville Pike
Pittsburgh, Pennsylvania 15205-9604
Phone 412/787-0220 Fax 412/787-0287

Falconbridge Limited
95 Wellington St. W., Suite 1200
Toronto, Ontario, Canada M5J 2V4
Phone 416/956-5700
Fax 416/956-5757

DECORATIVE NICKEL PLATING

The technology of decorative nickel plating has undergone many improvements over the years. The introduction of bright and semi-bright, nickel solutions, the development of multilayer nickel coatings, and the use of conventional, microporous and microcracked chromium in combination with multilayer nickel coatings are some examples.

Decorative Processes:

The solutions used for decorative plating differ from those for other applications in that they contain organic addition agents which modify the growth of the nickel deposit to produce fully-bright semi-bright and satin-like surfaces. The basic constituents — nickel sulfate, nickel chloride, and boric acid — serve the same purposes as they do in the Watts solution (Table III).

Nickel sulfate is the principal source of nickel ions; nickel chloride improves anode dissolution and increases solution conductivity; boric acid helps to produce smoother, more ductile deposits.

Anionic anti-pitting or wetting agents are required to reduce pitting due to the clinging of hydrogen bubbles to the products being plated. Nonfoaming wetting agents which lower surface tension are available for air-agitated solutions.

The composition and operating conditions given in Table III for the Watts solution are typical of many decorative nickel plating solutions, but wide variations in the concentrations of nickel sulfate and nickel chloride are possible. Since most decorative nickel plating processes are proprietary, composition and operating conditions should be controlled within the limits recommended by the suppliers.

Table III. Typical Compositions, Operating Conditions and Approximate Mechanical Properties of Deposits from Several Electrolytes

Constituents	*All Chloride*		*Chloride Sulfate*		*All Fluoborate*		*All Sulfate*		*All Sulfamate*		*Chloride Sulfamate*		*Hard Sulfamate*		*Watts*		*Hard Watts*	
Typical Electrolyte Compositions—g/L(oz/gal)																		
Total nickel	75	(10)	86.4	(11.5)	75	(10)	70	(9.3)	84	(11.2)	84	(11.2)	45	(6)	78	(10.4)	60	(8)
Nickel chloride	300	(40)	158	(21)							22.5	(3)	7.5	(1)	60	(8)	45	(6)
Nickel sulfate			188	(25)			330	(44)							300	(40)	262	(35)
Nickel sulfamate									450	(60)	428	(57)	248	(33)				
Nickel fluoborate					300	(40)												
Boric acid	30	(4)	37.5	(5)	30	(4)	30	(4)	37.5	(5)	37.5	(5)	30	(4)	30	(4)	30	(4)
Anti pitter	X		X		X				X		X		X				X	
Addition agent													Optional stress reducer				Optional stress reducer	
Operating Conditions																		
Temperature °C (°F)	55	(130)	55	(130)	55	(130)	55	(130)	60	(140)	60	(140)	55	(130)	55	(130)	50	(122)
pH	2.0		3.0		2.7		1.5		4.0		4.0		5.0		3.0		5.0	
Current density, A/m² (A/ft²)	540	(50)	540	(50)	320	(30)	400	(40)	540	(50)	540	(50)	600	(60)	540	(50)	540	(50)
Mechanical Properties																		
Tensile strength, MPa(ksi)	690	(100)	517	(75)	400	(58)	480	(70)	413	(60)	758	(110)	896	(130)	413	(60)	1170	(170)
Hardness, DPN (100 g load)	240		230		150		170		190		300		470		150		350	
Elongation, % in 50.8 mm (2 inches)	14		20		30		28		30		5		6		28		2	
Internal stress, MPa(ksi)	345	(50)	220	(32)	138	(20)	117	(17)	14	(2)	69	(10)	Variable according to addition agent		138	(20)	Variable according to addition agent	

NICKEL CHEMICALS

- Nickel Acetate
- Nickel Carbonate
- Nickel Chloride
- Nickel Sulphate
- Nickel Sulphamate
- Nickel Nitrate

Call us for a total listing of the chemicals, solutions and compounds we produce for the metal finishing industry.

CP/PhibroChem
A Division of Philipp Brothers Chemicals, Inc.
1 Parker Plaza, Fort Lee, NJ 07024
1-201-944-6020

CHEMISTRY FOR PRECLEANING & SURFACE TECHNOLOGY

- METAL–AID™ Nickel Activator for precleaning or preplating
- Results in the highest quality plated parts

APPLICATIONS:

✓ Electronics Finishing
✓ Industrial & Decorative Nickel
✓ Precious Metals Plating

For details call Jeff Puma at:
PCT TECHNOLOGY
30 Downhill Lane
Wantagh, New York 11793
Phone or Fax: 516/221-4537

Bright Nickel Solutions:

Bright nickel solutions contain at least two classes of organic additon agents which complement each other and yield fully-bright nickel deposits.

The first class produces deposits that are mirror-bright initially, but are unable to maintain the mirror-like appearance of the deposit as its thickness is increased. This class includes compounds like benzene disulfonic acid, benzene trisulfonic acid, napthalene trisulfonic acid, benzene sulfonamide and sulfonimides, such as saccharin. The presence of the sulfon group and an unsaturated bond adjacent to the sulfon are critical characteristics.

Adsorption of the additon agent occurs by virtue of the unsaturated bond onto growth sites, points or edges of crystals and at dislocations. The organic compound is reduced electrochemically at the cathode, and this is accompanied by the reduction and incorporation of sulfur (as the sulfide) in the deposit. Fully bright nickel deposits typically contain 0.06 and 0.10% sulfur. These reactions control the structure and growth of the nickel as it is deposited.

The second class of addition agents may be termed leveling agents because they make the surface smoother as the thickness of the deposit is increased. They are sulfur-free, bath soluble organic compounds containing unsaturated groups and generally introduce small amounts of carbonaceous material into the deposit. Typical examples of second class brighteners are formaldehyde, coumarin, ethylene cyanohydrin and butynediol.

The combination of these two classes of organic addition agents makes it possible to obtain brilliant, lustrous deposits which are smooth over wide ranges of coating thickness. The deposits have a bonded structure consisting of closely spaced laminations believed to be related to the codeposition of sulfur.

Your #1 Source for Metal Finishing

BISON

INCO Nickel—All Types and Shapes • Metal Finishing Supplies and Equipment • Brighteners and Agents • Industrial Chemicals and Processes • Buffs • Compositions • Coated Abrasives • Cleaners • Acids • Alkalies • Anodes: Cadmium, Zinc, Brass, Copper, Lead, Tin.

BISON CORPORATION
(216) 455-0282
1935 Allen Ave., S.E., Canton, Ohio 44707

PAX

Technology For Metal Finishing

- *PAXBRITE*
  Brass, Cadmium, Copper & Zinc Plating Brighteners
- *VISTABRITE*
  Nickel and Bright Nickel Plating Processes
- *ENPAX & SPECLAR*
  Electroless Nickel Plating Systems
- *AURASTAN & PAXPLATE*
  Matte and Bright Tin and Tin-Lead Plating Processes
- *CHEMAX, PAXDIP & ALCROMAX*
  Conversion Coatings & Bright Dips

PAX SURFACE CHEMICALS, INC.
SYOSSET, NY 11791
516/822-7860 • Fax 516/932-9373
Distributor Inquiries Invited

Certain cations — zinc, selenium, cadmium — enhance the luster of electrodeposited nickel, and have been used in combination with the first class of brighteners.

Supply houses provide instructions for proprietary bright nickel processes, including the rates of replenishment and methods of analyses for the organic addition agents.

Semi-Bright Nickel:

Semi-bright nickel solutions contain nickel sulfate, nickel chloride, boric acid and a leveling agent. The most popular process makes use of coumarin as the principal additive. Coumarin-free processes are a more recent development.

As implied by its name, the process yields deposits that are semi-lustrous. The deposits are smooth and have a columnar structure unlike the bonded structure characteristic of fully bright deposits.

The solution was developed to facilitate polishing and buffing; i.e., semi-bright nickel deposits are easily polished to a mirror finish. Efforts to eliminate the need for polishing led to the combination of semi-bright and bright nickel deposits. This subsequently led to the greater use of multilayer nickel coatings, not only to minimize polishing, but to improve corrosion performance of decorative nickel coatings.

Single and Multilayer Nickel Coatings:

Single and multilayer nickel coatings are used to produce decorative coatings that resist corrosion. Single-layer bright nickel deposits are specified for mildly corrosive service where nickel thickness is about 5 to 12 micrometers (0.2 to 0.5 mil).

Double-layer coatings are specified for use in severe and very severe service. In double-layer coatings, the first nickel layer is deposited from a semi-bright bath. The second layer is then deposited from a bright bath.

In practice, the thickness ratio of the first to the second layer is 3:1; for example, in highly corrosive environments the thickness of the semi-bright nickel layer is about 22.5 micrometers (0.9 mil), whereas the thickness of the bright layer is about 7.5 micrometers (0.3 mil).

Triple-layer coatings may also be used in severe and very severe service. In this case, a special thin layer of bright, high-sulfur nickel is deposited between the initial layer of semi-bright nickel and the top layer of bright nickel.

The very thin layer should comprise about 10% of the total nickel coating thickness and must contain greater than 0.15% sulfur (as compared to 0.06 to 0.10 normally found in fully bright deposits).

Multi-layer nickel coatings provide improved protection because the highly active, sulfur-bearing nickel layer protects the underlying sulfur-free layer by sacrificial action.

Microdiscontinuous Chromium:

Electrodeposited chromium coatings are used in combination with decorative nickel to prevent the tarnishing reaction that slowly occurs when nickel is exposed to the atmosphere. The chromium coating is relatively thin compared to the nickel because electrodeposited chromium is not intrinsically bright and will become dull if thickness is increased beyond an acceptable level. The brightness is not affected if chromium thickness is on the order of 0.4 micrometers (15 microinches).

Studies of the corrosion performance of decorative nickel plus chromium coatings revealed a tendency to form one or two relatively large corrosion pits that would rapidly penetrate to the basis metal. This was believed to be due to the relatively low porosity of the top layer of chromium.

It was concluded by many investigators that a pore-free chromium electrodeposit should improve corrosion resistance. The pore-free chromium plating processes developed in the early '60s were short-lived when it was observed that the deposits did not remain pore-free in actual service.

Other investigations concluded that chromium deposits with high porosity or crack densities on a microscopic scale would be preferable. This led to the development of microdiscontinuous chromium deposits of two types: microporous and microcracked.

These processes greatly improve corrosion performance by distributing the available corrosion current over a myriad number of tiny cells on the surface of the coating. As a result, corrosion proceeds uniformly over the entire surface, instead of concentrating at one or two pores, and the rate of pit penetration is slowed dramatically.

Double-layer nickel coatings 40 micrometers thick (1.5 mils) electroplated with either microporous or microcracked chromium and applied uniformly resisted corrosion in severe service for more than 16 years.

The progress made in the technology of decorative nickel plating has led to great improvement of the corrosion resistance of nickel plus chromium coatings. What is not often appreciated is that this has been accomplished without increasing the thickness of the nickel coating. This has kept nickel plating practical and cost competitive.

ENGINEERING NICKEL PLATING

Engineering or industrial applications for electrodeposited nickel exist because of the useful properties of the metal. Nickel coatings are used in these applications to modify or improve surface properties, such as corrosion resistance, hardness, wear and magnetic characteristics.

Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in the preceding section are not usually required.

Engineering Plating Processes:

Table III gives typical compositions and operating conditions for many electrolytes suitable for engineering applications.

Mechanical Properties:

The mechanical properties are influenced by the chemical composition and the operation of the plating bath, as indicated by the information included in Table III. The tensile strength of electrodeposited nickel can be varied from 410 to 1170 MPa (60 to 170 psi), and the hardness from 150 to 740 DPN, by varying the electrolyte and the operating conditions.

The operating conditions significantly influence the mechanical properties of electrodeposited nickel. Figures 2, 3 and 4 show the influence of pH, current density and

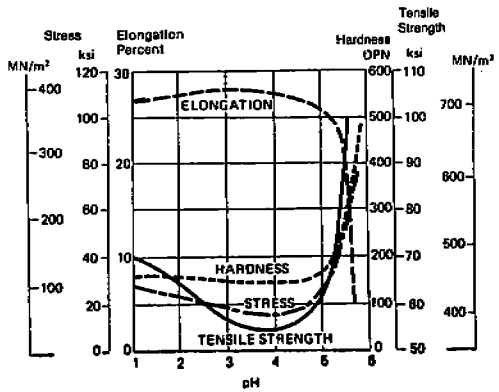


Fig. 2. Variation in internal stress, tensile strength, ductility and hardness with pH. Watts bath 54°C (130°F) and 495 A/m² (46 A/ft²).

Electroplating of Zinc Die Castings

by S.K. Jalota

225 pages $85.00

This book provides a quite exhaustive coverage of plating on zinc die castings starting with design and production with emphasis on its relation to plating. Subsequent chapters treat polishing, buffing and mass finishing, cleaning and pretreatment and the equipment for plating. The balance of the book runs the gamut of the various metals that can be deposited. Each chapter devotes a portion to troubleshooting, causes of defects and remedies. Concluding chapters concerning coloring, lacquering, stripping of deposits and analysis and testing.

Send Orders to:

METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service,
call (201) 487-3700 or
FAX your order to
(201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

C-12 ACTIVATOR™
Pat. Pend

FOR NICKEL OVER NICKEL, SILVER OVER NICKEL, CHROME OVER CHROME, GOLD OVER COPPER, PAINT OVER GLASS AND CERAMICS. REDUCES ALL METALLIC OXIDES TO INSURE PERFECT BOND.

ELECTROLESS NICKEL:

A 15 second immersion in our C-12 ACTIVATOR™ bath allows you to plate nickel over nickel. The second coat of nickel will have 100% adhesion over the first. Passivation is eliminated. PUMA C-12 ACTIVATOR™ is environmentally responsive.

PUMA™
PUMA CHEMICAL CORP.
P.O. Box 1388 W. Babylon
New York 11704-1388 USA
Phone: 800/831-0762 FAX: 516/491-7372
For Puma products and service in Western United States contact Millhorn Chemical & Supply Co., Maywood, CA 90270. Ph. (213) 771-8301.

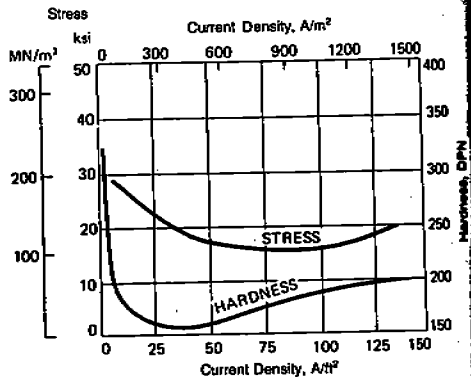


Fig. 3. Variation in internal stress and hardness with current density. Watts bath 54°C (130°F) and pH 3.0.

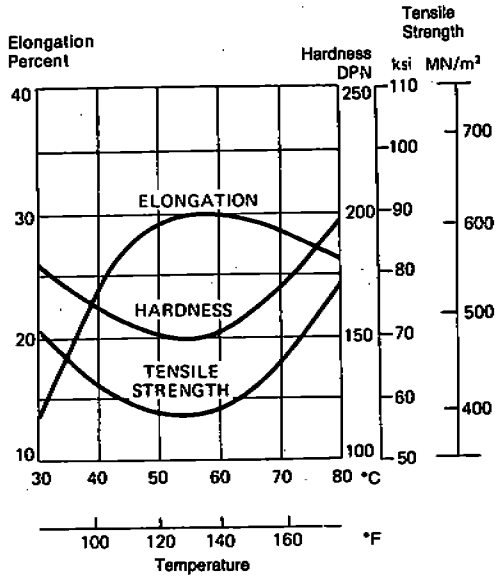


Fig. 4. Variation in elongation, tensile strength and hardness with temperature. Watts bath pH 3.0 and 495 A/m² (46 A/ft²).

temperature on the properties of nickel deposited from a Watts bath. Additional information is given in Tables IV and V which describe how various properties are affected by changes in operating variables and solution composition.

The mechanical properties of electrodeposited nickel vary with the temperature to which the coatings are exposed, as summarized in Fig. 5. The tensile strength, yield strength and ductility of electrodeposited nickel decrease steadily with an increase in temperature from −240 to 870°C (−400 to 1600°F).

The ductility of electrodeposited nickel reaches low values above 480°C (900°F). Nickel deposits from sulfamate solutions are stronger at cryogenic temperatures than deposits from the Watts bath. The electrolytes used to prepare the deposits for these studies are those given in Table VI.

Table IV. Variables Which Affect Mechanical Properties of the Deposit-Watts Solution

Property	*Operational* / *Solution Composition*	
Tensile strength	Relatively independent of plating solution temperature within range suggested.	Increases with increasing nickel content.
	Relatively independent of changes in cathode current density.	Increases with increasing chloride content.
	Relatively independent of pH variation within range suggested.	
Elongation	Increases with temperature to 55°C (130°F) followed by slight decrease at higher temperature.	Decreases with increasing nickel content.
	Relatively independent of pH variation within range suggested.	
Hardness	Decreases with temperature rise to 55°C (130°F) but increases with higher temperatures.	Increases with increasing nickel content.
	Decreases significantly with increasing cathode current density to 540 A/m² (50 A/ft²). At higher current densities the hardness increases with increasing current density.	Increases with increasing chloride content.
Internal stress	Relatively independent of plating solution temperature.	Increases slightly with increasing nickel content.
	Decreases slightly, then increases with increasing cathode current density.	Increases markedly with increasing chloride content.
	Relatively independent of pH variation within range suggested.	

Table V. Variables Which Affect Mechanical Properties of the Deposit-Nickel Sulfamate Solution

Property	*Operational*	*Solution composition*
Tensile strength	Decreases with increasing temperature to 49 °C (120 °F), then increases slowly with further temperature increase.	Decreases slightly with increasing nickel content.
	Increases with increasing pH.	
	Decreases with increasing current density.	
Elongation	Decreases as the temperature varies in either direction from 43 °C (110 °F).	Increases slightly with increasing nickel content.
	Decreases with increasing pH.	Increases slightly with increasing chloride content.
	Increases moderately with increasing current density.	
Hardness	Increases with increasing temperature within operating range suggested.	Decreases slightly with increasing concentration of nickel ion.
	Increases with increasing solution pH.	Decreases slightly with increasing chloride content.
	Reaches a minimum at about 1300 A/m² (120 A/ft²).	
Internal stress	Decreases with increasing solution temperature.	Relatively independent of variation in nickel ion content within range suggested.
	Reaches a minimum at pH 4.0-4.2.	Increases significantly with increasing chloride content.
	Increases with increasing current density.	

Fig. 5. Effect of temperature on the tensile strength, yield strength and elongation of electrodeposited nickel.

Table VI. Composition and Operating Conditions of Typical Industrial-Type Electrolytes

	Plating Bath		
Constituent and Conditions	*Watts*	*All-Chloride*	*Sulfamate*
Nickel sulfate, $NiSO_4 \cdot 7\,H_2O$	300 g/L (40 oz/gal)	—	—
Nickel chloride, $NiCl_2 \cdot 6\,H_2O$	60 g/L (8 oz/gal)	300 g/L (40 oz/gal)	—
Nickel sulfamate, $Ni(H_2NSO_3)_2$	—	—	400 g/L (60 oz/gal)
Boric acid, H_3BO_3	37.5 g/L (5 oz/gal)	37.5 g/L (5 oz/gal)	30 g/L (4 oz/gal)
pH	3.0	3.0	4.5
Temperature	60 °C (140 °F)	60 °C (140 °F)	57 °C (135 °F)
Current density, A/m² (A/ft²)	430 (40)	430 (40)	430 (40)

Note: Proprietary wetting agents were used to prevent pitting.

Corrosion Resistance:

Engineering nickel coatings are frequently applied in the chemical, petroleum, food and beverage industries to prevent corrosion, maintain product purity and prevent contamination. As a general rule, oxidizing conditions favor corrosion of nickel in chemical solutions, whereas reducing conditions retard corrosion.

Nickel also has the ability to protect itself against certain forms of attack by developing a passive oxide film. When an oxide film forms and is locally destroyed as in some hot chloride solutions, nickel may form pits. In general, nickel is resistant to neutral and alkaline solutions, but not to most of the mineral acids.

Corrosion resistance in engineering applications is controlled by optimizing nickel thickness. The thickness of the nickel to be used is dependent on the severity of the corrosive environment. The more corrosive the service conditions the greater the thickness of nickel required. Thickness generally exceeds 0.003" (75 μm).

Nickel Plating and Fatigue Life:

Thick nickel deposits applied to steel may cause significant reductions in the composite fatigue strength in cyclical stress loading. The reduction in fatigue strength is influenced by the hardness and strength of the steel and the thickness and internal stress of the deposits.

Elimination of, or the lowering of, internal stress of the deposits is an important factor. Fatigue life is enhanced by increasing the hardness and strength of the steel, and by specifying the minimum deposit thickness consistent with design criteria.

Compressively stressed nickel deposits are beneficial. Shot peening the steel prior to plating helps minimize reduction in fatigue life upon cyclical stress loading.

Hydrogen Embrittlement:

Highly stressed, high strength steels are susceptible to hydrogen embrittlement during normal plating operations. Because nickel plating is highly efficient, hydrogen embrittlement is unlikely to occur as a result of nickel plating, per se.

The pretreatment of steel prior to plating, however, may require exposing the steel to acids and alkalies. During these operations, excessive amounts of hydrogen may be evolved which may damage steels susceptible to hydrogen embrittlement.

Steels that are susceptible to hydrogen embrittlement should be heat treated at 205°C (440°F) for several hours to remove the hydrogen. The time required may vary from eight to 24 hours depending on the type of steel and the amount of hydrogen to be removed.

NICKEL ELECTROFORMING

Nickel electroforming is the production or reproduction of products by electroplating on a mandrel which is subsequently separated from the deposit.

Nickel Electroforming Processes:

The composition, operating conditions and mechanical properties of deposits from two electrolytes most often used for electroforming are given in Table VII. Nickel sulfamate solutions are the most popular because the deposits are low in stress, high rates of deposition are possible and thickness of the deposit is less affected by variations in current densities than are deposits from Watts solutions.

Table VII. Nickel Electroforming Solutions

	Watts Nickel	Nickel Sulfamate
Electrolyte composition, g/L (oz/gal)	$NiSO_4 \cdot 6H_2O$—225-300 (30-40) $NiCl_2 \cdot 6H_2O$—37.5-52.5 (5-7) H_3BO_3—30-45 (4-6)	$Ni(SO_3NH_2)_2$—315-450 (42-60) H_3BO_3—30-45 (4-6) $NiCl_2 \cdot 6H_2O$—0-22.5 (0-3)
	Operating Conditions	
Temperature	44-66°C (115-150°F)	32-60°C (90-140°F)
Agitation	Air or mechanical	Air or mechanical
Cathode current density	270-1075 A/m² (25-100 A/ft²)	50-3225 A/m² (5-300 A/ft²)
Anodes	Soluble nickel	Soluble nickel
pH	3.0-4.2	3.5-4.5
	Mechanical Properties	
Tensile strength:		
MPa	345-482	410-620
ksi	50-70	60-90
Elongation, %	15-25	10-25
Hardness (Vickers hardness, 100 g load)	130-200	170-230
Internal stress:		
MPa	125-186 tensile	0-55 tensile
ksi	18-27	0-8

High-Speed Nickel Sulfamate Solution:

A typical high-speed nickel sulfamate solution for electroforming has a nickel sulfamate concentration of 550 to 650 g/L, a nickel chloride concentration of 5 to 15 g/L and a boric acid concentration of 30 to 40 g/L. It is operated at a pH of 4.0, a temperature of 140 to 160°F (60 to 71°C) and at current densities as high as 800 A/ft².

The high rates of plating are made possible by the high nickel concentration. When the bath is properly conditioned and operated, it is possible to control internal stress and vary it over broad ranges.

The conditioning, which can be done continuously, involves electrolyzing the solution in a separate tank using an anode of low activity; i.e., regular electrolytic nickel. The conditioning tank should have 10 to 20% of the capacity of the plating tank so that the entire solution can be circulated through the conditioning tank from two to five times per hour.

The average current density on the anode and cathode in the conditioning tank should be 5 to 10 A/ft². The current in the conditioning tank should be about 3% of the current through the main tank.

The anode material used in the main tank should be the active type; i.e., electrolytic nickel with sulfur. With a correctly conditioned bath, zero deposit stress can be achieved at 165 A/ft² at 140°F (60°C) or at 300 A/ft² at 158°F (70°C).

The internal stress in deposits from sulfamate solutions is influenced by reactions at the nickel anode material. When a nickel anode dissolves at relatively high potentials, a stress-reducing compound is produced by anodic oxidation of the sulfamate anion.

The use of pure nickel in the conditioning tank and active nickel in the main tank is designed to control the nature and amount of the stress-reducer formed in this high-speed bath. Although the process was developed many years ago, there appears to be renewed interest because of the need to obtain zero stress in certain critical applications.

Nickel electroforming is the first and oldest practical application of nickel plating and it remains an important industrial activity about 150 years after it was conceived.

NICKEL PLATING QUALITY CONTROL

Quality control is an important consideration whether the nickel plating process is used for decorative, engineering or electroforming purposes. Controlling quality involves maintaining the purity of the plating solutions and the properties of the deposits.

Purification of Solutions:

Nickel plating baths freshly prepared from technical salts contain a number of organic and inorganic impurities that must be removed before the bath is operated. Older baths gradually become contaminated from drag-over from preceding treatments, from components that are allowed to fall off the rack and are allowed to remain in the tank, from corrosion products from auxiliary equipment, from tools dropped into the tank and from other sources.

It is probably more effective to wage a continuous campaign to keep impurities out of the plating bath than to deal with rejects and production interruptions resulting from the use of impure solutions.

The maximum concentrations of impurities normally permissible in nickel plating solutions and recommended treatments for their removal are shown in Table VIII.

The electrolytic treatment referred to in the table involves placing a large corrugated cathode in the solution and plating at low current densities, 2 and 5 A/ft². Copper, lead and certain sulfur-bearing organic addition agents are best removed at 2 A/ft², whereas iron and zinc are more effectively removed at 5 A/ft².

A corrugated cathode is preferred because it gives a wider current density range. At 2 A/ft² impurities should be removed after the solution has been operated for 2 ampere hours per gallon; at 5 A/ft², 5 ampere-hours per gallon should be sufficient.

Table VIII. Maximum Permissible Concentration of Impurities

Iron	0.15	g/L
Copper	0.04	"
Zinc	0.05	"
Lead	0.002	"
Aluminum	0.06	"
Hexavalent chromium	0.01	"

Purification Treatments:

Impurity	*Treatment (See Text)*
Iron	High pH or electrolysis
Copper	High pH or electrolysis
Zinc	High pH or electrolysis
Lead	Electrolysis
Chromium	High pH. It may be necessary to precede this with a potassium permanganate-lead carbonate treatment, followed by lead removal.
Aluminum	High pH
Organic Impurities	Activated carbon, and activated carbon plus electrolysis.

The high pH treatment requires transferring the nickel solution to an auxiliary treatment tank. Sufficient nickel carbonate is added to bring the pH above 5.2. About 0.5 to 1.0 ml/L of 30% hydrogen peroxide is added.

The bath is agitated and kept warm for two hours. The pH is adjusted to the optimum level after the bath is filtered back into the main plating tank. The solution may then be electrolyzed at low current density until deposit quality is acceptable.

When organic impurities are to be removed, activated carbon is added prior to the high pH treatment described above. About 0.13 to 0.4 oz/gal (1 to 3 g/L) of activated carbon is commonly added to the solution in the auxiliary treatment tank.

The nickel carbonate and hydrogen peroxide are then added, and the solution is filtered. Electrolytic purification is often desirable at this point.

After a new bath has been prepared, the high pH treatment, treatment with activated carbon and electrolysis at low current densities are performed sequentially until the quality of the deposit as determined by the tests discussed in the next section is acceptable.

Controlling the Properties of Nickel Deposits:

Methods that measure thickness, adhesion and corrosion resistance of nickel coatings are available for quality control. Properties such as porosity, ductility, tensile strength, internal stress, hardness and wear resistance are important and are measured to control the quality of electroplated articles. These properties may be measured by the following methods.

Thickness:

Micrometer readings are often used to determine the thickness of a coating at a particular point when the deposit thickness exceeds 125 μm (0.005 ").

More intricate and accurate methods for determining the thicknesses of electrodeposited coatings can be found in ASTM standards. ASTM standard B 487 describes a method based on metallographic examination of cross-sections of the plated object. Alternate tests involve magnetic (ASTM B 530) and coulometric (ASTM B 504) measurements of thickness.

Corrosion and Porosity Tests:

Examination of the coated part after immersion in hot water for two to five hours for rust is one technique used in studying the corrosion resistance of plated steel. The number of rust spots in a given area is then used as the qualification for accepting or rejecting the piece.

Modifications of this test include immersion for up to five hours in distilled water, in distilled water saturated with carbon dioxide, or in distilled water containing 0.5% wt sodium chloride, at test temperatures of 82 to 85 °C (180 to 185 °F).

Several salt spray tests have been used to simulate marine environments. These tests are commonly used to evaluate nickel and nickel-chromium coatings on ferrous and nonferrous substrates.

The salt spray tests are also used as accelerated quality control tests and are described in the following ASTM standards:

1. Salt spray (ASTM B 117).
2. Acetic acid salt spray (ASTM B 287).
3. Copper accelerated acetic acid salt spray (CASS Test: ASTM B 368).

The ferroxyl test is another porosity test which is employed for coatings on ferrous metal substrates and involves the formation of Prussian blue color within exposed pits.

The solution utilizes sodium chloride and potassium ferricyanide as reagents to develop the color.

The only truly satisfactory method of establishing the relative performance of various coating systems is by service testing. Care should, therefore, be exercised in interpreting the results of accelerated corrosion tests.

Once an acceptable service life has been determined for a specific thickness and type of coating, the performance of other candidate coatings may be compared in accelerated corrosion tests to the performance obtained with the coating for which an acceptable service life has been established.

Hardness:

Hardness measurements involve making an indentation on the surface (or cross-section for thin coatings) of the deposit. The indenter has a specified geometry and is applied with a specified load.

In the case of industrial nickel coatings, the most common hardness determination is the Vickers method of forcing a diamond point into the surface under a predetermined load (normally 100 grams). This provides a measure of that surface to permanent deformation under load.

The figure obtained is not necessarily related to the frictional properties of the material nor to its resistance to wear or abrasion.

Tensile Strength:

The measurement of the tensile strength of an electrodeposited coating is performed after the coating is separated from the basis metal. The coating is then pulled in a tensile machine. In general, plating plant operators seldom perform this test.

Internal Stress:

The magnitude of internal stress obtained in deposits is determined by plating onto one side of a thin strip of basis metal and measuring the force causing the strip to bend.

One method used in commercial practice involves plating the exterior surface of helically wound strip and measuring the resultant change of curvature. Another method is based on the flexure of a thin metal disc.

Ductility:

Most of the tests that have been used for evaluating the ductility of plated coatings are rather qualitative in nature. Two bend tests are described in ASTM B 489 and B 490. Both of these procedures require a minimum amount of equipment.

Another method for measuring the ductility of thick deposits is to determine the elongation of a specimen in a tensile testing machine. This method is limited to relatively thick foils of controlled geometry and thickness. A method specifically designed for plated thin foils has been used and is known as the hydraulic bulge test.

Adhesion:

The adhesion of a coating to the basis material is important. In general, the adhesion between a nickel coating and the basis material exceeds the tensile strength of the weaker material.

As a result, when a force is applied to a test specimen which tends to pull the coating away from the basis metal, separation occurs within one of the two metals rather than at the boundary between the basis metal and the nickel coating.

A number of qualitative tests have been used which utilize various forces applied in a multitude of directions with regard to the composite basis metal and coating, such as hammering, filing, grinding and deforming.

NICKEL ANODE MATERIALS

Significant developments in nickel anode materials and their utilization have taken place. Of utmost significance was the introduction of titanium anode baskets in the 1960s. Today the use of expanded or perforated titanium anode baskets filled with nickel of a selected size has become the preferred method of nickel plating.

Titanium anode baskets are preferred because they offer the plater a number of advantages. Primary forms of nickel can be used, which provide the least costly nickel ion source. Anode replenishment is simple and can be automated. The constant anode area achieved by keeping baskets filled improves current distribution and conserves nickel.

Several forms of primary nickel are currently being used in baskets. These include electrolytic nickel squares, rectangles, or rounds which contain a small controlled amount of sulfur. Nickel pellet produced by the carbonyl process and pellets containing a controlled amount of sulfur are also in use.

Prior to the introduction of titanium anode baskets, wrought and cast nickel anode materials were widely used. These are still used, but not to the extent they were before 1960.

The wrought and cast anode materials comprise rolled bars containing about 0.15% oxygen; rolled nickel containing about 0.20% carbon and 0.25% silicon; and cast bars containing about 0.25% carbon and 0.25% silicon. Soluble auxiliary anodes are generally carbon and silicon-bearing small-diameter rod.

With the exception of the sulfur-bearing materials, nickel anodes require the presence of chloride ion in the plating bath to dissolve efficiently. Rolled or cast carbon-bearing materials are used up to about pH 4.5. Oxygen-bearing, rolled depolarized anode bars can be used above pH 4.5.

Thermal Spray Coatings: New Materials, Processes and Applications

by F.N. Longo 146 pages $52.00

The major areas involved with thermal spray coatings are covered in this book proceedings. Emphasis is on the practical aspects with 10 papers on applications. Remaining papers provide an overview of the process, discuss new coatings, equipment and processes, test methods and other topics.

Send Orders to: METAL FINISHING, Three University Plaza, Hackensack, NJ 07601

For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

PALLADIUM AND PALLADIUM-NICKEL PLATING

by Ronald J. Morrissey

Technic Inc., Providence, R.I.

PALLADIUM

Palladium has been electroplated from a wide variety of systems which can be broadly categorized as ammoniacal, chelated, or acid processes. Of these, the most numerous are the ammoniacal systems, in which palladium is present as an amine complex such as palladosamine chloride, $Pd(NH_3)_4Cl_2$, or the diaminodinitrite, $Pd(NH_3)_2(NO_2)_2$, which is known popularly as the P-salt. Some representative formulations are shown as follows:

P-salt/Sulfamate:

Palladium as $Pd(NH_3)_2(NO_2)_2$	10-15 g/L
Ammonium sulfamate	100 g/L
Ammonium hydroxide to pH	7.5-8.5
Temperature	25-35 °C
Current density	0.1-2.0 A/dm²
Anodes	platinized

Palladosamine chloride:

Palladium as $Pd(NH_3)_4Cl_2$	10-15 g/L
Ammonium chloride	60-90 g/L
Ammonium hydroxide to pH	8.0-9.5
Temperature	25-50 °C
Current density	0.1-2.5 A/dm²
Anodes	platinized

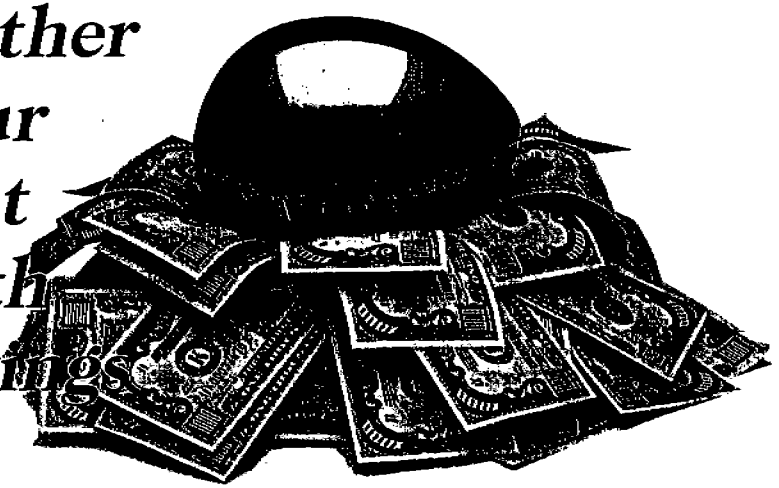
Ammoniacal electrolytes, particularly at pH values above 8.0, tend to cause tarnishing of nickel, copper, and copper alloys. Consequently, work to be plated in ammoniacal palladium solutions is often struck with gold or silver prior to plating. Chelated palladium plating solutions contain palladium in the form of an organometallic complex. These species are operable in non-tarnishing electrolytes such as phosphates, citrates, or combinations thereof. Plating solutions of this type can be applied directly to nickel, copper, and copper alloys without the use of a strike. Chelated palladium plating solutions currently available are proprietary. Requisite details can be obtained from the manufacturers.

Acid palladium plating systems have been used for producing heavy deposits of very low stress. Such systems are ordinarily based on the chloride, although a proprietary sulfate solution containing a sulfite complex has recently been reported. A representative formulation for the chloride system is as follows:

Acid Chloride:

Palladium as $PdCl_2$	50 g/L
Ammonium chloride	30 g/L
Hydrochloric acid	to pH 0.1-0.5
Temperature	40-50 °C
Current density	0.1-1.0 A/dm²
Anodes	pure palladium

Feather Your Nest With Savings...



PallaTech...

As Good As Gold

AT&T PallaTech products, used to electroplate palladium and palladium alloys, have been the processes of choice for AT&T over the past decade. Thanks to PallaTech, we've saved over

$70,000,000.00

We think AT&T PallaTech should be your palladium and palladium alloy *"future connection"*. We invite you to consider some of the unique advantages of our products.

AT&T
The right choice.

AT&T Nassau Metals • 286 Richmond Valley Road • Staten Island, NY 10307 • 1-800/221-6316
AT&T Bell Laboratories • 600 Mountain Avenue • Murray Hill, NJ 07974 • 908/582-3407

The acid chloride system yields deposits having an entrained hydrogen content on the order of 3% or less. Current efficiency is 97 to 100%. The bath is highly sensitive to contamination by copper, which can displace palladium from solution. Work to be plated must accordingly be struck, preferably with gold.

PALLADIUM-NICKEL

Palladium readily forms alloys with other metals, and has been electroplated in numerous alloy formulations. To date, the most important electroplated alloy of palladium is palladium-nickel, which can be deposited as a homogeneous alloy over a composition range from about 30 to 80% palladium by weight. A formulation suitable for plating an alloy of about 75 weight percent palladium is as follows:

Palladium-Nickel Alloy:

Palladium as $Pd(NH_3)_2(NO_2)_2$ (palladium metal 3 g/L)	6 g/L
Nickel sulfamate concentrate (nickel metal 3 g/L)	20 ml/L
Ammonium sulfamate	90 g/L
Ammonium hydroxide to pH	8-9
Temperature	20-40 °C
Anodes	platinized

This formulation is operable at room temperature over a range of about 0.5 to 1.0 A/dm². A strike of gold or silver is recommended for most basis metals prior to plating.

Handbook of Printed Circuit Design, Manufacturing, Components and Assembly

by G. Leonida

569 pages $95.00

This book provides information on the manufacture and assembly of printed circuits emphasizing quality and reliability. It covers electronic design and includes a basic explanation of all the steps needed in the physical construction of anything that is designed and expressed as a wiring diagram.

Send Orders to:
METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service, call (201) 487-3700
or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

PLATINUM PLATING

by Ronald J. Morrissey

Technic Inc., Providence, R.I.

Electroplating solutions for the deposition of platinum are generally similar to those employed for palladium. However, while palladium ions in solution are almost always divalent, platinum exhibits stable valences of +2 or +4. Divalent platinum ions can become oxidized to quadrivalent at the anode, particularly in alkaline solution. Such oxidation can lead to progressive, sometimes erratic losses in current efficiency. For this reason, it is often useful to separate the anode compartment in electroplating solutions of this type.

For plating platinum directly onto titanium for fabricating anodes, the dinitroplatinite sulfate formulation has been employed, as follows:

Dinitroplatinite sulfate — Sulfuric acid:

Platinum as $H_2Pt(NO_2)_2SO_4$	5 g/L
Sulfuric acid to pH	2.0
Temperature	40 °C
Current density	0.1-1 A/dm²
Anodes	Platinum

An alternate acid formulation is based on chloroplatinic acid, as follows:

Chloroplatinic acid:

Platinum as H_2PtCl_6	20 g/L
Hydrochloric acid	300 "
Temperature	65 °C
Current density	0.1-2 A/dm²
Anodes	Platinum

In chloroplatinic acid, platinum has a valence of +4, rather than +2 as in the dinitroplatinite sulfate. Plating formulations based on chloroplatinic acid can also be operated at neutral to alkaline pH, as follows:

Chloroplatinic acid — Ammoniacal:

Platinum as H_2PtCl_6	10 g/L
Ammonium phosphate	60 "
Ammonium hydroxide to pH	7.5-9
Temperature	65-75 °C
Current density	0.1-1 A/dm²
Anodes	Platinized

The alkaline formulation can be applied directly to nickel-based alloys without the use of a preplate. Both of the acid baths shown require a preplate, preferably gold, on most basis metals.

RHODIUM PLATING

by Alfred M. Weisberg

Technic Inc., Providence, R.I.

Although several different electrolytic baths for rhodium plating have been proposed, the only baths to achieve commercial significance have been:

1. Phosphate—for very white and reflective deposits.
2. Sulfate—for general jewelry and industrial deposits.
3. Mixed phosphate-sulfate—for general decorative deposits.

DECORATIVE PLATING

The jewelry and silverware industries were the primary users of rhodium electroplates until quite recently. Although both the phosphate and sulfate baths gave bright white deposits, the phosphate bath was preferred for soft soldered jewelry, especially before the general adoption of bright nickel plating. Cold nickel did not always cover the soft solder and the acid electrolyte attacked and dissolved some of the solder. Lead in a rhodium bath gave dull and dark deposits and destroyed its decorative white finish. Phosphoric acid attacked the solder less than did the sulfuric acid, so phosphate rhodium was preferred. After the introduction of bright nickel, most of the industry changed to sulfate because it could operate at a slightly lower rhodium concentration. The phosphate-sulfate solution was used because some felt that the color was a bit whiter or brighter.

The typical rhodium electroplate on costume or precious jewelry is 0.000002-5" and is produced in 20 seconds to one minute at about 6 V in the following baths:

Phosphate Rhodium Bath:

Rhodium as phosphate concentrate	2 g/L
Phosphoric acid (85% CP grade)	40–80 ml/L
Anodes	platinum/platinum clad
Temperature	40–50°C
Agitation	none–moderate
Current density	2–10 A/dm²

Sulfate Rhodium Bath:

Rhodium as sulfate concentrate	1.3–2 g/L
Sulfuric acid (95% CP grade)	25–80 ml/L
Anodes	platinum/platinum clad
Temperature	40–50°C
Agitation	none–moderate
Current density	2–10 A/dm²

RHODIUM SULPHATE TP/ PHOSPHATE/ S-LESS Bright compressive stress rhodium.

SILVER PLATINUM

RUTHENIUM

PALLADIUM

PALLASPEED High speed high efficiency for continuous plating and barrel plating. **PALLASPEED 88**

RUTHENIUM U Mirror bright, decorative and industrial.

PLATINUM AP
PLATINUM TP

BRUSH PLATING SOLUTIONS

RHODIUM	TIN
PLATINUM	GOLD
PALLADIUM	NICKEL
SILVER	COPPER

TECHNI-SILVER E Mirror bright cyanide bath.

ELECTROLESS IMMERSION PALLAMERSE (PALLADIUM) STANOMERSE (TIN) ARGENTOMERSE (SILVER) RHODOMERSE (RHODIUM) OROMERSE (GOLD) NICKELMERSE

TECHNI-SILVER EHS-2 Ultra High Speed, no immersion.

TECHNI-SILVER E-2 Mirror bright, high speed industrial.

SPECIALIZED EQUIPMENT PLATING CONSOLES 1 to 200 gallons. CONTINUOUS PLATING UNITS Strip, Stripe, Spot and PC. PLATINUM CLAD ANODES

TECHNI-SILVER CY-LESS NON-CYANIDE bright silver.

Send for:
- Product Checklist
- Equipment Checklist
- Latest Govt. Gold Specs
- "What Gold To Use"

TECHNIC INC. GOLD/RHODIUM/SILVER

RHODE ISLAND: 401-781-6100
ILLINOIS: 312-262-2662/TEXAS: 214-790-8500
CALIFORNIA: 408-287-3732 / 714-632-0200
CANADA: 416-283-7400 / 514-684-4563
EUROPE / HONG KONG / KOREA

Phosphate-Sulfate Rhodium Bath:

Rhodium as phosphate concentrate	2 g/L
Sulfuric acid (95% CP grade)	25–80 g/L
Anodes	platinum/platinum clad
Temperature	40–50°C
Agitation	none–moderate
Current density	2–10 A/dm²

Tanks for these baths should all be made of glass, pyrex, plastic, or plastic-lined steel. If plastic is used, it should be leeched once or twice with 5% sulfuric or phosphoric acid for 24 hours before the rhodium is added. In mixing a new solution, distilled or deionized water should be used and the acid should be added to the water carefully and mixed thoroughly before the rhodium concentrate is added. This will prevent precipitation of the rhodium.

Rhodium is, of course, plated out and also lost through drag-out. Because of the expense of rhodium, the first rinse after plating should be a stagnant drag-out rinse, also contained in a glass or plastic tank. As water is lost from the plating solution, it should be replaced with this drag-out rinse so some of the "lost" rhodium is returned for reuse. Even with two drag-out tanks, the actual amount of rhodium lost will be about 25 to 30% of the rhodium plated, therefore, rhodium should be replenished at the rate of 5 grams per 18–20 ampere-hours of flash plating. Because the drag-out is so high in jewelry plating, sulfuric (or phosphoric) acid should also be replenished at the rate of 5 ml per 18–20 ampere-hours. This recommended replenishment is only an average value. If possible, it should be checked by analysis.

Bright nickel is the preferred base for decorative rhodium electroplates. It provides a bright base for rhodium and it also prevents the rhodium solution from attacking a brass, copper, steel, lead or tin base. All of these metals adversely affect the color, tarnish and corrosion resistance, as well as the covering power of the rhodium solution. Nickel, of all the metals, has the least adverse effect on a rhodium solution. Baths can tolerate as much as 1 to 2 g/L and still give a satisfactory deposit. There are no truly satisfactory methods to purify a contaminated rhodium plating solution.

DECORATIVE BARREL PLATING

The usual decorative barrel finish is also 0.000003–5". A variation of the sulfate-rhodium bath is always used. It is necessary, however, to reduce the metal concentration and to raise the acid concentration in order to get economical and satisfactory deposits. With many parts in the barrel, it is necessary to plate quite slowly so that the parts have time to mix and be evenly exposed to the plating solution. This ensures that they are all plated to a similar thickness, before more than 0.000005" is deposited. It is not advisable to slow the rate of plating by decreasing the current density (and voltage) as this may lead to non-adhering deposits over a bright nickel base. Therefore, the plating rate is best slowed by decreasing the cathode current efficiency by raising the acid and lowering the rhodium. A typical formulation for decorative barrel plating would be:

Rhodium as sulfate concentrate	1 g/L
Sulfuric acid (95% CP grade)	80 "
Anodes	platinum/platinum clad
Temperature	45 to 50°C
Current density	0.5–2 A/dm²

ELECTRONIC/INDUSTRIAL PLATED RHODIUM

The emerging electrical/electronics industry in the 1950's and 1960's made considerable use of rhodium electrodeposits for many diverse uses, but it was particularly used on sliding and rotating contacts, printed circuit switches and commutators, and high frequency switches and components.

There are many requirements for rhodium deposits of 0.000020" to 0.0002" over nickel or occasionally silver. These may be plated from the following solution:

Rhodium metal as sulfate concentrate	5 g/L
Sulfuric acid (95% CP grade)	25–50 ml/L
Anodes	platinum/platinum clad
Temperature	45 to 50°C
Current density	1–3 A/dm²
Current efficiency	70–90% with agitation
	50–60% without agitation

See the previous section under Decorative Plating for instructions on leeching the plating tank before use. It is preferable to use water jacket heating of the solution to prevent local overheating by an immersion heater or steam coil. Even a short exposure to temperatures over 160°F will result in chemical changes to the solution that will result in permanent increase in stress of the deposit. The stress will be present even if the bath is later operated within the correct temperature range.

Because of the expense of the solution, it is advisable to plate with as low a rhodium concentration as possible in order to achieve the desired plating thickness and finish. If some of the plating is to be 0.0002" and over, it will be necessary to raise the rhodium concentration to 7½ or 10 g/L.

Replenishment is based upon ampere-hours plated and the cathode current efficiency. It is best determined by analytical control; however, an approximation would be to replenish five grams of rhodium for every five to ten ampere-hours of plating. The actual value will depend on the average thickness plated and the current density used.

The cathode current efficiency is quite low, even with agitation, and hydrogen gas bubbles will tend to cling to the work and leave imperfections. This effect may be minimized by adding a 1% solution of sodium lauryl sulfate to the bath. The rate of addition should be one to five ml of a 1% solution per gallon of the plating bath.

INDUSTRIAL BARREL PLATING

Not only the expense of rhodium but the high drag-out of barrel plating recommends the use of a low metal concentration. Coatings in the millionth inch range can be produced with as little as one gram of rhodium per liter. Thicker deposits must use proportionally higher concentrations. Deposits of 0.000020" may be achieved with 2½ g/L; 0.000050" with as little as 3½ g/L; 0.0001" with as little as 4 g/L and deposits of 0.0002" and over with 5 g/L. If the holes in the barrel are very small and the parts have a high surface area, it will be necessary to use higher concentrations to compensate for poor solution transfer.

Otherwise, the formulations for barrel plating are the same:

Rhodium metal as sulfate concentrate	2½–5 g/L
Sulfuric acid (CP grade)	20 ml/L
Anodes	platinum/platinum clad
Barrels	horizontal, submerged
Temperature	45–50°C
Current density	0.5–2 A/dm²

CARE OF RHODIUM SOLUTION

Contamination of the rhodium solution is the cause of most rhodium plating problems. The major contaminates are:

1. Organics.
2. Rhodium basic salts.
3. Rhodium complexes.
4. Inorganics:

a) Iron	c) Copper	e) Nickel
b) Lead/Tin	d) Gold/Silver	f) Other

The most common contaminants are organics. These are dust, dirt, adhesives from masking tape, stop-off paints, printed circuit board material and organics from improperly leached plastic tanks. They are usually easily removed by batch-type carbon treatment. It is imperative that the carbon used be very low in acid-soluble residues. It is also important not to use a diatomaceous earth filter aid. If a single carbon treatment does not clean the solution, a second treatment may be necessary, or a treatment with a carbon designed for the removal of very short chain organic molecules. Carbon treatment will frequently eliminate stress brittleness and flaking of the deposit. It will also often cure finger staining or apparent tarnishing of the deposit.

Basic rhodium salts will precipitate from a rhodium solution and act as a contaminant if the pH of the bath rises above 2. The acidity of the solution should be controlled and never be allowed to fall below 25 ml/L. If plating is normally done at higher current densities of over 25 ASF, the acidity should be kept even higher. Levels of sulfuric acid of at least 50 ml/L are generally satisfactory. Phosphoric acid is not recommended for industrial plating baths.

Contamination and increased stress by unwanted rhodium complexes, as has been mentioned, can occur if the solution is overheated. Rhodium solutions should be indirectly heated and be thermostatically controlled.

Inorganic contaminants are usually introduced by the basis metal or base plates. The warm sulfuric acid electrolyte is extremely corrosive and work should never be allowed to hang in the tank without current. Preferably, work should be connected to the negative power source before it is introduced into the rhodium tank. This may occasionally require a flying cathode bar or, in the case of barrel plating, a cathodic battery clamp and wire to be attached to the barrel before it is lowered into the tank. Of course, dropped parts should immediately be removed from the bottom of the tank.

Copper, iron, tin and lead, even after exhibiting a brief brightening effect in the parts per million range, will cause highly stressed heavy rhodium deposits. They also will cause dark and stained deposits and skip plating.

Most metallic impurities, theoretically, can be precipitated from a rhodium solution by potassium ferrocyanide. But, in practice, the procedure is very difficult, time-consuming and not too successful, especially with solutions used for heavy rhodium deposits. The best practice is to prevent metallic contamination.

The parameters that will tend to decrease the stress and brittleness of a rhodium deposit are:

1. Increased rhodium metal concentration.
2. Increased sulfuric acid concentration.
3. Increased temperature.
4. Carbon treatment of the bath.
5. Decreased inorganic contaminants.

Low stress rhodium proprietary baths are available that contain trace amounts of selenium and indium. Although the stress, and attendant stress cracking, is almost totally eliminated, the baths operate like conventional sulfate baths.

Modern Electroplating
by F. Lowenheim
801 pages $95.00

This is the third edition of this valuable textbook. Numerous authorities have contributed summaries on the principles of plating and metal finishing, control, maintenance, deposit properties and troubleshooting. A worthwhile reference.

Send Orders to:

METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service,
call (201) 487-3700 or
FAX your order to
(201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

A Complete Line of

PLATINUM COATED ANODES

Platinum Coated Titanium
And
Platinum Clad Columbium

- FOR GOLD and RHODIUM PLATING
  Available in expanded mesh or solid sheet in a variety of standard stock sizes or made to order.
- FOR COPPER-NICKEL-CHROME
  Designed to meet your requirements for plating thickness and long life.
- WE CAN RECOAT YOUR PRESENT ANODES
  Call us for price and delivery information.

Write for free product information on platinum coated and platinum clad anodes.

INTREPID

P.O. Box 443
Whitehouse Station
NJ 08889
Tel. 908/534-5300
FAX 908/534-4338

RUTHENIUM PLATING

by Alfred M. Weisberg

Technic Inc., Providence, R.I.

Electroplated ruthenium is the second best electrical conductor, produces the hardest deposit, and is the least expensive of the platinum group metals. In addition, it has the highest melting point of the platinum metals that can be deposited from an aqueous solution. Nonetheless, it has not been used as an electroplated finish until quite recently. It is used to a limited extent as a barrier layer, a finish on reed switches, and as a novel dark finish on jewelry and other decorative items.

A general purpose bath is:

Ruthenium (as sulfamate or nitrosyl sulfamate)	5.3 g/L
Sulfamic acid	8 "
Anodes	Platinum
pH	1-2
Temperature	80-140 °F (sulfamate) 70-190 °F (nitrosyl sulfamate)
Current density	10-30 ASF
Current efficiency	20%
Time to plate 0.0001"	30-40 min at 20 ASF

The low pH of this solution requires that the ruthenium be plated over a gold or palladium flash.

Decorative flash deposits may be produced from:

Ruthenium (as nitroso salt)	2.0 g/L
Sulfuric acid	20 "
Current density	20-30 ASF
Temperature	120-180 °F

This bath also requires a flash underplate of gold.

The hardness of ruthenium deposits can be 800 to 1300 KHN, harder than a rhodium deposit, however, the ruthenium has less internal stress.

SILVER PLATING

by Alan Blair

AT&T Bell Laboratories, Irvine, Calif.

Electrodeposition of silver from cyanide electrolytes has changed little since first performed about 1840. The use of soluble silver anodes, free potassium or sodium cyanide to aid anode corrosion, and the presence of carbonate salts to aid conductivity has been the standard approach. Development of additives, grain refiners and brighteners were the only form of evolution in silver plating until 1970. Several attempts have been made to introduce non-cyanide systems, but in all cases these processes have exhibited shortcomings, so the traditional formula has remained.

The first major innovation in silver plating technology since the mid-1970's occurred with the new demands imposed by the electronics industry. Here, semi-conductor components, such as lead frames, require selective plating with silver as rapidly as possible, using equipment that prohibits the inclusion of soluble anodes.

Traditional Electrolyte:

A traditional formulation for rack or barrel work would be:

Silver, as $KAg(CN)_2$	5-40 g/L (0.7-6 oz/gal)
Potassium cyanide (free)	12-120 " (1.6-16 oz/gal)
Potassium carbonate (min.)	15 " (2 oz/gal)
Temperature	20-30 °C (70-85 °F)
Current density	0.1-4.0 A/dm² (1-40 ASF)

Higher concentrations of silver and cyanide are required for rack plating than for barrel application. A typical solution for plating flatware might contain 36 g/L silver (4 oz/gal) and 100 g/L (13.5 oz/gal) free-potassium cyanide.

As with all alkaline solutions of precious metal, there is a tendency to form immersion coatings on less noble metal surfaces, even when "live" loading the plating solution. The inevitable result of this phenomenon is poor adhesion of the deposit. In order to minimize this effect, a silver strike coating should be applied prior to the main deposit. A typical silver strike formula is:

Silver, as $KAg(CN)_2$	3.5-5 g/L (0.5-0.7 oz/gal)
Potassium cyanide (free)	80-100 " (10-13 oz/gal)
Potassium carbonate	15 " (2 oz/gal)
Temperature	15-25 °C (6-80 °F)
Current density	0.5-1.0 A/dm² (5-10 ASF)

Normally no rinsing is required between a silver strike solution and the main plating tank.

These electrolytes will produce coarse, chalk-white deposits which are soft (< 100 Knoop). Fully bright, harder deposits (100 to 200 Knoop) can be produced by employing brighteners. These additives usually consist of either a sulfur-containing compound, which may be organic in nature, or a complex containing a group VA or VIA element, such as selenium, bismuth or antimony. As a general rule, organic brighteners give

better electrical properties (such as lower contact resistance) but antimony or selenium-brightened silver is harder and has better wear resistance.

Anode purity and quality is of paramount importance since typical impurities, such as copper, iron, bismuth, lead, antimony, sulfur, selenium, tellurium and the platinum group metals will not only cause solution contamination, but may cause anode filming which inhibits proper dissolution. Anode shedding (i.e., break off of small particles) can result from using anodes with incorrect grain size. This is usually the result of poor annealing during manufacturing, after rolling, casting, or extruding the anode. Shedding or improper dissolution, however, can also occur due to operation with insufficient anode area or insufficient free-cyanide concentration. The optimum anode area to cathode area ratio is 2:1 and the maximum anode current density should be approximately 1.25 A/dm² (13.5 ASF).

Non-Cyanide Systems:

Almost every known silver compound has been investigated as an electrolyte base for silver plating. Many compounds are unsuitable simply because of their photosensitivity.

Two proprietary formulations are perhaps worthy of individual mention; these being based on silver succinimide and silver sulfite/thiosulfate. In both cases, coherent, reasonably bright silver deposits can be obtained with acceptable deposition rate. However, tarnish resistance of the deposits is inferior to those obtained from the cyanide system and both processes are more expensive to operate than the traditional one.

The Chemical Analysis of Electroplating Solutions

by T.H. Irvine

182 pages $41.50

Chapters in this work are divided into groups in accordance with the periodic table of elements. Procedures are traditional, but theoretical aspects and other information are also provided. Anyone who studies this book carefully will derive a helpful understanding of what he or she is doing so that unexpected results can be searched out for causes and corrected.

Send Orders to:
METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service, call (201) 487-3700
or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

We *Deliver* What Others Will *Promise*

Price • Purity • Reliability

Silver ▪ Gold

ANODES ▪ SALTS
SILVER WIRE, RODS & STRIPS ▪ REFINING

Anodes
- all shapes and sizes
- consistent, reliable 99.95 + purity
- annealed uniform grain structure

Salts
- Ag, KAg, $AgNo_3$, $KAuCN_2$
- guaranteed content

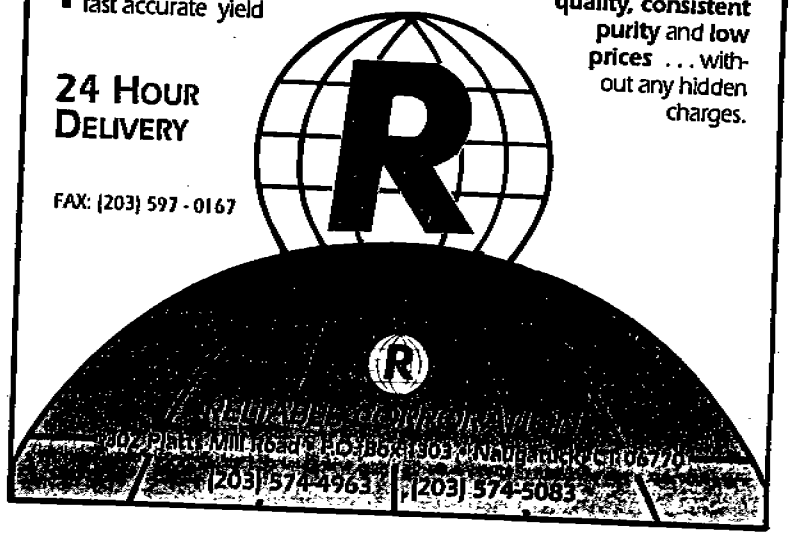
Silver Wire, Rods & Strips
- 99.95 + purity
- fabricated to specification

Refining
- modern lab
- fast accurate yield

We've passed the test of time – as **Reliable** approaches its first decade of steady growth. Reliable has proven that its customers' **success** is its own success – so we leave no stone unturned to DELIVER success to your door. We guarantee to execute your orders within 24-hours! Our ***guaranteed delivery*** means you can stop stockpiling and start **saving $ $**. Our in-stock & custom programs will surpass your expectations. Reliable also guarantees your satisfaction with **quality, consistent purity** and **low prices** . . . without any hidden charges.

24 HOUR DELIVERY

FAX: (203) 597 - 0167



High Speed Selective Plating:

Silver epoxy and ultrasonic bonding techniques for silicon chips and aluminum wire have enabled semiconductor manufacturers to utilize silver electrodeposits in place of gold on many devices.

In order to meet production speed requirements, it became necessary to deposit 100 to 150 microinches (2.5 to 3.75 μm) of pure silver in 1 to 4 seconds. Due to the design of selective plating equipment, insoluble platinum or platinized titanium anodes must be employed. These conditions cause rapid deterioration of traditional cyanide solutions due to polymerization/oxidation of cyanide at the anode. To meet this new challenge, formulations were developed which contain essentially no free-cyanide. Conductivity is provided by a conducting salt, such as phosphate, and the solution is buffered at a pH value between 8.0 and 9.5. A typical electrolyte would operate as follows:

Silver, as $KAg(CN)_2$	65-85 g/L (8-10 oz/gal)
Conducting/buffering salts	60-120 " (8-16 oz/gal)
pH	8.0-9.5
Temperature	60-70°C (140-160°F)
Current density	32.5-380 A/dm² (300-3500 ASF)
Agitation	Jet plating
Anode material	Pt or Pt/Ti

Additives are available which impart full brightness, or partial brightness to the silver deposits. Immersion deposit inhibitors have been investigated which will enable direct deposition of silver onto copper or copper alloy substrates. Where the substrate is nickel or nickel-iron, it is preferable to utilize a copper, silver or gold strike in order to ensure good adhesion of the silver deposit.

RFE INDUSTRIES
WHERE METALLURGY MAKES SAVINGS A SCIENCE
RFE Industries
19 Crows Mill Road
Keasbey, NJ 08832
908/738-5200

THE "SILVER CONNECTION"
RFE fulfills all your silver plating needs:
ANODES: "POPCORN" Anodes plus Cones • Slabs • Bars
SALTS: Silver Cyanide and Potassium Silver Cyanide
RECLAMATION EQUIPMENT:
Electrolytic-Resin Recovery
Contact us today for all your silver plating/recovery needs

SUNCAST
SILVER ANODES
Flat Anodes
Corn Flakes
Ball Anodes
Gum Drop Anodes
Rod Anodes
Cone Anodes
419 Commerce Lane, Suite One, Berlin, NJ 08009
800/969-3331 • 609/768-5707 • Fax: 609/753-0482

TIN-LEAD, LEAD AND TIN PLATING

by Stanley Hirsch

Leeam Consultants Ltd., New Rochelle, N.Y.

Tin fluoborate, lead fluoborate and fluoboric acid, in various proportions, can be used for plating all percentages of tin-lead (solder), 100% lead and 100% tin. In addition, some proprietary non-fluoborate tin-lead baths are now available. In tin plating, other baths in use are stannous sulfate and sodium or potassium stannate.

TIN-LEAD PLATING

The 60/40% tin-lead solder bath (the most commonly used proportions) is prepared from liquid concentrates of stannous (tin) fluoborate, lead fluoborate and fluoboric acid. The bath requires use of boric acid for stability and an addition agent. These chemicals are mixed as directed in the manufacturer's makeup specification.

The addition agent is critical in the operation of the solution. Up until about 15 years ago, almost all the baths used powdered peptone as the addition agent. Today a liquid peptone or a non-protein liquid addition agent proprietary system is used, thereby simplifying the process.

The following are advantages of liquid proprietary addition agents: the solution remains clear; the grain structure of the deposit is improved; the throwing power of the bath is improved; better rinsing is possible and drag-out is reduced.

Chemical and Physical Properties of Bath Constituents:

Fluoboric Acid—Average Analysis:

	wt %	g/L	oz/gal
Fluoboric acid, HBF_4	48.0	656	87.5
Boric acid, free H_3BO_3	1.4	19	2.6
Hydrofluoric acid, free HF	None	—	—

Physical properties:

Appearance ..... clear, colorless solution
Specific gravity at 20°C(68°F) 1,365
The solution weight is about 11.4 lbs per gallon.

Lead Fluoborate—Average Analysis:

	wt %	g/L	oz/gal
Lead fluoborate, $Pb(BF_4)_2$	51.0	873.0	116.4
Lead, Pb(equivalent)	28.1	480.1	64.1
Fluoboric acid, free HBF_4	0.6	10.5	1.4
Boric acid, free H_3BO_3	3.0	48.0	6.4

Physical properties:

Appearance ..... clear, colorless solution
Specific gravity at 20°C(68°F) 1.71
The solution weight is about 14.3 lbs per gallon.

Stannous (Tin) Fluoborate—Average analysis:

	wt %	g/L	oz/gal
Stannous fluoborate, $Sn(BF_4)_2$	50.0	800	106.0
Tin, Sn(equivalent)	20.0	320	42.7
Fluoboric acid, free HBF_4	3.0	48	6.4
Boric acid, free H_3BO_3	3.0	48	6.4

Physical properties:

Appearance ..... clear, colorless solution
Specific gravity at 20 °C(68 °F) 1.60
The solution weight is about 13.3 lbs per gallon

Composition and Operating Conditions for Standard 60/40 Solder Bath:

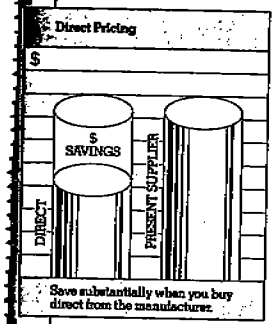
	Optimum		Range	
	oz/gal	g/L	oz/gal	g/L
Stannous tin	7.5	56.3	7–8	52.5–60
Lead	3.5	26.3	3–4	22.5–30
Fluoboric acid	13.3	99.8	13–20	98–150
Boric acid	3.5	26.3	3–5	22.5–37.5
Liquid peptone	2.6	19.5	2–3	15–22.5
or				
Peptone	0.7	5.3	0.6–0.9	4.5–7
Current density, ASF	30		25–35	
Anode to cathode ratio	2:1			
Anodes	60/40 tin lead bagged with Dynel or polypropylene.			
Temperature, °F	70		60–80	
Agitation	Mild cathode rod			
Filtration	Continuous is recommended to maintain a clear solution.			

For through-hole plating of printed circuit boards, the following bath formulation has been found useful.

Composition and Operating Conditions of High Throw 60/40 Solder Bath:

	Optimum		Range	
	oz/gal	g/L	oz/gal	g/L
Stannous tin	2	15	1.6–2.7	12–20
Lead	1.3	10	1.1–1.9	8–14
Fluoboric acid	53	400	47–67	350–500
Boric acid	3.5	26.3	3–5	22.5–37.5
Liquid peptone	2.6	19.5	2–3	15–22.5
or				
Peptone	0.7	5.3	0.6–0.9	4.5–7
Current density, ASF	15		15–25	
Anode to cathode ratio	2:1			
Anodes	60/40 tin-lead alloy bagged with Dynel or polypropylene.			
Temperature, °F	75		60–100	
Agitation	Mild cathode rod			
Filtration	Continuous is recommended to maintain a clear solution.			

ATTENTION:
All Buyers Of Non-Fluoborate Plating Products:
Your Costs Just Went Down

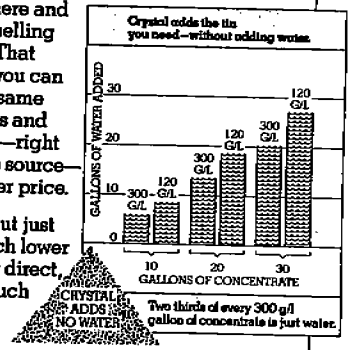


Chances are we already produce the non-fluoborate plating products you buy—we are the world's largest manufacturer. But for the past 10 years, we have been private labeling non-fluoborates for the suppliers who have been selling them to you.

We've been supplying all the popular tin, lead and acid solutions, but now you can buy direct from the manufacturer. And to make it even easier, we back it all with trained engineers and service technicians who can provide all the technical support you'll need.

Plus, for those of you with water balance problems, only our exclusive crystal lets you add tin to your bath without having to also add water.

It's all here and we are selling direct. That means you can get the same products and support—right from the source—at a lower price.



To find out just how much lower and how direct, get in touch today.

PITT METALS & CHEMICALS, INC.
P.O. Box 279, State Route 980
McDonald, PA 15057
412-796-1511
FAX: 412-922-6657

The Right Chemistry

Cut This Coupon and You've Just Cut Your Non-Fluoborate Costs

I need direct answers on how much I can save. Contact me.

NAME _____
PHONE _____
COMPANY _____
ADDRESS _____
CITY _____
STATE _____ ZIP _____

Other compositions of solder can be formulated by using the total metal concentration of the bath as 11 oz/gal, the acid concentration of 30 oz/gal, plus the usual amounts of boric acid and peptone. Multiply 11 oz/gal by the percentage of tin and lead desired, and be sure to use the right anode composition to correspond to the alloy desired.

A low concentration of addition agent and lower than recommended current densities will reduce tin in the deposit. Factors affecting the throwing power and grain structure of the deposit include addition agent concentration and organic contamination. Since most of the baths in printed circuitry encounter organic coatings, a buildup of organics in the bath is unavoidable. This results in darkened deposits with poor throwing power and may affect the composition of the deposit, usually reducing the tin. Organics will adversely affect the solderability of the coating; therefore, the bath should be carbon treated periodically. Carbon treatment will remove the addition agents, which should be replaced before plating is resumed.

Contaminants such as antimony and arsenic reduce tin in the deposit, sometimes drastically. Iron can reduce the throwing power of the bath. Copper can affect throwing power and increase the grain size.

Troubleshooting Tin-Lead Bath

Problem	*Cause*	*Remedy*
Treeing	Low replenisher	Add peptone
Edge feathers	Too high a current density	Lower current density
Grainy deposit	Organic contamination	Carbon treat
Burning	Too high a current density	Lower amperage
	Too low metal content	Add stannous fluoborate Add lead fluoborate
	Low acid content	Add fluoboric acid
Wrong alloy composition	Incorrect bath composition	Adjust bath composition
	Wrong current density	Plate 25-30 ASF
	Insufficient addition agent	Replenish with peptone
	Improper agitation	Cathode rod agitation recommended
Poor throwing power	Low acid	Add fluoboric acid
	Too high anode to cathode ratio	Remove some anodes
	Low addition agent	Add peptone
Roughness	Chloride or sulfate drag-in	Improve rinsing
	Torn anode bags	Replace anode bags
	Oxidation of tin from too violent agitation.	Look for air leak in filter, if used.
Poor reflow	Insufficient deposit—minimum should be 0.00025"	Do not reflow unless thickness above minimum
	Wrong alloy	Check reason for wrong alloy
	Organic contamination	Carbon treat
	Metallic contamination	Dummy
	Substrate not active or clean	Check cleaning cycle

Harstan Printed Circuit Board Chemicals Make The Cut By Being The Most Consistent Source On The Circuit.

There are no finer chemicals used in the manufacture of printed circuit boards than products from Harstan. Harstan has earned this reputation by providing quality and service for over 30 years.

The printed circuit board industry has come to trust and rely on our quality and our nationwide distributor network assures products are promptly available no matter where they are in the United States.

So, when you need fluoborates, copper sulfate, cupric chloride, nickel sulfamate, printed circuit grade sulfuric acid, printed circuit board hydrochloric acid, or etch back grade sulfuric acid, call us toll-free at 800-325-3332.

You'll appreciate the top flight chemistry.

HARSTAN
A DIVISION OF
Chemtech

1655 Des Peres Road • St. Louis, Missouri • 63131

LEAD PLATING

Lead fluoborate is the accepted electrolyte for commercial lead plating. An interesting use is the preparation of internal and conforming anodes for chromium plating. The following formula is used for plating lead from the fluoborate bath:

Composition and Operating Conditions of Lead Bath for Still and Barrel Plating:

	Optimum		*Range*	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Lead fluoborate	50	375	45–55	337–412
Lead	29	218	26–32	195–239
Fluoboric acid	3	22.5	2–4	15–30
Boric acid	4	30	3–5	22.5–37.5
Liquid peptone	2.6	19.5	2–3	15–22.5
or				
Peptone	0.7	5.3	0.6–0.9	4.5–7

pH	Less than 1
Current density, ASF	20–70
Anode to cathode ratio	1:1
Anodes	Pure lead
Temperature, °F	70–100
Agitation	Mechanical
Filtration	Will insure smooth deposits. If solution is maintained under a constantly operated filter pump it will assure the best agitation and filtration.

An alloy of 7% tin/93% lead is also commonly used for bearing plating. This is easily accomplished with a 4.6% addition of stannous fluoborate by volume (2 oz stannous tin per gallon) to the lead fluoborate bath above and using 7% tin/93% lead anodes.

Troubleshooting Lead Bath

Problem	*Cause*	*Remedy*
Lack of adhesion	Improper cleaning	Check cleaner
Rough deposit	Current too high	Lower current
	Agitation too low	Increase agitation
	Boric acid content too low	Hang anode bag filled with boric acid in tank
	Fluoboric acid too low	Add fluoboric acid
	Addition agent too low	Add addition agent
	Suspended material	Filter
Deposit bright, but thin	Current too low	Raise current
	Metal concentration too low	Add lead fluoborate
Deposit dark and non-adherent	Organic contamination	Carbon treat

TIN PLATING FROM STANNOUS (TIN) FLUOBORATE

Tin, one of the easiest metals to plate, is widely used because of its unique properties. Plated tin coatings are non-toxic, ductile, and resistant to both corrosion and tarnishing. In contrast to hot tin dipping, tin plating allows accurately controlled and uniformly thick tin coatings. The high throwing power of tin plating baths makes it possible to plate items of unusual shapes without using internal anodes.

Tin plating operations can be carried out with minimal control and only minor problems. Four electrolytes are available for commercial use: stannous fluoborate, stannous sulfate, sodium or potassium stannate and the "halogen" tin process.

The stannous fluoborate bath has excellent throwing power and requires very little control, since it operates at almost 100% anode and cathode efficiency. This bath produces a whiter plate than that from a stannate tin bath. Satin, semi-lustrous deposits are produced which are very smooth and fine-grained. Plating takes place two to three times as fast and uses as little as 10% of the electricity of a stannate bath. This results from using tin with a valence of +2 in the fluoborate bath, compared to tin with a valence of +4 in the stannate bath.

The stannous fluoborate bath can be adapted to rack, barrel, wire and strip plating over an extremely wide range of current densities, at room temperature or slightly above.

Addition Agents:

Addition agents are essential for all stannous fluoborate baths in order to produce fine-grained deposits and to improve throwing power. A variety of agents is available

Tin and Tin Lead Alloys Plating Processes

TINOLS – Brilliant, Bright Finishes
TINOMATS – Satin, Matte Finishes

BATHS:
- Fluoboric Acid Baths – Fluoborates
- Sulfonic Acid Baths – Non Fluoborates
- Sulfuric Acid Baths – Sulfates

APPLICATIONS:
- Excellent for All Types of Reel-to-Reel Applications Including Plating of Preformed or Bandoliered Contacts, High Speed Wire and Strip Material
- Excellent for All Types of Rack and Barrel Plating

DEPOSITS:
- Bright and Matte Finishes – Best Quality
- Meet All Applicable Specifications for Electronics and Semi-conductors

MACLEE
MACLEE CHEMICAL CO. INC.
2065 N. SOUTHPORT, CHICAGO, IL 60614 (312) 929-9792 FAX (312) 929-0698

for this purpose including combinations of peptone, gelatin, β-naphthol, catechol and hydroquinone.

In the past 10 years, proprietary addition agents have been formulated, simplifying the procedure and eliminating the problems associated with the aforementioned agents.

Composition and Operating Conditions of Still and Barrel Plating Tin Bath:

	Optimum		*Range*	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Stannous fluoborate	12.5	94	10–15	75–113
Tin	5	37	4–6	30–45
Fluoboric acid	30	225	25–35	188–263
Boric acid	4	30	3–5	22.5–37.5
Addition agent	As recommended by manufacturer			
Anodes	Pure tin, bagged with Dynel or polypropylene			
Anode current density, ASF	20–25			
Filtration	Constant filtration using a non-silicated filter aid is desirable, although not necessary; such treatment keeps the solution clean and affords agitation.			
Temperature, °F	90–120			
Agitation	Mild, mechanical			
Cathode current density, ASF	1–80			

Composition and Operating Conditions of Wire and Strip Plating Bath:

	Optimum		*Range*	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Stannous fluoborate	35	262.5	30–40	225–300
Tin	7	52.5	6–8	45–60
Fluoboric acid	35	262.5	30–40	225–300
Boric acid	4	30	3–5	22.5–37.5
Addition agent	As recommended by manufacturer			
Anodes	Pure tin			
Cathode current density, ASF	Up to 300			
Anode current density, ASF	Do not exceed 25			
Temperature, °F	90 to 130			
Agitation	Mechanical			
Filtration	Constant filtration using a non-silicated filter aid is desirable, although not necessary; such treatment keeps the solution clean and affords agitation			

Operating Hints:

Addition agent is slowly consumed during plating and has to be replenished. When deposits appear dark and smudged, carbon treating the bath will restore the whiteness of the plate.

It is important to prevent the introduction of air into the bath when filtering. Air will oxidize the tin, and insoluble stannic salts will form. This is indicated by a white precipitate and may cause roughness.

In wire plating, rough deposits may be caused by too high a current density. If gassing is noticed in the plating tank, the current density should be lowered.

It is a good practice not to exceed 25 ASF on the anode. Too high a current density on the anode will cause it to dissolve too rapidly, and therefore elevate the tin content of the bath.

Coast to Coast... General Chemical meets your Fluoborate needs.

We are America's largest Fluoborate supplier to the printed circuit board industry–and the only one with modern, state-of-the-art manufacturing facilities, backed by a nationwide network of strategically located, mixed-load warehouses for fast, responsive delivery.

Quality products...Fast delivery...Nationwide distribution...

Just a few more reasons why at General Chemical, *The Customer Is King.*

For more information call or write:
General Chemical Corporation
90 East Halsey Road, P.O. Box 393, Parsippany, NJ 07054-0393
(201) 515-0900 Customer Service Center, toll free (800) 631-8050

Cupric Fluoborate • Nickel Fluoborate • Zinc Fluoborate
Ammonium Fluoborate • Sodium Fluoborate • Potassium Fluoborate
Stannous Fluoborate • Lead Fluoborate • Peptone

General Chemical

Where the customer is king

Troubleshooting Stannous (Tin) Fluoborate Bath

Problem	*Cause*	*Remedy*
Trees	Low replenisher Low acid	Add addition agent Raise acid content
Roughness	Solids in bath	Filter
Graininess	Low replenisher Too low metal	Add addition agent Add stannous fluoborate
Burning	Too high current density	Lower current density
Blistering	Poor cleaning	Correct cleaner
Streaking or pitting	Low replenisher	Add addition agent
Reduced throwing power	Low replenisher Low acid Low metal	Add addition agent Raise acid Add stannous fluoborate
Gassing	Too high current density Low replenisher	Lower current density Add addition agent

TIN PLATING FROM STANNOUS (TIN) SULFATE

The sulfate bath contains stannous sulfate and sulfuric acid plus addition agents. Advantages of this bath are its high current efficiency, high cathode efficiency, (close to 100%), operation at room temperature and ease of control. In fact, the most critical factor in operating this solution is control of the addition agents. Either Hull cell tests or sample cathodes plated directly in the tank may be used for good control. The bath has good throwing power.

Addition agents are essential for operation of this bath. They inhibit the oxidation of stannous tin, produce smooth, dense deposits and prevent treeing. Among those in

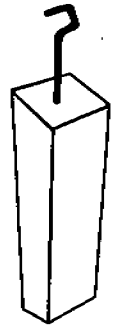
Composition and Operating Conditions for Stannous (Tin) Sulfate Bath:

	Optimum		*Range*	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Stannous sulfate	4	30	2–6	15–45
Stannous tin	2	15	1–3	7.5–22.5
Sulfuric acid	23	172	18–28	135–210
Addition agent	As recommended by manufacturer			
Anodes	Pure tin			
Anode current density, ASF	20		25 max	
Cathode current density, ASF	20		1–25	
Voltage	0.4		0.4–0.8	
Temperature, °F	70		55–85	
Agitation	Mechanical, cathode rod			
Filtration	Constant filtration using a non-silicated filter aid is desirable, although not necessary; such treatment keeps the solution clean and affords agitation			

WHY HANG-UP CASH-FLOW IN TIN OR SOLDER ANODES ???

LET YOUR AMES DISTRIBUTOR ACT AS YOUR WAREHOUSE!!

HE'LL SAVE YOU $$$ THRU....



- ☐ Minimizing In-House Inventories
- ☐ Efficient Fast Restocking of Depleted Production Stocks
- ☐ Low, Low, O.E.M. Pricing
- ☐ Virgin Metal Quality

SERVICE IS THE KEY

STANDARD SHAPES
RECTANGULAR: 1" X 3" X length required
16 POINT STAR: 2¾" X up to 36" lengths
DRILLED and TAPPED at one end at NO CHARGE

AMES H.P. (High-Purity) SOLDER & TIN ANODES are made exclusively, from Electrolytically Pure LEAD (99.99% Min.) and NEW VIRGIN TIN to assure consistent performance and quality.

CALL YOUR NEAREST DISTRIBUTOR

A-Bright Co., TX	214-638-0465	MacDermid, Inc., MN	612-944-9141
Allied-Kelite, Witco Div., IL	800-949-9767	Maltz Sales Co. MA	617-341-0430
Belke Mfg. Co., IL	312-626-4606	Metafin, Inc., IL	312-894-0107
Brookfield Chemical Co., WI	414-782-0555	OMI International, MI	313-497-9100
Electrochem, MO	314-894-9300	Plating Services, CT	203-496-7608
Finishing Eq. & Supply, MN	612-452-1860	Southbrook Metals, FL	305-899-1290
W.D. Forbes Company, MN	612-378-1917	Stutz Co., The, IL	312-287-1068
Frederick Gumm Chem. Co., NJ	201-460-7900	Sunbelt Systems, TX	214-790-5127
Kocour Co., IL	312-847-1111	Tally Metal Sales, IL	312-729-8822
Lafferty-Baublitz, Inc., MD	301-727-6770	Waite Industrial Distributors, SC	803-782-9777

AMES METAL PRODUCTS CO.
4323 S. Western Blvd. • Tel. 312-523-3230 • Chicago, IL 60609

Troubleshooting Stannous (Tin) Sulfate Bath

Problem	*Cause*	*Remedy*
Trees	Low replenisher Low acid	Add addition agent Add sulfuric acid
Roughness	Solids in bath	Filter
Graininess	Low replenisher Too low metal	Add addition agent Add stannous sulfate
Dark or discoloration, still bath	Too low temperature Too low replenisher	Raise temperature Add addition agent
Burning	Too high current density	Lower current
Blistering	Poor cleaning	Correct cleaner
Streaking or pitting	Low replenisher	Add addition agent
Reduced throwing power	Low replenisher Low acid Low metal	Add addition agent Add sulfuric acid Add stannous sulfate
Gassing	Too high current density	Lower current density
Polarized anodes	Anode current density too high	Add anodes or lower current density
Brittle deposits	Organic contamination	Carbon treat

use are: phenol- or cresol-sulfonic acid, gelatin, β-naphthol and resorcinol. Proprietary addition agents which are easier to use are also available for the purpose of preventing oxidation of stannous tin and obtaining desirable results.

Bright tin plating can be accomplished through the addition of other proprietary chemicals. Solderability, corrosion resistance and leveling characteristics are essentially the same in bright or mat plating, but it is questionable whether bright tin plating is superior to mat in resistance to whisker growth and tin pest as has been claimed.

TIN PLATING FROM STANNATE BATHS

Alkaline baths are also used for tin plating, with sodium stannate and potassium stannate as the two available baths. Both will produce similar satisfactory results. The criteria for choosing one over the other is related to cost and speed of plating.

Potassium stannate is generally preferred over sodium stannate for the following reasons:

1. Higher plating rates in situations where full use can be made of this characteristic.
2. Greater conductivity, especially in barrel plating.
3. Less likelihood for sludge formation.

The plater is cautioned to choose one or the other bath, and not to mix them. Caustic potash should be used with the potassium stannate bath and caustic soda with the sodium stannate. While the "mixed" bath is operable and satisfactory results can be obtained, analytical control is quite difficult.

Simply The Best...

REDRING ELECTRIC
(TIN & SOLDER PRODUCTS)
MADE SOLELY WITH MALAYSIAN STRAITS TIN

- One & Two Pound Bars
- Bars (rectangles, ovals, stars)
- Nuggets
- Balls
- Hemispherical Anodes

For Unsurpassed Quality!

(800) 435-4644

829 Highams Court
Woodbridge, Virginia 22191

Chromium Plating

by R. Weiner and A. Walmsley

239 pages $90.00

A thorough and well-written book on both decorative and engineering (hard) chromium plating. It will be of interest to anyone engaged in production chromium plating and also to students, researchers and design engineers. Anyone contemplating the installation of chromium plating facilities will find it of special value.

Send Orders to:

METAL FINISHING
Three University Plaza
Hackensack, NJ 07601

For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

TIN CHEMICALS

TinSol™ Process
Stannolume™ 160 Process
Stannospeed™ Process
Potassium Stannate
Sodium Stannate
Stannous Sulfate
Stannous Chloride
Stannous Oxide
Stannasol®
Stannous Methanesulfonate
Lead Methanesulfonate
Methanesulfonic Acid
Bri-Tin® Process
Ultra Stan-100® Process
Tin Anodes

For immediate help, call 908-302-3500
For literature: 800-833-1234

M & T Harshaw
Two Riverview Drive
P.O. Box 6768
Somerset, NJ 08875-6768

M&T HARSHAW
Quality Plating Technologies

Composition and Operating Conditions of Stannate Baths:

Sodium Stannate Bath:

	Rack		Barrel	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Sodium stannate	12	90	24	180
Tin metal	5.3	40	10.6	80
Free sodium hydroxide	1.6	12	3	22.5
Cathode current density, ASF	15–20		5–15	
Anode current density, ASF	25		15–25	
Voltage	3–4		3–4	
Temperature, °F	170–180		165–175	

Potassium Stannate Bath:

	Rack		Barrel	
	oz/gal	*g/L*	*oz/gal*	*g/L*
Potassium stannate	13.3	100	26.6	200
Tin metal	5.3	40	10.6	80
Free potassium hydroxide	2	15	3	22.5
Cathode current density, ASF	30–100		1–100	
Anode current density, ASF	30–40		10–30	
Voltage	4–8		4–14	
Temperature, °F	150–180		150–180	

Anodes:

Anodes used in the stannate bath may be made of pure tin, a tin alloy with 1% aluminum (known as "high speed" anodes), or of inert materials such as steel, nickel and stainless steel.

Critical to the operation of the stannate bath is the formation and maintenance of the film on the anodes. The primary cause of poor tin deposits is the improper filming on the anodes. To film tin anodes a "surge" of current, at higher-than-normal current density must be impressed on them for a few seconds to a minute, after which the current is reduced to its regular value. The anodes must be refilmed after each shut-down before plating again, as the film dissolves rather quickly.

Advantages of the high-speed anode are its greater current density range and its consistent efficiency at higher current density.

Inert anodes have the advantage of avoiding difficulty in filming, and the fact that stannous tin cannot form due to the production of oxygen at the anode. Furthermore, they do not change shape in use. Use of inert anodes has previously been somewhat limited, because of the need for chemical replenishment of the bath. Presently, the chemical replenishment by a tin oxide solution has made their use practical. These solutions are usable only with the potassium stannate systems.

Practically all problems in the use of stannate baths will be resolved when proper anode operation is achieved.

Stannate Anode Film Characteristics

	Pure Tin	*Tin + 1% Al (High Speed)*	*Inert Anode*
Color of film formed	Yellowish	Olive green	No film
Anode current density, ASF	15–40	30–80	No limits

FOR OVER 65 YEARS...THE FINEST ANODES MADE... IN USE WORLD WIDE

Anodes

- TIN
- LEAD
- SOLDER
- EXTRUDED
- MOST ANY SIZE & LENGTH REQUIRED

FASTEST DELIVERY IN U.S.A.

LOWEST COST PER LB. BASED ON LIFE-USE

Call or Write for Information and Prices

DIVISION LEAD

DIVISION LEAD LIMITED PARTNERSHIP
7742 WEST 61st PLACE
SUMMIT, IL 60501

CALL
TEL(708)458-4528
FAX(708)458-4842
1-800-457-5323

ESTABLISHED 1925

TIN PLATING ANODES

- 99.99%– Grade A.
- Also Tin-Cadmium, Tin-Lead/Solders (Electronic Grades to Gov't. & ASTM specs), Tin-Zinc. Standard & Special Compositions.
- Ball, oval, pieces, rectangular, round, special shapes.

Also Cadmium, Copper (Electrolytic, Phosphorized), Copper-Tin, Lead (Pure & Antimonial), Nickel, Zinc. Standard & Special Compositions & Shapes.

Belmont METALS INC
312 Belmont Ave. • Brooklyn, N.Y. 11207
718-342-4900 • FAX: 718-342-0175

Phibro

Metallic Fluoborates
Fluoboric Acid
Copper Fluoborate
Nickel Fluoborate
Tin Fluoborate
Ferrous Fluoborate
Cadmium Fluoborate
Lead Fluoborate

CP/PhibroChem
A Division of Philipp Brothers Chemicals, Inc.
1 Parker Plaza, Fort Lee, NJ 07024
1-201-944-6020

Troubleshooting Anode Problems in Stannate Baths

Problem	*Cause*	*Remedy*
Anodes gray or white	Initial current density not high enough to form film	Remove anodes and replace one at a time when current is on
Anodes brown or black, film passive	Free alkali too low Temperature too low Anode current density too high	Add KOH or NaOH Raise temperature Add anodes If above does not remove film, dip anodes in a 20% muriatic acid solution and rinse well before using
Excessive anodic gassing	Temperature too low Anode current density too high	Raise temperature Add anodes
Film lost after first forming	Free alkali too high Anode current density too low Temperature too high Poor anode contact	Lower with 10% solution of acetic acid Remove some anodes Lower temperature Clean contacts
No anodic film	Initial current density not high enough to form film	Remove anodes and replace one at a time when current is on
Low cathode efficiency	Temperature too low Metal content too low Caustic too high Current too high	Raise temperature Add stannate Add 10% acetic acid Lower current density
Low anode efficiency	Temperature too low Low caustic content Current density too high	Raise temperature Add KOH for potassium bath, NaOH for sodium bath Lower current density, or add more anodes
Plating range too narrow	Temperature too low Metal content too low if using sodium bath	Increase temperature Add stannate Switch to potassium bath
Conductivity too low	Temperature too low Caustic too low Metal content too low	Increase temperature Increase caustic Add stannate
Non-adherent deposits	Initial current density not high enough to form film	Remove a few anodes and put back one at a time while plating
Solution crystallizes	Carbonates too high	Freeze out carbonates and then filter
Rough, dark or spongy deposits	Stannous tin in solution	Treat with hydrogen peroxide

Solution should be light straw or light gray in color. Black solutions indicate Sn^{+2} is present; treat with hydrogen peroxide (2ml of 35% hydrogen peroxide/gal of solution). If frequent additions of peroxide are necessary, make sure alkali concentration is not too high, and/or anode current density is not too low.

A 10% solution of acetic acid is used to lower the free alkali content of the bath; one gallon of 10% acetic acid will neutralize 9¼ oz of NaOH (caustic soda) or 12¼ oz KOH (caustic potash). Acetic acid must be added slowly with constant stirring so that the stannic acid formed will redissolve.

Sludge removal should be done when parts being plated are rough from occluded dirt. Sludge usually consists of hydrated tin oxide and carbonates. Allow the bath to cool and settle overnight or over a weekend, then decant the clear solution to another tank. Shovel out the remaining sludge. Filtration of the stannate bath is very difficult.

REFLOWING TIN DEPOSITS

Tin can be plated either mat or bright. Although the characteristics of each are comparable, bright tin plating has its proponents and is quite successful, commercially.

Converting the mat finish of tin plate to a bright one can be accomplished by means of a process called reflowing, flow melting or flow brightening. The tin coating is heated momentarily to a temperature slightly above its melting point of 450°F, and then quickly quenched to produce the bright finish.

Among the methods used in heating the plated material are induction, conduction, radiant heating and immersion. The most commonly used method is immersion in hot oil or fat for a short time. The oil is usually a long chain fatty acid ester of glycerin such as tallow, palm oil or partially hydrogenated oil which has a sufficiently high flash point for the temperature used. It should also have some free fatty acid to serve as a flux.

It is best to reflow as soon as possible after plating. The heating to the molten stage should be completed within 2 to 10 seconds before removing and quenching. For best results, the time to melt the tin coating should be precisely calculated. Unsatisfactory results, in the form of dewetting or balling-up, can occur if the parts are left in the oil too long after the coating melts. The size of the oil bath is also important so that the immersion of cold parts does not reduce the oil temperature to the point that heating time must be prolonged.

A suitable quench to use is 4 to 6" of kerosene (acid-free) over water. The parts should be lowered into the quench slowly so that the molten tin coating solidifies in the kerosene layer. A spangled appearance will result if the molten tin comes in contact with the water. The water further lowers the temperature of the parts and also keeps the kerosene from being heated too near its flash point. The kerosene also serves to remove some of the oil from the tin surface.

Small parts are generally immersed in the hot oil in bulk in a suitable basket. They are then separated by pouring them slowly into the quench or by using a breaker which separates them before entering the quench. For flow-melting large parts, a compartment basket is recommended to prevent disfiguration of parts touching while the tin is molten.

The breakdown of free fatty acid content will gradually reduce the effectiveness of the oil, relative to whether it drains freely and evenly from the molten surface or whether a streaked appearance occurs. To maintain the oil suitably for proper draining, part of it (10 to 25%) must be replaced frequently.

Residual oil must be removed from the tin surface after flow-melting. Any ordinary degreasing method may be used, but the preferred method is vapor degreasing.

There are a number of factors which are critical in successful reflowing. Good cleaning, good plating and good rinsing practices are vital. Dewetting is more likely to occur on large flat areas rather than with rounded shapes.

Operating Conditions for Tin Reflowing:

	Optimum	*Range*
Plating thickness, in.	0.00025	0.0001–0.0003
Immersion time, sec.	6	2–10
Temp. of oil bath, °F	490	480–510
Acid neutralization value, mg KOH/gm of oil	2.7	2.3–6.6

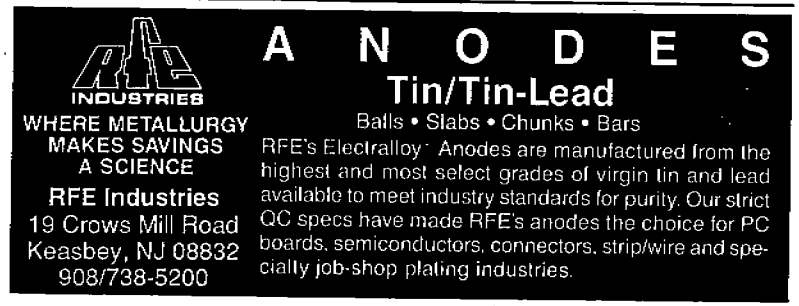
Troubleshooting for Tin Reflowing

Problem	*Cause*	*Remedy*
Etching	Acid neutralization value too high	Remove part of oil bath and replace with new oil
Dewetting	Tin coating too thick Part not cleaned well before plating	Plate for shorter time Check cleaning cycle
Streaky	Acid neutralization value too low	Add fatty acid flux
Not fully bright	Tin coating too thin	Plate for longer period of time
Spangling	Molten tin comes in contact with water in quench	Increase in quench. Lower parts more slowly

Determination of Acid Neutralization Value:

1. Weigh 6 to 10 grams oil in a 250-ml Erlenmyer flask and add approximately 50 ml of 3A alcohol (a methanol-ethanol mixture) previously neutralized to a pH of 7.0.
2. Carefully heat the solution on a hot-plate with stirring until one or two bubbles appear on the surface of the solution.
3. Remove the solution from the hot-plate, add five drops phenolphthalein indicator and immediately titrate with 0.1N sodium hydroxide from clear to a pink endpoint that persists for 10 seconds.

$$\text{Acid Neutralization Value mg KOH/gm oil} = \frac{\text{ml NaOH} \times 5.611}{\text{weight oil sample, gm}}$$



TIN-NICKEL ALLOY PLATING

by S. K. Jalota

Olin Corp., New Haven, Conn.

Tin-nickel may be electroplated directly on basis metals such as steel, copper, brass and on an undercoat of copper or nickel on zinc diecastings. The alloy is an intermetallic compound of approximately 65% tin and 35% nickel.

Tin-nickel alloy plating offers a replacement or an alternative to decorative chromium plating for a number of indoor and outdoor applications because of its attractive faint rose-pinkish color which gives it a very pleasant appearance. The alloy is resistant to corrosion and tarnish and has good contact and wear resistance. Its hardness lies between those of nickel and chromium. It has excellent frictional resistance and the ability to retain an oil film on its surface. Tin-nickel alloy plating solutions have deep throw so that where there is a problem in plating chromium in deep recesses, tin-nickel is an alternative. Because of these and a number of other properties, tin-nickel alloy has found its use in light engineering fields and in the printed circuit board manufacturing industry as an excellent etch resist and a substitute for gold.

Tin-Nickel Alloy Plating from Fluoride Baths:

Solution Composition:

Stannous chloride anhydrous ($SnCl_2$)	6.5	oz/gal	49	g/L
Nickel chloride ($NiCl_2 6H_2O$)	40.0	"	300	"
Ammonium bifluoride (NH_4HF_2)	7.5	"	56	"

Control Limits:

Stannous tin	3.5– 5.0	oz/gal	26–38	g/L
Nickel	8.0–11.0	"	60–83	"
Total fluoride	4.5– 6.0	"	34–45	"
pH	2–2.5			

The solution pH can be adjusted by additions of ammonium hydroxide (to raise) and ammonium bifluoride (to lower). The total fluoride content should be at least as high as the total tin content (both stannous plus stannic).

Operating Conditions:

Temperature	150°F	65°C
Voltage	2–4 V	
Cathode current density	25 amps/ft²	2.8 amps/dm²

Agitation is not necessary for thin deposits but mechanical agitation may be necessary for thick deposits. Continuous filtration is necessary to remove the suspended matter.

Anodes:

Only nickel anodes may be used. Alternately, tin anodes may be used in conjunction with nickel anodes in the ratio of 2:1 respectively. When tin anodes are used, they have to be taken out of the solution during idling periods. It is not necessary to take out the nickel anodes. When only nickel anodes are used, tin content of the solution is maintained by regular additions of anhydrous stannous chloride.

Solution Preparation:

The plating tank is 2/3 filled with water and heated. The required quantity of nickel chloride is dissolved first. Ammonium fluoride is added next. Stannous chloride is added when both the nickel chloride and ammonium bifluoride have been dissolved. Ammonium hydroxide is used to adjust the pH between 2 and 2.5. The solution is dummied for 4 to 6 hours while filtering it through activated carbon before it is put to use.

Effect of Process Variables and Contaminants:

For a given concentration of tin and nickel in a solution, the factor exerting the most profound influence on the deposit is the fluoride content. Since fluoride has complexing action on tin (stannous), an increase in fluoride content will decrease the tin content of the deposit and vice versa.

Free hydrofluoric acid content should be maintained between 6 and 12 g/L to avoid loss of brightness and burning in the high current density areas.

The presence of grease, oil and organic contaminants in the solution will give rise to serious pitting of the deposit. The presence of lead over 25 ppm is very harmful to the solution. Metallic impurities such as copper, antimony, iron, zinc, cadmium, etc, under 200 ppm have no detrimental effect on the deposit but can be removed by dummying.

Troubleshooting:

1. Cloudy deposits are due to lack of nickel content, low temperature or organic contamination.
2. Dark deposits in low current density areas are due to metallic contamination, copper in particular if more than 50 ppm.
3. Gray deposits in high current density areas are due to high tin (stannous) content, lack of free fluoride content, iron contamination above 750 ppm or chromium contamination over 50 ppm.
4. Burnt deposits are due to lack of tin content, low temperature, and pH imbalance.
5. Loss coverage is due to excessive iron contamination.
6. Poor solderability is due to surface passivation and aging.

Plating from Proprietary Baths:

Tin-nickel alloy may be electroplated with the use of proprietary additives in fluoride baths. Incorporation of proprietary additives allows the operation of the process at a little lower temperature range (120-130°F) and pH between 4 and 5, resulting in bright and ductile deposits.

Tin-Nickel Alloy Plating from Pyrophosphate Baths:

Because of the corrosive and toxic nature of fluorine in fluoride baths, pyrophosphate baths have been developed which operate at lower temperatures and near neutral pH.

Bright deposits of tin-nickel alloy have been successfully obtained from baths consisting of the following composition and operating parameters:

Stannous chloride ($SnCl_2 2H_2O$)	3.8	oz/gal	28.2	g/L
Nickel chloride ($NiCl_6H_2O$)	4.2	"	31.3	"
Potassium pyrophosphate ($k_4P_2O_3H_2O$)	25.8	"	192.2	"
Glycine	2.7	"	20.0	"
Temperature	122°F		50°C	
pH	7.5–8.5			
Current density	4.8–14	amps/ft²	0.5–1.5	amps/dm²

The composition of the alloy obtained from this solution does not vary with changes in pyrophosphate concentration, but variation in the content of individual metals, tin or nickel, changes the composition of the alloy. pH values below 7.5 or above 8.5 are undesirable.

ZINC PLATING

by Vijay Kansupada, Cliff Biddulph and Michael Marzano

Pavco Inc., Cleveland

The electroplater can achieve excellent results from bright zinc plating electrolytes when the baths are operated correctly. This article is designed to give quick reference to all vital data needed for the optimum bath performance. Discussion has been kept to a minimum in favor of tables in an effort to convey more useful information in a simplified form.

Although there are a number of electroplating baths operating such as acid sulfate and alloyed zinc, their numbers are a small percentage of the zinc electroplating industry. With that in mind, the present data concentrate on acid chloride zinc, alkaline noncyanide zinc, and cyanide zinc baths.

PLATING TANK CONSTRUCTION

The choice of plating tank construction material should fit the type of bath. All types of tank linings have advantages and disadvantages ranging from length of wear to economy.

Acid Chloride Baths:

Acid chloride zinc baths can use fiberglass tanks, or polypropylene tanks, but steel tanks must be lined with any of the following: fiberglass, PVC, or polypropylene. Tanks for chloride zinc must not be constructed of unlined steel.

Alkaline Noncyanide Baths:

Alkaline noncyanide zinc baths can use tanks constructed from steel, PVC, fiberglass lined with PVC, or polypropylene. Alkaline noncyanide zinc systems cannot use unlined fiberglass tanks.

Cyanide Baths:

Cyanide zinc baths can use tanks constructed of steel, fiberglass, PVC, or polypropylene.

TYPE OF SUBSTRATE TO BE PLATED

The selection of a bath to match the substrate characteristics is of major importance in the success of a zinc plating system. Regular steel substrates and leaded steel substrates both are compatible with acid chloride, alkaline noncyanide, and cyanide zinc systems. In fact, those materials are the only two recommended for alkaline and cyanide plating.

Acid chloride zinc is more flexible in compatibility with other substrates. Successful use of malleable, high carbon, heat treated, and carburized substrates can be accomplished with acid chloride zinc systems.

AUTOMATIC CONTROL EQUIPMENT

Automatic control equipment can play an integral role in the operation of a consistent, high-quality plating line. Both acid chloride zinc and alkaline noncyanide zinc systems can benefit from the use of starter, carrier, or refining agent automatic feeder systems. All three zinc baths are suited for the use of brightener feeders connected to rectifiers. An automatic pH controller can simplify and improve the operations of an acid chloride zinc bath.

Table I. Bath Compositions

	Zinc Metal[1]	*Sodium Hydroxide*[2]	*Sodium Cyanide*	*Ammonium*[3] *Chloride*	*Potassium*[3] *Chloride*	*Boric Acid*[4]	*pH*
ACID CHLORIDE ZINC:							
All Ammonium Chloride	2.0-4.0			16.0-20.0			5.0-6.0
Low Ammonium Potassium Chloride	2.0-4.0			4.0-6.0	16.0-20.0		5.0-6.0
Non Ammonium or All-Potassium Chloride	3.0-5.0				25.0-30.0	3.0-5.0	5.0-5.5
ALKALINE NON-CYANIDE ZINC:							
Low Chemistry	0.8-1.2	10.0-14.0					
High Chemistry	1.8-3.0	16.0-20.0					
CYANIDE ZINC:							
Low Cyanide	1.0-1.5	10.0-12.0	1.5-2.5				
Mid Cyanide	1.8-2.5	10.0-12.0	3.5-6.0				
High Cyanide	3.5-4.5	10.0-12.0	11.0-14.0				

All figures in oz/gal. Conversion to metric: oz/gal × 7.49 = g/L

1. Zinc metal source:
   Acid chloride zinc—zinc chloride.
   Alkaline noncyanide zinc—zinc oxide (preferably nonleaded).
   Cyanide zinc—zinc oxide or zinc cyanide.
2. Sodium hydroxide source: mercury cell grade or rayon grade.
3. Ammonium and potassium chloride source: untreated is preferred.
4. Boric acid source: granular preferred as powdered form creates a dusting problem.

SAFETY CONCERNS

The characteristics of zinc plating baths deserve consideration due to possible safety hazards. While acid chloride zinc and alkaline noncyanide zinc result in no toxicity to humans, cyanide zinc is highly poisonous. Platers should remember that the formulations of acid chloride zinc baths make them corrosive to equipment. Alkaline noncyanide and cyanide baths are noncorrosive to equipment.

Exposure to the chemicals in alkaline noncyanide zinc and cyanide zinc baths can be corrosive to living tissue, while acid chloride zinc appears to have little corrosive effect on tissue. Remember to follow all OSHA requirements, checking appropriate MSDS sheets prior to the handling and/or use of all chemicals whether general or proprietary in nature.

Table II. Bath Parameters

	Acid Chloride Zinc	*Alkaline Non-cyanide Zinc*	*Cyanide Zinc*
Wetting agents, refining agents or carrier	2 - 5% by volume	1 - 3% by volume	Not applicable
Brightener	0.05 - 0.2% by volume	0.05 - 0.2% by volume	0.2 - 0.5% by volume
Temperature[1]	60 - 130°F	60 - 110°F	60 - 100°F

1. Positive and negative effects are observed when a bath is operated above room temperature (75°F):
   a. Because of the solution evaporation, bath build-up problems can be minimized or eliminated.
   b. At higher temperatures, higher conductivity means less power consumption.
   c. Bath efficiency is higher at higher temperatures. This means less plating time is required.
   d. Operating at higher temperatures means savings in refrigeration cost.
   e. At elevated temperatures brightener consumption may be higher than at room temperature.

Table III. Properties of the Zinc Baths

	Acid Chloride	*Alkaline Non-cyanide Zinc*		*Cyanide Zinc*		
		LC	HC	LCN	MCN	HCN
Ductility[1] at higher thicknesses	Poor (>0.5 mil)	Poor	Fair/ Good	Good	Good	Good
Bath efficiencies	95-97%	70-75%	70-95%	65-70%	70-75%	75-80%
Stardusting	Yes	Yes	Yes	No	No	No
Plate distribution[2]	Poor	Good	Excellent		Good to Excellent[3]	
Commercial plating thickness requirements	Excellent	Excellent			Excellent	

1. Ductility is the ability of a material to be bent, molded, or formed without cracking, peeling, or chipping.
2. Distribution or throwing power is the ratio of the amount of zinc deposited in the high current density to the amount of zinc deposited in the low current density.
3. Plate distribution improves as cyanide to zinc ratio increases.

The Great Zinc Plating Beauty Contest

We'll grant you that our mascot Pat Pavco is no beauty, but you must admit that he's better looking than that other guy.

However, if you plate with cyanide you live with the old skull & crossbones, plus all of cyanide's other hassles, including expensive waste treatment and sludge disposal costs.

All that has changed since the introduction of easy-to-handle Alk2V3 non-cyanide alkaline zinc plating system.

Alk2V3 yields results equal toor better than cyanide without cyanide's toxicity or expensive waste treatment drawbacks.

Alk2V3 is the painless way to kick the cyanide habit. Alk2V3's advantages include:

- Outstanding distribution on large parts requiring low-current density coverage.
- No need to pump out and store over weekends or holidays – Alk2V3 can stay in the plating tank during shutdowns and still deliver superior coverage after start up without delayed blistering problems.
- Increased plating efficiency – up to 80% in some cases. Alk2V3 easily tolerates temperatures in excess of 100°F.

Do your product, your business, and your employees a favor. Try PAVCO Alk2V3 in your zinc plating operation and say goodbye to the cyanide blues. For more information or literature about PAVCO alkaline non-cyanide plating systems, call toll-free 1-800-321-7735, or write PAVCO, 8100 Grand Ave., Cleveland, OH 44104.

AESF mfsa

PAVCO

American Bred / World Class

Table IV. Miscellaneous Requirements and Properties

	Acid Chloride Zinc	*Alkaline Non-cyanide Zinc*	*Cyanide Zinc*
Anode polarization	Seldom	Yes	Yes
Conductivity of the bath solution (Higher conductivity lowers energy costs)	Excellent	LC-Poor, HC-Good	Fair
Agitation in rack operations	Required	Not required	Not required
Heating or cooling required	Yes	Yes	Yes
Filtration required	Yes	Yes	Not normally
pH adjustment required	Yes	No	No
Purifier needed to treat impurities	No	Yes	Yes
Chromate receptivity	Good	LC-Fair, HC-Excellent	Excellent
Waste treatment	Simple	Simple	Complex
Iron treatment by oxidation[1]	Yes	No	No

1. Hydrogen peroxide is most commonly used. When necessary, 20 ml/100 gal of bath is a typical addition. This addition should be diluted with water to a 10% solution before adding. Potassium permanganate may also be used; however, this generates a greater amount of sludge, possibly creating filtration problems and iron precipitation/filtration problems.

CHLOROSTAR
BRIGHT ACID ZINC PROCESS

★ DUCTILE
★ BRILLIANT DEPOSIT
★ EASY TO CONTROL AND CHROMATE
★ INEXPENSIVE TO OPERATE
★ NON-CHELATED
★ EXCEPTIONALLY GOOD THROWING POWER
★ HIGH CATHODE CURRENT EFFICIENCY
★ SINGLE ADDITIVE

Starlite Chemicals, Inc.
1319 WEST NORTH AVENUE ★ CHICAGO, ILLINOIS 60622 ★ 312/772-2278

IMPORTANT DATA
from the NEW LEADER in Innovative Metal Finishing Technology
A BRITE COMPANY

- Nickel Plus Bright Nickel Technology
- ABZ NO CY Zinc Systems
- AZ and KZ Zinc Systems
- Chromates up to 500 hours
- Alkleen, Aluma Etch & Aldeox Aluminum Processes
- My T Kleen, Sparkleen and Pickleen Pre-Treatment Products
- Phoseal Phosphate Systems
- Briteguard Protective Products
- Polyfloc, Polycat, Dropout & Equipment for Waste Treatment
- Processing Equipment & Accessories

8005 Sovereign Row • Dallas, TX 75247
Ph: 214 / 638-0485 • FAX: 214 / 630-4849

metal finishing suppliers
. . . gain a competitive edge
sell our ZINC BRIGHTENERS
under your private label

- market 'your own' brighteners in addition to the other brands you currently sell.
- increase your profits with our superior quality and lowest distributor prices.
- Acid Chloride Zinc
- Alkaline Non-Cyanide Zinc
- Cyanide Zinc
- Acid Tin
- Separate Brightener Components

COLUMBIA™ CHEMICAL
3097 Interstate Parkway
Brunswick, Ohio 44212
Phone: 216/255-3200
Telex: 980131 WDMR
Fax: 216/255-1499

U.C.R., Inc.
Suppliers to the Metal Finishing Industry
Ni Brightener Systems
ZN Brightener Systems
CD Brightener Systems
CU Brightener Systems
TN Brightener Systems
Manufacturers of soak, electro cleaners and strippers
- *Complete lab. facilities available.*
- Specialists in chemical engineering.
- Distributor Inquiries Invited

826 East Sumner Avenue
Indianapolis, IN 46227
Phone: 1-317-783-3188
Fax: 1-317-787-4715

ZINC
Anodes, Balls & Special Shapes

Also Cadmium Balls;
Copper Anodes & Wire;
Nickel 1x1, D-Crowns & S-Rounds;
Tin Balls & Anodes

TALLY
Metal Sales, Inc.
1850 Johns Drive
Glenview, IL 60025
30 years of experience

Call Toll-Free
800-323-1310
In Illinois 708-729-8822
Fax 708-729-1564

ZINC ALLOY PLATING

Ed Budman

Dipsol Gumm Ventures Inc.

and Robert R. Sizelove

Frederick Gumm Chemical Co. Inc., Kearny, N.J.

The application of sacrificial coatings onto steel and other ferrous substrates has long been established as an effective and reliable standard of the industry for corrosion protection. Due to its low cost, zinc has been the predominant coating, although cadmium has also been widely used where zinc fails to provide the necessary corrosion protection for certain applications. Recent demands for higher quality finishes, and, more specifically, longer lasting finishes, have prompted a move to alloy zinc deposits. This has been especially true in the automotive industry, but is also true in the aerospace, fastener, and electrical component fields, among others. Additionally, cadmium users are under increased pressure to stop using it due to its toxic nature.

Several different alloy zinc systems have been introduced, giving deposits of somewhat different properties. The differences come not only from the choice of alloying metal, but from the electrolyte system used as well. Much of the recent research work on alloy zinc electroplating processes was done in Europe, and in Japan, where cadmium was effectively outlawed during the 1970s. The alloying elements successfully used with zinc have been iron, cobalt, nickel, and tin. Except for the tin, which is typically an alloy of 70% tin and 30% zinc alloy, zinc comprises from 85–99% of the alloy deposit. At these compositions, the deposit maintains an anodic potential to steel, yet remains less active than pure zinc. Analogous to conventional zinc, each of the alloys requires a chromate conversion coating to obtain improved corrosion resistance. Indeed, the chromate in this case is more effective on the alloy deposits than on the pure metal.

ZINC-NICKEL

Zinc-nickel can be plated from acid or alkaline noncyanide solutions. The acid bath typically gives a higher nickel content than the alkaline (i.e., 10–14% nickel versus 6–9%). Corrosion protection increases with increasing nickel content until approximately 15% is reached. Beyond that level, the zinc-nickel deposit becomes more noble than the substrate, thus losing its corrosion protection properties (see Table I). Additionally, at a nickel content above 10%, the deposit becomes more passive, and therefore less receptive to forming a consistent,

Table I. Bath Parameters for an Acid Zinc-Nickel Bath

Parameter	*Rack*	*Barrel*
Zinc chloride	130 g/L	120 g/L
Nickel chloride	130 g/L	110 g/L
Potassium chloride	230 g/L	—
pH	5.0–6.0	5.0–6.0
Temperature	24–30°C	35–40°C
Cathode CD	0.1–4.0 A/dm²	0.5–3.0 A/dm²
Anodes	Zinc and nickel separately. In some cases, separate rectifiers and bussing are required.	

Table II. Bath Parameters for an Alkaline Zinc-Nickel Bath

Zinc metal	8.0 g/L
Nickel metal	1.6 g/L
Sodium hydroxide	130 g/L
Ratio zinc/nickel	5.0/1
Temperature	23–26°C
Cathode CD	2–10 A/dm²
Anode CD	5–7 A/dm²
Anodes	Pure zinc

effective chromate conversion coating. Finally, the deposit from the acidic solution tends to have poor thickness distribution and significant alloy variation from high to low current density areas.

Compared with the acid bath, alkaline zinc-nickel produces a deposit with a lower nickel content, but one that is far more uniform in terms of both thickness of deposit and alloy composition; however, this is done at the sacrifice of plating speed (see Table II). The alkaline bath produces a columnar structure rather than the laminar structure as deposited from the acidic electrolyte. Thus, the alkaline system maintains better deposit integrity when the part is formed, bent or crimped after plating. This bath is very simple to operate, being quite similar to conventional alkaline noncyanide zinc processes.

Zinc-nickel has consistently achieved the highest corrosion protection as shown by accelerated corrosion testing, with the exception of the SO_2 (Kesternich) test, which favors zinc-cobalt. Zinc-nickel does, however, retain high corrosion resistance after forming of parts, such as fuel lines, or after heat treating of fasteners and other parts. The ability to continue to deliver good corrosion properties after heat treating has, in some cases, allowed parts to be baked after chromating rather than before chromating, eliminating the need for double handling.

Another area where zinc-nickel was found to offer excellent protection is in plating of fasteners, which are to be used in contact with aluminum, safely replacing cadmium in this application.

ZINC-COBALT

Commercial zinc-cobalt baths are essentially conventional low ammonium or ammonium free acid chloride zinc baths, with the addition of a small amount of cobalt. The resulting deposit is generally up to about 1% cobalt, the balance being zinc. This bath has a high cathode efficiency and high plating speed, with reduced hydrogen embrittlement compared to alkaline systems. But the thickness distribution of the deposit varies substantially with the current density. An alkaline bath is also available (see Tables III and IV for acid and alkaline bath parameters).

Table III. Bath Parameters for an Acid Zinc Cobalt Bath

Parameter	*Rack*	*Barrel*
Zinc metal	30 g/L	30 g/L
Potassium chloride	180 g/L	225 g/L
Ammonium chloride	45 g/L	—
Cobalt (as metal)	1.9–3.8 g/L	1.9–3.8 g/L
Boric acid	15–25 g/L	15–25 g/L
pH	5.0–6.0	5.0–6.0
Temperature	21–38°C	21–38°C
Cathode CD	0.1–5.0 A/dm²	1–50 A/dm²
Anodes	pure zinc	pure zinc

Table IV. Bath Parameters for an Alkaline Zinc-Cobalt Bath

Zinc metal	6–9 g/L
Caustic soda	75–105 g/L
Cobalt metal	30–50 mg/L
Temperature	21–32°C
Cathode CD	2.0–4.0 A/dm²
Anodes	Steel

ZINC-IRON

The primary advantage of zinc iron is its ability to develop a deep, uniform black conversion coating. Additionally, the alloy has good weldability and workability, and can readily be used on electroplated strip steel. It is also used as a base for paint. Of the alloys being considered, zinc-iron will generally give the least improvement in corrosion resistance compared with conventional zinc. Also, if the iron content of the bath gets too high, blistering problems, including delayed blistering, may occur (see Tables V and VI for acid and alkaline bath parameters).

Table V. Bath Parameters for an Acid Zinc-Iron Bath

Ferric sulfate	200–300 g/L
Zinc sulfate	200–300 g/L
Sodium sulfate	30 g/L
Sodium acetate	20 g/L

Table VI. Bath Parameters for an Alkaline Zinc-Iron Bath

Zinc metal	20–25 g/L
Iron metal	0.25–0.50 g/L
Caustic soda	120–140 g/L
Temperature	18–23°C
Cathode CD	1.5–3.0 A/dm²
Anodes	Steel

TIN-ZINC

A number of electrolytes are available for deposition of tin-zinc alloys. These include acid, alkaline and neutral formulations. In general, an alloy of 25–30% zinc with 70–75% tin is produced. This range of composition produces optimum corrosion resistance, especially in sulfur dioxide atmospheres, along with excellent solderability. As with the other zinc alloys, a chromate conversion coating is required in order to achieve the optimum corrosion protection. In any event, the tin-zinc deposit has good frictional properties, and excellent ductility for use on parts that may be formed after plating; however, being very soft, it is also susceptible to mechanical damage. Electrical contact resistance of the tin-zinc alloy is low, and it is somewhat superior to pure tin for resistance welding of coated mild steel sheet. Additionally, tin-zinc coatings do not undergo bimetallic corrosion, and can be used, for example, on steel fasteners for aluminum alloy panels.

Table VII. Comparison of Zinc Alloy Plating Processes

		Bath Type				
		Alkaline Zinc	*Alkaline Zinc-Nickel*	*Neutral Tin-Zinc*	*Alkaline Zinc-Iron*	*Acid Zinc-Cobalt*
Deposit Properties	Appearance	Good	Good	Fair	Good	Excellent
	Solderability	Fair	Fair	Excellent	Fair	Fair
	Abrasion Resistance	Fair	Good	Poor	Fair	Fair
	Whisker	Fair	Good	Fair–Good	Fair	Fair
	Ductility	Fair	Fair	Excellent	Fair	Fair
Corrosion Resistance				As Plated		
	To White Rust	Fair	Excellent	Fair	Excellent	Fair
	To Red Rust	Fair	Excellent	Excellent	Good	Good
				Heat Treated		
	To White Rust	Poor	Good	Poor	Poor	Poor
	To Red Rust	Poor	Good	Fair	Poor	Poor
				After Bending		
	To White Rust	Fair	Good	Fair	Fair	Fair
	To Red Rust	Fair	Good	Excellent	Fair	Fair
Bath Characteristics	Throwing Power	Good	Excellent	Poor	Good	Poor
	Plating Speed	Fair	Poor	Good	Fair	Good
	Covering Power	Fair	Fair	Excellent	Fair	Fair
	Bath Control	Good	Fair	Fair	Fair	Fair
Analysis and Measurement				Thickness		
	X-Ray Fluorescence	Good	Good	Good	Good	Good
	Coulometric	Good	Good	Good	Good	Good
				Alloy Ratio		
	X-Ray Fluorescence	Good	Good	Good	Poor	Poor
	Wet Analysis	Good	Good	Good	Fair	Fair
Anodes		Separate	Zinc	Alloy	Zinc	Zinc

CHROMATING

As with conventional zinc or cadmium plating, a chromate conversion coating used in conjunction with the deposit greatly increases corrosion protection compared with a nonchromated surface. However, the presence of the alloying elements affects both the chemistry of the chromate needed to produce an appropriate conversion coating, and the protective mechanism provided by that film. For example, with zinc-nickel, the reaction of the chromating solution on the deposit dissolves some of the zinc from the surface, leaving a nickel-rich layer. This layer provides far superior corrosion resistance than a conventional chromate film. Cost factors, however, may make tin-zinc the last of the alloy deposits to be considered, except in cases where its unique properties are essential.

HOW TO SELECT A FINISH

Unfortunately, there is no single answer as to the best substitute for zinc or cadmium (see Table VII). Each application must be examined to determine which parameters in the

specification are most important. Compatibility of the process with existing equipment may also be a determining factor. For example, an existing acid chloride zinc line may be readily converted to acid zinc-cobalt, if that finish will meet the requirements of the part to be plated; however, if the part is to be heat treated after plating, zinc-cobalt is not indicated as the preferred deposit. An analysis must be made of cost versus quality, and a decision made based on a company's philosophy. Table VII presents data highlighting some of the areas of differences among the finishes described.

CURRENT APPLICATIONS

As in Japan and Europe, where industrial application of alloy zinc finishes has preceded the U.S., the automotive industry has led the way to successful use of these processes. In particular, parts such as fuel lines and rails, fasteners, air conditioning components, cooling system pumps, coils and couplings have made the switch to alloy zinc. Additionally, nonautomotive uses include electrical power transmitting equipment, lock components and maritime, military and aerospace applications. Lengthy testing programs and specification rewriting have slowed the introduction of these processes, but as an increasing number of successful heavy-duty applications become known, the industry's confidence level will rise, resulting in a broader range of uses.

Zinc Plating

by H. Geduld *360 pages* *$100.00*

This book contains 15 chapters including a history, cleaning procedures, equipment and plant layout, cyanide, zincate and acid baths, post-plate treatments, troubleshooting, special operations such as mechanical and strip and wire continuous processing, control of solutions and waste treatment. It is a practical volume written for the practitioner and chemist.

Send Orders to:
METAL FINISHING
Three University Plaza, Hackensack, NJ 07601
For faster service, call (201) 487-3700 or FAX your order to (201) 487-3705

All book orders must be prepaid. NY, NJ and MA residents add appropriate sales tax. Please include $5.00 shipping and handling for delivery of each book via UPS to addresses in the U.S.; $8.00 for Air Parcel Post shipment to Canada; and $20.00 for Air Parcel Post shipment to all other countries.

QUIN-TEC
"THE PLATER'S EDGE"

GREAT IDEAS TO INCREASE CORROSION RESISTANCE

- **ZINC-IRON 680** Full bright low alloy plate with amazing salt spray
- **QUIN-CAD CADMIUM-930** Neutral process to give unbelievable high salt spray test
- **BRIGHT & SEMI-BRIGHT NICKEL** Single additive. Customized mixes
- **ACID COPPER 770** No dye single additive. High leveling

Call us today for ideas to "Make Things Simple"

1-800-521-1094

QUIN-TEC INC.
14057 Stephens, Warren, MI 48089
(313)774-8010 Fax (313)775-8460

PLATING PROCEDURES

BARREL PLATING

by Raymund Singleton

Singleton Corp., Cleveland

DEFINITION

In barrel plating a bulk work load is tumbled in a rotating vessel incorporating electrical contacts to attract metals out of solution onto the work. This is the most effective method for treating bulk parts and any pieces which do not require individual handling. The workpieces, in effect, are part of the plating equipment because they become bipolar electrical contacts to the other pieces in any work load. This inherent feature greatly contributes to the higher efficiencies experienced in barrel plating since the entire surface of the work load, in the current path at any time, is in cathode contact.

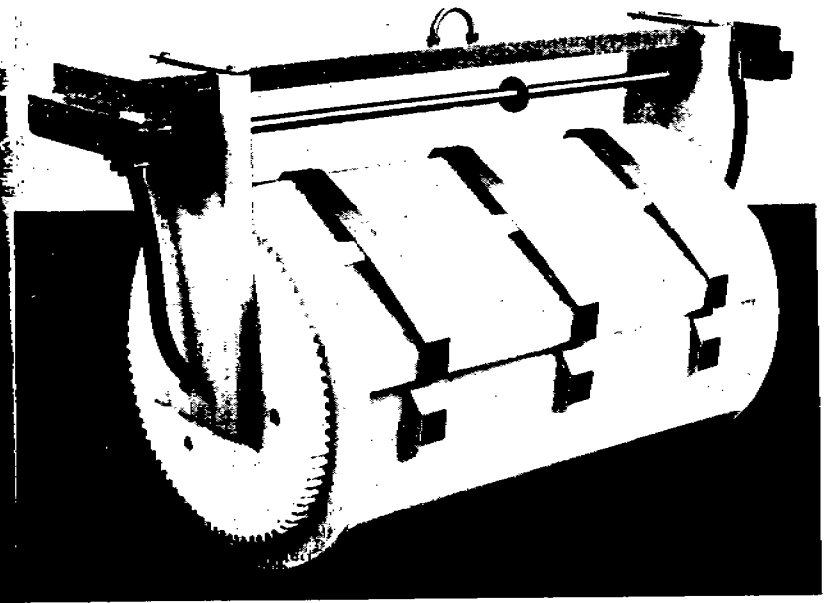


Fig. 1. Typical horizontal barrel and superstructure assembly showing inverted "V" type contacts.