ELECTROPLATING SOLUTIONS

BRASS PLATING

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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:

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/ft^2 (2.2 A/dm^2).

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.