Decorative applications for alloy plating

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Alloy plating (the co-deposition of metals) is becoming more commonplace in the metal finishing industry. While most of the emphasis has been in functional applications (i.e. zinc alloyed with cobalt, nickel or iron) there have been many exciting new developments in alloy decorative plating. Many of the new, innovative processes provide improved covering power and wear resistance, as well as giving end users a variety of choices in finishes. The purpose of this paper is to discuss the various chemistries, properties and attributes of the different technologies available.

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Typically when platers think of alloy plating, they first think of zinc alloys. Zinc, when alloyed with other metals such as cobalt, iron, nickel and tin to enhance the corrosion protection performance of the deposit. Alloy plating is, however; equally common for decorative plating, to provide new, more durable, environmentally friendly, cost effective finishes.

One of the first, and often forgotten decorative alloy finishes is brass. Brass of course is an alloy of zinc and copper, whose origins can be traced back to ancient times. Egyptian Pharaohs had death masks made from brass and gold using mercury amalgams and the plating was done mechanically. Most brass plating today tends to be limited to decorative applications, generally 60-70 percent copper and 30- 40 percent zinc.

Electroplated brass is used as a decorative finish on ferrous metals applied as a thin plate on top of copper or nickel, so that a bright finish is obtained. Corrosion protection is provided by means of the initial electrodeposit. Less often, heavier plate thickness are applied and brushed or polished to the desired finish.

To prevent the brass from tarnishing, it is usual to lacquer or alternatively passivate the subsequent deposit. Care should be taken as not to alter the finish of the brass.
There are three basic types of solutions used for brass plating. First is the conventional low temperature solution (70-100 degrees F) with a wide range of compositions and alloys plated. Second is a similar solution operated at a temperature above 110 degrees F. Third is a solution with a hydroxide content above 7.5 grams per liter and usually a higher metal content. Below is a typical solution make up.

Copper cyanide	32g/l
Zinc cyanide	10 g/l
Sodium cyanide	50 g/l
pH	~10

A second type of solution uses the same basic formula, but at higher concentrations. This allows the bath to operate at a higher temperature, resulting in a faster plating rate and better solution evaporation.[1]

One of the most important considerations in brass plating is the deposit color. Some people prefer the redder deposit achieved with a more copper rich deposit, while others prefer the more greenish hue achieved by a more zinc rich plate. The deposit alloy is typically controlled by altering the bath chemistry and through ammonia additions. Ammonium hydroxide complexes the zinc as an amine, allowing it to more readily deposit, resulting in a greener finish.[2]

Occasionally the zinc in the deposit will contribute as much as 50% of the allow resulting in a white deposit. This form of plating is aptly called white brass. Such deposits are extremely brittle, so only very thin deposits can be applied. It is most common for white brass to be plated on top of nickel, and followed by chrome plating.

Not only is copper alloyed with zinc, it is also alloyed with tin to form bronze. Common applications include decorative fittings, corrosion protection of builder's hardware and bearing surfaces. Alloys with 10-12% tin have a golden color, which is sometimes used as a gold replacement in costume jewelry. A typical formulation is as follows:[3]

Sodium cyanide	64 g/l
Copper cyanide	30 g/l
Sodium stannate	35 g/l
Sodium hydroxide	45 g/l
Rochelle salts	45 g/l

A variation of the bronze solution which produces a plate that is about 40% tin, has a pewterlike finish. This alloy is known white bronze or speculum. A typical formulation is as follows:

Sodium cyanide	37 g/l
Copper cyanide	20 g/l
Sodium stannate	100 g/l
Sodium hydroxide	10 g/l
Rochelle salts	38 g/l

Operation of this is very similar to the standard bronze solution. Control of the alloy depends on the analysis of the deposit since the color does not vary with minor changes in analysis. Fairly frequent addition of stannate salts is necessary due to the large tin content of the deposit.[4]

Nickel is another element commonly used in decorative alloys. It can be combined with tin to produce either a black or silver finish, as well as with cobalt as a replacement for decorative hexavalent chromium.

One of the earliest nickel alloy baths that was developed was tin nickel. These fluoride based solution produced a "pinkish" silver deposit approximately 65% tin and 35% nickel. Both the corrosion resistance and throwing power of these solutions were acceptable, making them a suitable replacement for hexavalent chromium. While much of the technology associated with this chemistry is proprietary, a typical formulation is as follows:

Stannous Tin	20-35 g/l
Nickel metal	50-80 g/l
Total F	30-50 g/l

These baths also contain proprietary complexing agents, grain refiners and wetting agents to improve the deposit properties. Operating solutions are typically run at a slightly acidic pH (4.0-6.0) and at temperatures ranging from 120-140 degrees F.

There are many different applications for"silver" tin zinc. Small parts that are typically barrel plated have been successfully processed in this type chemistry. Applications where corrosion protection is required, perhaps at the expense of deposit hardness, or electronic parts where solderability is a concern, all can be processed in tin nickel.

There is no unusual plating equipment needed for processing tin nickel. Plastic lined steel tanks are commonly used along with fluoride resistant heater. Anodes are either pure nickel or carbon, and very low rectification is needed. Rack plated parts are typically processed at 1 volt, 20 ASF and barrel parts at 3 volts, 5 ASF. While the cathode efficiency is high, ventilation is still normally recommended, as this is an acid-fluoride based solution.

A decorative, black deposit can be achieved by maintaining the same core chemistry, only substituting a phosphate based electrolyte. This type finish has recently grown in popularity, as it is much simpler to run and offers many advantages over other black alternatives such as black nickel or black chrome. These advantages include a harder deposit, more uniform color, no lacquer or oil topcoat required and ease of make up. As is the case with the fluoride version of this process, outstanding corrosion protection and covering power are typical of this technology.

What is interesting about this finish is it has the same metallurgical make up (65% tin 35% nickel) as the silver version. The bath chemistry, and of course the deposit appearance is drastically different. Again, much of the technology associated with this chemistry is proprietary; a typical formulation is as follows:[5]

Stannous Tin	2-3 g/l
Nickel metal	6-2 g/l
Total Phosphate	40-50 g/l

These baths also contain proprietary complexing agents, grain refiners and wetting agents to improve the deposit properties. Operating solutions are typically run at a slightly acidic pH (5.0-6.0) and at temperatures ranging from 120-130 degrees F.

As you can see, the metal concentrations for the black chemistry are much lower than the silver type plating solutions. This has proven to be a major advantage to applicators, as the cost of waste treatment is significantly reduced. Also, by replacing the fluoride-based chemistry with phosphate based, the attack on equipment is reduced as well.

Not only is tin commonly alloyed with nickel, it is also often combined with cobalt to produce a silver, chrome like finish.

Tin-cobalt finishes typically consist of 78% cobalt and 22% tin deposit that has the appearance of decorative chrome but without the environmental and health & safety problems associated with hexavalent chromium. These type chemistries give a deposit appearance similar to that obtained from decorative chromium (bluish-white) and the deposit is resistant to tarnishing and atmospheric corrosion.   The deposit has good abrasion resistance. It is a good replacement for decorative chrome in certain applications.

Typically, tin-cobalt baths are made up as follows:

Tin metal	2-3 g/l
Cobalt metal	1-2 g/l
Conductivity salts	30-60 g/l
pH	7.5-8.5
Temperature	100-120 degrees F

These baths also contain proprietary complexing agents, grain refiners and wetting agents to improve the deposit properties. Operating solutions are typically run at a slightly acidic pH (7.5-8.5) and at temperatures ranging from 100-120 degrees F.

Covering power, or the ability to achieve plating at very low current densities is perhaps one of the most important characteristics of all these type chemistries. This allows even the most intricate parts to be uniformly plated, but also the ability to bulk process small parts in barrels. Now, small parts that could previously only be barrel plated in bright nickel can be cost effectively topcoated with either a black or silver finish improving both the functional performance and the decorative appeal. This allows manufactures to “match” parts, for example fasteners used in conjunction with door hinges.

Decorative coatings make up a large percentage of the plating that is done worldwide. As technology improves, and industry moves towards more environmentally friendly alternatives, alloy plating has become more prominent. Decorative alloy plating also provides more variety in appearance, corrosion protection and wear properties, than was previously available. As decorative alloy plating becomes more prevalent, we should expect to see more and more of these finishes in circulation.

References

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