Blackening of Metals*

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Although it does not represent one of the major applications of metal finishing, the blackening of metals, both for decorative and functional purposes, does occupy an interesting and certainly commercially prominent place in the field.

One of the obvious methods of blackening a metal surface is to apply a black organic coating (paint, plastic, etc.) to the surface. This technique, of course, is widely used and is thoroughly practical. Because it is a specialized field, this method of blackening will not be discussed in any detail other than to state that it certainly is available and can always be considered and evaluated as a blackening option.

Most inorganic blackening of metals is accomplished by one of the following methods:

Fig. 1—Black chromium on bright nickel plate for optical frames.

1. Electrodeposition of a black or at least dark coating onto the metal surface.
2. Chemical conversion of the metal surface into an oxide or other black compound.
3. Anodic treatment of the metal surface to produce an oxide film, either initially black or capable of subsequent blackening.
4. Chemically producing a film or coating on the metal surface and further treating it to generate a black or dark finish.

Some inorganic blackening is also done by the thermal oxidation method, and some by immersion or electroless plating.

Black Electroplating

Black electroplating is usually independent of the metal on which it is being deposited. Provided the basis metal will accept the black plate, the coating generally will follow the character of the substrate surface, yet exhibit the color and properties of the particular electrodeposit. A variety of plating processes, both proprietary and non-proprietary, are used to produce black or gray-black electrodeposits. Arsenic, black chromium, black nickel and nickel-molybdenum alloy plating have been described in the literature and have been used to some extent for many years. Table 1 summarizes some of the formulations and suggested operating conditions for these baths.

The arsenic plating bath produces a grayish, thin, relatively soft and fairly uniform deposit, which probably consists largely of arsenious oxide. The deposit has little corrosion resistance and is used primarily to produce antique finishes. The system is in limited use due to the toxicity associated with arsenic. Proprietary modifications of the basic arsenic plating formulation have produced systems that develop darker and more consistent deposits.

The black chromium plating bath produces a deep black, hard, abrasion and corrosion-resistant deposit consisting of a mixture of elemental chromium and chromium oxide. Black chromium plating requires a relatively high current density and does not have good covering power. Additionally, the process normally requires cooling to maintain the bath within the operative temperature range, and the system must be kept free of sulfate contamination. Because of its hardness and resistance to abrasion and corrosion, the black chromium deposit is particularly well suited for blackening applications in which the finished part will be subjected to outdoor exposure or require very good wear resistance.

Modification of the basic black chromium bath has resulted in proprietary systems that can provide uniform, consistently high-quality finishes with properties similar to those of decorative chromium electrodeposits. The photo of the optical frames shows the black finish produced on a bright nickel plate from a proprietary black chromium system (Fig. 1). The part was processed at 21°C (70°F) at a current density of 26.9 A/dm^2 (250 A/ft^2) for 3 min.

Modifications of the black nickel plating systems have produced proprietary black nickel and nickel-alloy baths that are much easier to control, more reliable in performance and consistent in providing a uniform color. The coatings produced from these baths are not as black as the black chromium deposits, nor are they as hard or as corrosion resistant. The photo of the belt buckles (Fig. 2) shows the black finish produced on a bright nickel plate from a

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Fig. 2—Belt buckle in center is plated with black nickel-tin alloy over bright nickel.

Fig. 3—Commemorative coins with coating produced by hot alkaline blackening.

proprietary black nickel-tin alloy formulation operated at 70°C (158°F) and 1.0 to 2.1 A/dm^2 (10 to 20 A/ft^2). The part was plated for 2 min and coated with a clear lacquer.

The operating conditions and equipment requirements for the various proprietary systems generally are similar to those for the parent baths, *i.e.*, the requirements of the black chromium system would resemble those for standard decorative chromium. Specific recommendations, naturally, would be available from the supplier.

Preparation of the part for black electroplating will depend on the final finish desired, the basis metal being processed, and the black system being utilized. If a matte, dull final finish is desired, the part may require sandblasting, etching or other types of mechanical pretreatment. An undercoat of semibright nickel, copper or brass then can be applied, if needed, followed by the black plate. Bright black finishes are produced by plating the black deposit onto a bright surface. Bright nickel serves as an excellent undercoat. It affords a corrosion-resistant, hard, uniform and lustrous base for the final black deposit. Where practical, the black deposit also can be plated directly onto the basis metal.

Chemical Conversion

By reacting a metal with a suitable chemical solution, the surface of that metal can be blackened by the formation of a black salt or oxide at the surface. One of the simplest and most familiar methods of blackening copper is to immerse the substrate into a water solution of a soluble sulfide. The reaction between the sulfide and the copper produces a thin layer of black copper sulfide salt at the surface. Table 2 lists a number of formulations cited in the literature to produce black coatings on different metals by chemically converting the metal surface. The table also indicates the type of black coating produced.

As with the black plating systems, most of the chemical blackening is done commercially with proprietary products. These materials may be based on some of the listed formulations with modifications to improve their performance.

The hot alkaline baths for blackening brass, copper and steel are used widely and produce reliable and consistent black finishes. The coatings are durable and uniform, but are relatively thin, only fairly hard and do not afford any great degree of corrosion resistance. Both coatings usually are oiled, waxed or lacquered to enhance

Table 1
Formulation & Conditions for Some Black Electroplating Systems*

Electrolyte Composition		Operating Conditions
Gray Arsenic		
Arsenic trioxide	120 g/L (16 oz/gal)	27-40°C (80-104°F)
Sodium hydroxide	120 g/L (16 oz/gal)	0.3-2.2 A/dm^2 (3-20 A/ft^2) at 1 - 6 V
Sodium cyanide	4 g/L (0.5 oz/gal)	Steel anodes
Copper cyanide	4 g/L (0.5 oz/gal)	
Black Chromium		
Chromic acid	250 g/L (33.5 oz/gal)	27-30°C (80-86°F)
Fluosilicic acid	0.25 g/L (0.033 oz/gal)	16.1-48.4 A/dm^2 (150-450 A/ft^2)
		Lead alloy anodes
Black Nickel		
Nickel sulfate	75 g/L (10 oz/gal)	pH 5.6-5.9
Nickel ammonium sulfate	45 g/L (6 oz/gal)	50-55°C (120-130°F)
Zinc sulfate	37.5 g/L (5 oz/gal)	0.1-1.6 A/dm^2 (1.0-15.0 A/ft^2)
Sodium thiocyanate	15 g/L (2 oz/gal)	
Nickel - Molybdenum		
Nickel sulfate	144 g/L (19 oz/gal)	pH 4.3-4.7
Ammonium molybdate	30 g/L (4 oz/gal)	55-80°C (130-176°F)
Boric acid	22.5 g/L (3 oz/gal)	0.2-0.5 A/dm^2 (2.0-5.0 A/ft^2)

**Compiled from D. Fishlock, Metal Colouring, Robert Draper, Ltd, Teddington, Middlesex, UK, 1970 and personal experiences.*

their appearance and wearability. If not protected by an organic coating, both black oxide finishes are sensitive to acidic environments. The alkaline blackening system, particularly the one utilized for steel, is very difficult to rinse and considerable care must be taken when processing recessed parts to avoid solution entrapment and retention. The steel blackening solution, because of the temperature and concentration at which it is operated, presents a potentially hazardous situation. Salts should never be added to the hot solution; they should be dissolved in cold water, allowed to cool, and then slowly added to the bath. When adding water, the hot solution should be agitated or at its boiling point to insure that the water is mixed immediately; otherwise, an eruption may occur.

The photo of the commemorative coins (Fig. 3) shows the black coating produced with the hot alkaline blackening system. The blackened part was treated in a proprietary solution at a concentration of 180 g/L (24 oz/gal) and a temperature of 93°C (200°F). The blackened part was treated for 4 min and coated with a clear lacquer.

A number of proprietary systems based on soluble selenium compounds are being marketed for chemical blackening. These solutions are acidic, operate at room temperature and can produce a black finish on aluminum, copper alloys, silver and steel. The black coating produced from these compositions is composed of either a black metal selenide (copper, iron, silver) or elemental sele- nium and metal selenide. The coating is thin, durable, fairly soft and has a tendency to be powdery or smutty. It is usually lacquered, waxed or oiled to increase its wearability and to enhance its appearance. These systems, because they operate at room temperature, are not energy intensive, but tend to have a high chemical cost. A solution of this type cited in the literature for blackening steel consists of 10 g/L (1.3 oz/gal) of selenous acid, 10 g/L of copper sulfate, and 2 to 4 mL/L of nitric acid.

Proprietary chromate dips are available for the chemical blackening of cadmium, zinc and some zinc alloys. These systems produce uniform, adherent, deep black coatings with excellent corrosion resistance. The coatings generally are applied to electrodeposits having a minimum thickness of 7.6 μm (0.3 mil). These chromate solutions make use of a soluble silver salt, and hence are very sensitive to chloride contamination. When these baths are used after chloride zinc or cadmium plating, thorough rinsing must be employed to prevent drag-in of chloride into the chromate dip.

Anodic Treatments

Aluminum is most commonly blackened by anodic oxidation, followed by dyeing of the anodized surface. The aluminum generally is treated as the anode in a 15 percent by weight solution of sulfuric acid at 20°C (68°F), and a current density of 1.1 to 2.7 A/dm^2 (10 to 25 A/ft^2) for 30-45 min. This porous aluminum oxide coating then is immersed in a suitable organic or inorganic coloring bath. The color is absorbed into the aluminum oxide film, which is then sealed with water or a weak solution of nickel acetate maintained at 95°C (203°F). The black organic dyes used for coloring generally are employed at a concentration of 6.0 to 10 g/L (0.8 to 1.3 oz/gal) at a pH of 6 to 7. The black dyes currently available have good color-fastness and resistance to fading.

Inorganic blackening of the aluminum oxide can be accomplished by successively immersing the anodized surface into a 1 percent solution of cobalt acetate and then sodium sulfide. A black insoluble precipitate of cobalt sulfide is formed within the aluminum oxide film. The inorganic black finishes are more weather-resistant than those produced with the organic dyes.

Zinc can be blackened anodically in a proprietary system consisting essentially of sodium dichromate. These systems operate at room temperature and at 0.5 to 5.4 A/dm^2 (5 to 50 A/ft^2) in a pH range of 2.5 to 4.5 and produce a black coating having excellent

Fig. 4—Stages involved for black antiquing of medals.

resistance to abrasion and corrosion. For maximum resistance, the coating is sealed by immersion in a proprietary solution at 82 to 100°C (180 to 212°F) for 5 to 15 min.

Chemical Coating/Dyeing

Aluminum and steel can be treated in proprietary formulations and then dyed or colored black. A proprietary system for aluminum makes use of an alkaline solution controlled at a pH of 11.9 to 12.0 and operated at 23 to 26°C (74 to 79°F). The aluminum is treated in the bath for 20 to 40 min and then immersed in a proprietary dye bath. The finish produced from this system is durable, fairly hard and uniform, but has only fair corrosion resistance.

Steel can be blackened by phosphating in the conventional manner and then modifying the phosphate coating and dyeing. One proprietary system treats the phosphate layer in a stannous solution, converting the coating to a tin phosphate. This coating is dense and adherent and readily accepts an organic dye to produce a black finish that has good corrosion resistance and that also retains the other properties of the phosphate film.

Applications

Uniform black finishes are applied to a wide variety of products to enhance their appearance and marketability. These applications include auto trim, jewelry, marine hardware, builders' goods, furniture, plumbing components, and lighting fixtures.

In addition to these "uniform" black applications, extensive use is made of black coatings to produce the so-called "antique" look. With this technique, a black coating is applied by any of the previously indicated methods. The black coating then is partially removed by mechanical means from certain areas of the part to produce a contrasting effect between the color of the basis metal and that of the black coating. The photo of the medals (Fig. 4) illustrates the various stages involved. A zinc-base die casting was plated with 6.3 μm (0.25 mil) of brass and then an electrodeposit of black nickel alloy was applied. The part subsequently was mechanically relieved using a fine wire brush. Lacquering completed the operation.

This same procedure could be used on solid brass, plated copper, tin, silver, etc. The "look" and appearance of the antiqued part depends to a large extent on the mechanical relieving. The choice in the type of polishing wheel, compound and other tools will determine whether the finished part will have a satin, polished or scratch-brushed look. Parts that lend themselves to bulk handling can be blackened and relieved by tumbling or burnishing.

Table 2
Formulations & Conditions for Chemical Conversion Blackening*

Substrate	Chemistry		Conditions
Aluminum:	Ammonium molybdate Ammonium chloride ***Coating: Molybdenum oxides***	10-20 g/L (1.4-2.8 oz/gal) 15 g/L (2 oz/gal)	Temperature: 90°C (194°F) to boiling Immersion time: 1 - 5 min.
Brass and copper:	Sodium hydroxide Sodium chlorite ***Coating: copper oxide***	55-230 g/L (7.5-31 oz/gal) 5-150 g/L (0.7-20 oz/gal)	Temperature: 90°C (194°F) to boiling Immersion time: 1 - 10 min.
Cadmium:	Ammonium molybdate Ammonium chloride Potassium nitrate Boric Acid ***Coating: Molybdenum oxides***	12.5 g/L (1.7 oz/gal) 25 g/L (3.4 oz/gal) 6.25 g/L (0.84 oz/gal) 6.25 g/L (0.84 oz/gal)	Temperature: 60-70°C (140-158°F) Immersion time: 10 - 30 sec
Copper:	Polysulfide ***Coating: Copper sulfide***	2-4 g/L (0.26-0.53 oz/gal)	Temperature: 20-25°C (68-77°F) Immersion time: 45 - 90 sec
Iron and steel	Sodium hydroxide Sodium nitrite ***Coating: Black iron oxide***	750 g/L (100 oz/gal) 250 g/L (34 oz/gal)	Temperature: 135-145°C (275-293°F) Immersion time: 5 - 30 min.
Silver #1:	Ammonium polysulfide ***Coating: Silver sulfide***	10-20 g/L (1.4-2.8 oz/gal)	Temperature: 30-40°C (86-104°F) Immersion time: 10 - 30 sec.
Silver #2:	Tellurium dioxide Hydrochloric acid ***Coating: Silver telluride or oxide***	4 g/L (0.5 oz/gal) 250 g/L (34 oz/gal)	Temperature: 30-45°C (86-113°F) Immersion time: 15 - 90 sec.
Tin and tin alloys:**	Nitric acid Copper sulfate ***Coating: Tin-tin oxide***	5-10% by volume 2.5-5.0 g/L (0.33-0.66 oz/gal)	Temperature: 20-30°C (68-86°F) Immersion time: 15 - 90 sec.
Zinc:	Ammonium molybdate Ammonia	20-30 g/L (2.8-8.0 oz/gal) 40-50 mL	Temperature: 30-45°C (86-113°F) Immersion time: 1 - 10 min.

**Compiled from D. Fishlock, Metal Colouring, Robert Draper, Ltd, Teddington, Middlesex, UK, 1970 and personal experiences.*
***From Metal Finishing Guidebook and Directory, Elsevier Science, Tarrytown, NY, 1982. (Using current publisher info, 2003; reference year for formulation, 1982.).*

As noted earlier, when a part is to be antiqued, it is preferable to select, if possible, a blackening system that produces a relatively soft coating. This will usually make the subsequent relieving easier.

Besides being used for decorative applications, black coatings also have many functional uses. They are employed to reduce glare and reflectivity in optical systems, cameras and military hardware, to name a few. Some of the black coatings are used as a base prior to painting. Black oxide coatings on copper are used in printed circuitry to promote bonding in multilayer applications.

The emphasis on solar-energy development has created an intense interest in black coatings for solar collectors. Ideally, the black coating should absorb the maximum amount of heat energy and emit as little as possible. The ratio of the solar absorptance (called "alpha") to thermal emittance (called "epsilon") is a measure of the efficiency of the surface in collecting solar energy. The higher the ratio, the better the efficiency. Black chromium and black nickel plating systems, as well as the copper oxide chemical types, have very good alpha-to-epsilon values and are used in the production of solar collectors. However, in choosing the most suitable black coating for solar collectors, factors other than solar efficiency must be considered. The cost and ease of application of the black coating, as well as the corrosion resistance, must be taken into account.

Blackening of metals, although still to some degree an art form, is rapidly reaching a point at which it is no longer in the realm of black magic. *P&SF*