

How to Apply Statuary and Patina Finishes

Copper and copper alloys are widely used in architectural applications to take advantage of their inherent range of colors. While these metals may be used in their natural color, as fabricated, it is sometimes desirable to chemically color pure copper (C11000*), commercial bronze (C22000), architectural bronze (C38500) or other alloys referred to as "bronze" in architectural parlance.

The most common colors to be produced are referred to as brown or statuary finishes for bronze and green or patina finishes for copper. This data sheet outlines procedures and formulations for producing both. While the chemical solutions described are those generally accepted in the metal finishing trade, many variations exist.

The wide range of colors and shades which may be achieved are largely a matter of craftsmanship and experience. Chemical coloring techniques depend upon time, temperature, surface, preparation, mineral content of the water, humidity and other variables which influence the ultimate result. This data sheet presents the technology which underlies the craftsmanship and art involved in producing these colored finishes.

Brown Statuary Finishes

Statuary finishes are conversion coatings. In conversion coatings, the metal surface is either converted into a protective film, usually an oxide or sulfide of the metal involved, or a compound is precipitated which forms a surface film.

The use of chemical solutions is generally termed "oxidizing," although the oldest method and the one which produces the widest range of brown to black stages on copper alloys actually produces not an oxide but a metal sulfide finish by the use of alkaline sulfide solutions. Originally *liver of sulfur* was employed, this being a crude mixture of potassium polysulfides and thiosulfate, also called potassium and sulfuret.

Modifications of these formulas called for the use of sodium, potassium, barium, and ammonium sulfides, which were claimed to produce different shades, but almost all sulfide colors are now produced from solutions of polysulfides which are sold in concentrated form under a number of trade names, usually called "oxidizing liquid."

All sulfide films require wet or dry scratch brushing for good appearance and will look better longer if protected by oiling, waxing or, more permanently, by a good top coat of clear lacquer. The desirable contrast in color can be produced by scratch brushing with a pumice paste, or by use of a "greaseless" polishing compound on a buffing wheel. In any case, the sulfide solution employed should be fairly dilute, since concentrated solutions can result in a brittle film which may be non-adherent.

Cleaning

The metal surface should be degreased with trichloroethylene, or similar solvents. This not only cleans the surface, but enhances the cutting quality of abrasives if subsequent mechanical finishing is to be done before applying the color.

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UNS No.	Common Name	Nominal Composition	Available Wrought Forms
C11000	Electrolytic Tough Pitch Copper	99.90 Cu	Bar, extrusions, forgings, pipe, plate, rod, sheet, strip, tube
C22000	Commercial Bronze	90 Cu-10 Zn	Bar, extrusions, pipe, plate, rod, sheet, strip, tube
C23000	Red Brass	85 Cu-15 Zn	Pipe, sheet, strip, tube
C28000	Muntz Metal	60 Cu-40 Zn	Bar, plate, rod, sheet, strip, tube
C38500	Architectural Bronze	57 Cu-40 Zn-3 Pb	Bar, extrusions, forgings, rod

Clean to a bright satin finish using a mixture of 5% oxalic acid and water together with fine India pumice powder. The cleaning should be done using a fairly stiff short-bristled cleaning brush in the direction of the grain. The metal should be recleaned using the above mixture and a wet, virgin clean white cloth and applied in conformance with the original motion. The work should be cleaned with a virgin cloth rinsed in clean clear water and allowed to dry.

Finish the metal with abrasive belts, abrasive pads or wheels, or greaseless abrasive compounds on portable buffing wheels.

As the final operation, give the metal a hand rub with a fine abrasive pad (e.g., *Scotch-Brite*) and a slurry of pumice and water in order to insure complete removal of all surface films of oil and grease. Then remove all traces of pumice by wiping with a clean damp cloth or sponge.

Statuary Finishes on Bronze

Statuary finishes can be produced in light, medium and dark brown depending on both the concentration and the number of applications of the coloring solutions.

Solutions of 2%-10% aqueous ammonium sulfide, potassium sulfide (*liver of sulfur*) or sodium sulfide (*liquid sulfur*) are swabbed or brushed on. Oxide pre-treatment may be employed to enhance adherence. Final hand toning or blending may be required to achieve acceptable color match and color uniformity.

The following should produce a medium shade of brown:

A. Ammonium Sulfide Process

1. With a sponge or pad fairly well wrung out, swab on a thin film of a solution containing 5% to 10% by volume of polysulfide (dark) and water.
2. Rinse thoroughly.
3. Immediately follow this with a slightly heavier film of either a 5% solution of copper sulfate in water or a 0.5% solution of sulfuric acid in water. Apply by swabbing with a sponge or pad.
4. Do not contaminate the solutions by using the same sponge to apply both.
5. Rinse thoroughly.
6. Tone by rubbing in the direction of the grain with a fine abrasive pad (e.g., *Scotch-Brite*) while still wet.
7. Remove solution residue by wiping with a clean damp cloth or sponge and dry.
8. Repeat until the desired depth of color is achieved.
9. Alternately, small objects may be immersed in the ammonium polysulfide copper sulfate solutions.

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B. Potassium Sulfide Process

1. One gal of 1.5% sharp water (2oz oxalic acid in 1 gal tap water).
2. Fine beach sand.
3. Potassium sulfide (*liver of sulfur*) mixed in tap water (1/4 lb *liver of sulfur* to 1 gal water).

Clean the metal. Wipe down the solution of potassium sulfide using a virgin clean white cloth, in the direction of the grain of the metal. Wash down with a clean white towel wrung out in sharp water. Apply fine beach sand with another clean wet towel going against the grain to even out the color.

This procedure is followed until a medium statuary color is attained. It may have to be repeated several times before uniformity appears. After the desired uniform color is attained, neutralize the work with a wash of clear water.

C. Other Processes/Procedures

1. Clean with fine pumice (0, 1/2) on a clean cloth moistened with a 10%-20% solution of oxalic acid and water.
2. Wipe off with a clean soft cloth.
3. Apply a 5%-10% solution of potassium sulfide or ammonium sulfide using another soft cloth dipped in the solution and well wrung out.
4. Follow while still wet with a wipe of sharp water (about 2 oz of oxalic, sulfuric, or nitric acid in 1 gal water) using a clean soft cloth well wrung out.
5. Repeat steps 3 and 4 to achieve a depth of color slightly darker than the desired shade.
6. Relieve the surface by rubbing with fine beach sand on a clean damp cloth until the desired color is reached.
7. Rinse and dry.

Statuary Finishes on Copper

1. Clean copper with pumice and water or pumice and solvent to remove all dirt, grease, oil or tarnish.
2. Brush entire surface with a 2% solution of liquid ammonium sulfide (technical grade) in water.
3. Let dry. Even out color by rubbing lightly with pumice and water, using a stub or fine brass wire brush.
4. Repeat steps 2 and 3 to obtain the desired color.

Maintenance

Regularity is the key to a successful maintenance program. A schedule should be arranged providing periodic cleaning with regular inspections in the interim. The schedule should differentiate between interior and exterior surfaces and those surfaces subject to handling, scuffing and abrasion. When a regular maintenance program is followed, most installations can be maintained by oiling or waxing, some by lacquering and a few by polishing.

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Surfaces prefinished or naturally weathered to the statuary bronze shades should be maintained by periodic oiling with Lemon Oil, U.S.P.; Lemon Grass Oil, Native E.I.; or a high grade paraffin oil.

Mixtures of Carnauba wax and wood turpentine as well as quality commercial paste waxes have been found satisfactory. The comparative costs of waxing versus oiling should, however, be weighed.

Oil and wax coatings look best when applied with a well-impregnated, clean soft cloth followed by rubbing with a second, clean soft cloth to remove excess oil or wax. Frequency of oiling or waxing is as important as the oil or wax used. Newly installed metal should be oiled weekly for the first month in order to build up a protective film. Metals subject to heavy traffic should be oiled or waxed at one to two-week intervals. Where traffic is moderate to light, monthly treatment may suffice. In non-traffic areas, quarterly or semiannual applications are feasible.

Considering a typical building entrance, door handles, push plates or bars, and kick plates as well as the door stiles and rails, would normally be exposed to heavy traffic. The door frame and adjacent window wall framing usually receive less handling and would be considered a moderate to light traffic area. Transoms, canopies and similar metal elements normally out of reach would be classed as non-traffic areas.

Restoration

Bronze and other copper alloys can be restored to their original appearance even after years of neglect. Restoration of neglected surfaces may require the advice of specialists engaged in maintenance work.

To restore statuary finishes, the surfaces may be cleaned with a 5% oxalic acid and water mixture together with finely ground India pumice powder. Wipe dry with soft clean cloths and apply the statuary finish solution as outlined.

Lacquering

Long-term protection can be achieved by applying a clear organic coating.* Air-drying formulations are the most convenient to use and among them the INCRALAC formulation has proven to be the most protective.

INCRALAC is an air dry, acrylic lacquer for field or shop coating of copper and copper alloys. In research initiated by the International Copper Research Association (INCRA),** INCRALAC provided the best protection of all air dry coatings tested.

When applied to a properly cleaned metal surface, INCRALAC provides excellent protection indoors or outdoors, even in highly corrosive industrial and marine atmospheres.

The use of abrasive pads (e.g., *Scotch-Brite*) followed by washing with a cleaning solvent, provides a surface for maximum performance. Steel wool should not be used because it sometimes contains a corrosion inhibitor which may cause discoloration later on.

If abrasive pads are not available, the surface should be thoroughly washed with a solvent or alkali cleaning solution, or by vapor degreasing.

INCRALAC is designed for spray application and should not be brushed. Conventional spray equipment can be used, applying first a mist coat, followed by a wet coat. Two coats are recommended, with at least 30 minutes air dry between coats.

*Further information on clear protective coatings for copper and copper alloys is available in three CDA Application Data Sheets listed in the bibliography.

**Now, the International Copper Association, Ltd.

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Green Patina Finishes

The much admired natural protective coating of a blue-green patina characterizes older copper roofs, including ancient cathedrals as well as bronze statues and other copper metal surfaces exposed to the weather. Because of the time required to achieve this, much research has been done on artificial patination, with varying success.

In natural patination the major coloring agent in the film is basic copper sulfate. Carbonate and chloride salts of copper may also be present in varying concentrations. In seacoast locations, chloride salts may form an essential part of the patina film. The basic chloride salts of copper are not only fairly soluble, but photosensitive as well.

In artificially producing or accelerating the formation of a patina, success seems to depend on the manner in which the solutions are applied, the weather conditions under which the treatment is carried out, and perhaps most important, on the climate to which the treated surfaces are exposed.

Because of the number of variables involved, chemically induced patinas are prone to lack of adhesion, excessive staining of adjacent materials or inability to achieve reasonable color uniformity over large surface areas. These potential shortcomings should be considered when attempting to artificially duplicate a weathering process which may take from five to seven years in coastal or industrial environments, longer in rural areas, and may perhaps never develop in some climates and atmospheres.

Artificial patinas for architectural applications such as copper roofs, grilles, and statues have an inherent requirement which dictates that the solution has to be one which can be brushed or sprayed because of the large surface areas normally involved.

Cleaning

The copper surfaces to be colored must be clean, as any dirt, oil or grease on the surface will interfere with the chemical action of the solution. This involves removal of the residual film of oil left on copper and brass sheets from mill rolling operations, and fingerprints and dirt deposited on the surface during handling and installation.

A few hard rainstorms may clean the surfaces sufficiently to start operations. However, it is always advisable, particularly if the coloring is to be done immediately after installation, to go over the surface with a commercial chemical metal cleaner. Cleaners of the trisodium phosphate type should be satisfactory. Avoid cleaners which leave a coat of oxide on the copper surface.

Follow cleaning with a thorough rinsing to remove all traces of the cleaning compound. If cleaning has been properly done, the rinsing water will spread uniformly without beading (the formation of globular droplets); in other words, the water should wet the copper surface uniformly. If necessary, cleaning should be repeated until this condition is obtained.

Oxide film on the copper will cause poor adherence of the patina. Copper roofs which have weathered for six months or more should have the oxide film removed before the coloring operations start. This is done by swabbing the surface with a cold, 5%-10% solution of sulfuric acid. **The operator must wear rubber gloves and take care to prevent spilling any acid on himself or on adjacent wood or stonework.** Immediately after this swabbing, the surface should again be thoroughly rinsed with clean water. This should leave a roof surface, whether old or new, in good condition for coloring.

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Coloring

Of the three basic processes for accelerated patina formation, one uses a sulfate solution and two utilize chloride salts. Their formulas are as follows:

A. Ammonium sulfate

	<u>per liter</u>	<u>per gal</u>
ammonium sulfate	— 111.0 g	15.0 oz
copper sulfate	— 3.5 g	.5 oz
conc. ammonia	— 1.6 ml	.2 fl oz
tap water	— 1.0 l	1.0 gal

The quantities required per 1,000 sq ft of roof surface are:

ammonium sulfate	—	6 lb
copper sulfate	—	3 oz
concentrated ammonia	—	1.3 fl oz
tap water	—	6.5 gal
Total Solution	—	7.25 gal

The ammonium sulfate should be “technical grade.” Agricultural grade may be used if the solution is filtered to eliminate dirt. Copper sulfate is commonly known as *blue vitriol*. The concentrated ammonia should have a specific gravity of 0.900. One fluid ounce of concentrated ammonia contains 0.936 oz by weight of ammonia.

Preparation of The Solution—The solution should be prepared in a corrosion resistant plastic-lined container. Wooden barrels and tubs are also satisfactory if all exposed metal parts are lead covered.

First dissolve the ammonium sulfate in the water. When completely dissolved, add the copper sulfate. This is best done by removing a few gallons of the ammonium sulfate solution and dissolving in it as much of the copper sulfate as will dissolve. Then pour this back into the original solution and remove another batch, repeating the operation until all the copper sulfate has been dissolved.

Then add the concentrated ammonia **slowly**, while **constantly** stirring the solution. It is important that the quantity of ammonia be **exact**, as the correct ratio of ammonia to water must be maintained.

Method of Application—The solution should be applied by spraying. A satisfactory sprayer is an ordinary, plastic or galvanized steel, garden-type tank sprayer, with the inside coated with bituminous paint. Spraying should be done rapidly, using a fine spray. Avoid large drops, which tend to run together, causing streaks. It is better to use too little rather than too much solution at a time.

Allow the solution to dry after the first spraying (about 10 to 15 minutes on a warm, dry, sunny day; longer on a cool or cloudy day). Spraying and drying are repeated five or six times.

The color does not show up immediately. When the spraying has been completed, the copper surface should appear to be covered with a “glassy” coating somewhat resembling a dark, heavy coat of varnish.

The development of color depends on suitable weather conditions. Rain within six or eight hours may wash away some of the solution before it has had a chance to act on the copper.

Ideal weather conditions following the treatment are a moderate to heavy dew, a light mist or fog, or other condition of high enough atmospheric moisture to give a relative humidity of 80% or more. The atmospheric moisture combines with the deposited solution to react chemically with the copper, and the desired

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blue-green patina results. The colored layer should be of a satisfactory depth, if the action continues undisturbed for at least six hours.

Where this has occurred, the next rain should wash off the remaining deposit and bring out the blue-green patina, but it should weather into a natural color in time; the time depending on climatic conditions.

B. Ammonium chloride (sal ammoniac)

Dissolve sufficient ammonium chloride crystals (commercial *sal ammoniac*) in water to form a saturated solution, that is, until no more will dissolve. Brush or spray on a thoroughly clean copper surface. Several applications may be required.

This formula was favored by Frank Lloyd Wright. Wright specified that the solution be mixed 24 hours prior to its use. Two applications were made with a lapse of 48 hours between the two. Twenty-four hours after the final application, the copper was sprayed with a cold water mist. Wright emphasized the fact that dry weather was required throughout the entire period.

Although this coloring method was used with apparent success on the Price Tower in Bartlesville, Oklahoma, it failed to last on the copper roof of a residence in Dallas, Texas. After five years, the blue-green patina which had developed initially completely disappeared, leaving the copper a light russet brown. The ammonium chloride solution tends to chalk and flake if applied too heavily, and is also apt to dissipate in heavy rain. Both factors may have contributed to this failure.

C. Cuprous chloride/hydrochloric acid

Dissolve the following in a small amount of warm water:

	<u>per liter</u>	<u>per gal</u>
cuprous chloride	— 164 g	22 oz
hydrochloric acid	— 117 ml	15 fl oz
glacial acetic acid	— 69 ml	9 fl oz
ammonium chloride	— 80 g	10.5 oz
arsenic trioxide	— 11 g	1.5 oz

When dissolved, dilute with water to either 1 liter (1,000 ml) or 1 gal.

Apply by spray, brush, or stippling. Store and use in nonmetallic containers; do not use aluminum containers. **Wear suitable protective clothing and equipment. The solution is both acid and toxic.** It can be applied to either bright or weathered copper. If possible, the desired color should be attained in a single application. Reapplication—particularly in direct sunlight—may cause a reaction between the solution and the salts initially deposited, producing a smooth, hard, colorless film similar in appearance to varnish.

Maintenance

No maintenance is required for an existing natural patina or one which is in the process of formation.

If a *natural* statuary finish is desired on copper, weathering can be arrested at the desired point by applying a suitable oil, e.g., raw linseed oil or lemon oil. Depending on the prevailing climatic conditions and the degree of exposure, the frequency of oiling may be at intervals of from one to three years. Instances have been recorded where the initial oiling applied in two thin coats has preserved the statuary finish in excess of ten years.

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Copper and its alloys are made of nature's pure elements and as such harmonize with other natural materials with which people find an instinctive affinity. The fact that they change color as they weather gives them, and the building they adorn, an extra measure of life and character as first class building materials.

Copper, brass and bronze are resistant to destructive corrosion. The patina which forms naturally is in fact a protective film. The copper metals are light-weight, easy to work, easy to join, attractive and extremely durable. This accounts for their use for centuries for roofs, fascias, gutters, downspouts, flashing, storefronts, railings, grilles and other architectural applications of many descriptions.

Selected Bibliography

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2. Hughes, Richard and Rowe, Michael, "The Coloring, Bronzing and Patination of Metals," Crafts Council, London. (1982)
3. Fishlock, David, **Metal Colouring**. Teddington, England, Robert Draper Ltd., 1970. 393 pages.
4. **Metal Finishing Guidebook & Directory**. Metals and Plastics Publications, Inc., 1 University Plaza, Hackensack, N.J.
5. **CDA Application Data Sheets 108/9, 114/9 and 161/0** on clear organic coatings.

Source Of Materials

Ammonium sulfide, ammonium sulfate and ammonium chloride (*sal ammoniac*), potassium sulfide (*liver of sulfur*), sodium sulfide (*liquid sulfur*), copper sulfate (*blue vitriol*), oxalic acid, cuprous chloride, hydrochloric acid, arsenic trioxide and acetic acid are available from metal finishing and chemical supply houses. Abrasive pads are available from building supply and hardware stores. INCRALAC clear lacquer is available from:

Seagrave Coatings Corp.
PO Box 187 • 320 Paterson Plank Road
Carlstadt, NY 07072
(800) 426-0496

Stan Chem, Inc.
401 Berlin Street
East Berlin, CT 06023
860/828-0571

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