

CONSERVATION OF CUPREOUS METALS

Here the nonspecific term cupreous metals is used for copper and the alloys such as brass and bronze where copper predominates. In general it matters little what the specific alloy is, for they are usually treated in the same way. Care needs to be taken only when there is a high percentage of lead or tin, both of which are amphoteric metals and dissolve in alkaline solutions. There are a considerable number of chemical treatments for copper, bronze and brass, and most are not satisfactory for cupreous metals from marine sites. Consult the bibliography at the end of this section for further information.

In a marine environment the two most commonly encountered copper corrosion products are cuprous chloride and cuprous sulfide. However, the mineral alterations in the copper alloys are more complex than those of just copper. Once any cupreous object is recovered and exposed to the air, it continues to corrode by a process referred to as bronze disease. Cuprous chlorides in the presence of moisture and oxygen are hydrolyzed to form hydrochloric acid and basic cupric chloride. The hydrochloric acid in turn attacks the uncorroded metal to form more cuprous chloride. The reaction continues until no metal remains. Any conservation of chloride contaminated cupreous objects requires that 1) the cuprous chlorides be removed, 2) the cuprous chlorides be converted to harmless cuprous oxide, or 3) the chemical action of the chlorides be prevented.

Chemical Cleaning Techniques

I. ACIDS

All acid treatments require a solid metal core. All acids can and will strip off corrosion layers down to bare metal and many will even etch the bare metal. All acid treatment methods will completely remove patina and adhering corrosion layers and/or encrustation from cupreous metals. With all treatments, the artifact is usually placed in an acid solution to soak and the acid solution is changed when it becomes discolored (blue to green). On particular pieces localized spot treatments may be required. Drops of acid can be applied to specific areas and allowed to work. Repeated spot applications may be necessary and it is essential that the area be blotted and traces of the acid be neutralized once treatment is completed. During treatment with acid by immersion, especially citric and formic acids, a coating of copper is often deposited on the surface of the object. Usually the redeposited copper (copper ions come from the copper released from the corrosion layers) can be brushed away. Sometimes it is very difficult to remove, especially in areas where cuprous chloride are converted to adherent metallic copper plating on the surface of the object.

A. Citric Acid

This acid is useful for removing cupric oxides, but does not readily attack cuprous oxides. It is also very good for separating cupreous objects corroded together. It softens carbonates and is good for inscriptions. One problem is that it is not volatile and if not thoroughly rinsed from the object, it can continue attacking and etching the metal.

Kitchen technique-- juice of one lemon plus 1 teaspoon of salt to clean objects. This technique is not recommended in conservation.

1. Citric Acid (pH 1.90)
40 grams Citric Acid, monohydrate
1 liter D.I. water

There is an initial etching that proceeds rapidly with tin bronzes in the presence of corrosion products. The addition of BTA does not lessen the etching affect of citric acid.

2. Buffered Citric Acid (pH 4.0)
25 grams Citric acid, monohydrate
14 ml ammonium hydroxide
1 liter D.I. water

Buffered citric acid has very little etching affect on uncorroded metal, even after several hours. It is possible to control the etching by controlling the pH of the solution -- the higher the pH of citric acid, the less etching there is.

3. 5-10% Citric acid (50-100 grams)
1-2% Thiourea (1-2 grams)

The presence of thiourea protects the metal from being attacked by organic acids. Pearson recommends uses this formula for cleaning corroded cupreous object. After treatment, the objects are followed by a 1% sodium sesquicarbonate wash to neutralize the acid and remove more chlorides. The addition of the sodium sesquicarbonate treatment, following a citric acid treatment insures a more stable artifact, especially if it came from a marine environment.

B. 5-10% Sulfuric Acid (H₂SO₄)

This acid is good for removing superficial tarnish, which is usually consists of cuprous oxide. It attacks cuprous compounds more readily than citric acid.

C. 5-30% Formic Acid (HCOOH)

Formic acid is preferred over other acids because it completely vaporizes at 125°F. Merely heating in boiling water removes all residue of the acid. It is good for removing superficial corrosion from bronzes or copper corrosion products from silver. There is some danger of etching and

redepositing of copper on the surface of the metal, making a bronze, brass, silver object look like a copper object. Problems of plating are more common with formic acid.

II. Alkaline Sequestering Agents

This process characteristically removes cupric compounds much more readily than cuprous compounds. All cupric compounds are green to blue in color.

A. Alkaline Glycerol (pH 13.3)

150 gms NaOH
40 ml glycerol
1 liter D.I. water
Treatment time, 30 minutes

Where it is necessary to remove cuprous compounds, this treatment is followed by adding 100 ml. of 10Vol hydrogen peroxide to the solution.

Because of the strong alkalinity of this chemical, it should not be used on high lead or tin alloy bronzes. Both Pb and Sn are amphoteric, and thus soluble in strong alkalis.

In tests, tin bronzes were etched fairly rapidly using this treatment. The etching was accelerated in the presence of corrosion products.

On leaded tin bronzes, there was very little etching when corrosion products were not present. When corrosion products were present, the degree of etching was considerably enhanced.

B. Alkaline Rochelle (pH 13.6)

50 gms NaOH
150 gms Sodium Potassium Tartrate (Rochelle Salts)
1 liter D.I. Water
Treatment time 1-3 days

Obviously, from the treatment time, you can see that this treatment is much slower. In general, it is recommended over Alkaline Glycerol.

When necessary to remove cuprous compounds, this treatment is followed by immersion the object in a separate bath of 10% sulfuric acid.

In a 60 minute test on tin bronzes, the depth and degree of etching was considerably less using the Alkaline Rochelle process than Alkaline Glycerol. With leaded tin bronzes, in the absence of corrosion products, the speed and extent of etching was greater than A.G. In the presence of corrosion products, the speed of etching was slower.

Both alkaline sequestering agents quickly dissolve cupric compounds, but they only slowly dissolve cuprous compounds. As always, the use of heated solutions speed up the treatment. After cleaning with either, there is usually a pinkish to reddish appearance of freshly exposed cuprous oxide on the surface. To remove this layer and if necessary, to completely strip the corrosion layers, the cuprous compounds can be removed by following the treatment with 10% sulfuric acid.

or alternatively

...add 100 ml of 10 vol hydrogen peroxide to the Alkaline glycerol solution. The addition of the hydrogen peroxide H_2O_2 oxidizes any cuprous compounds to a cupric state, thus allowing the A.G. to continue its attack on the cupric compounds. The addition of hydrogen peroxide works best with A.G., but works also with A.R. Caution should be exercised, for hydrogen peroxide can etch metal.

Adding BTA to the A.R. and A.G. treatment has been shown to be more effective in guarding a copper/bronze piece against further attack than when BTA is used as a pretreatment. This allows an object to left in the solution longer with safety.

III. Sequestering agents that dissolve cupric salts more readily than cuprous salts, even though they slowly act to dissolve cuprous compounds.

A. Ethylenediaminetetraacetic acid EDTA, 10% solution

EDTA, di-sodium (pH 4.5)
EDTA, tri-sodium (pH)
EDTA, tetra-sodium (pH 11.5) best all around for copper/bronze

Immerse artifact in the solution, and if needed, heat the solution to speed up the reaction. This chemical solution removes cupric compounds as do the alkaline sequestering agents; however, it continues to remove cuprous oxides with only slightly less rapidly. Effective for removal of all the copper minerals.

B. Sodium Hexametaphosphate, 5-15% solution (pH 8.5)

50-150 gms sodium hexametaphosphate
1 liter D.I. water

15% Sodium hexametaphosphate is a stripping solution (the brand name Calgon was 100% sodium hexametaphosphate in the past). You will see the name Calgon in the older literature as a source for sodium hexametaphosphate. Now Calgon is sodium phosphates and sodium carbonate). It is slower reacting than EDTA, but in stronger concentrations of 15% it maintains a steady reaction against cuprous oxide and also strips off any patina. Soak the artifact in a heated solution for best results. It removes insoluble deposits of calcium and magnesium by complexing with them to form soluble salts. In short, it is effective for removing calcareous deposits, cupric oxide and cuprous oxide.

In tests, in the absence of corrosion products, there was no complete etching. In the presence of corrosion products, there is very quick etching.

Pretreatment, by immersion in 1% aqueous benzotriazole (BTA) for 6 hours completely prevented metal samples from being etched during a 1 hr. test period.

In weaker 5% solution, the patina is maintained on cupreous pieces. 5% solutions can also be used on completely mineralized objects. Artifacts can be soaked in repeated baths of this solution to remove all soluble salts, but 5% sodium sesquicarbonate is better for long term rinsing.

All stripping solutions should be carefully controlled to avoid etching any exposed metal while removing unwanted corrosion products. Ideally, a non-interacting environment of a controlled pH is desired so that the rate of attack on any exposed metal can be reduced. This insures that the least harm is done to the object being treated, while still removing unwanted corrosion products and calcareous deposits.

Sodium Sesquicarbonate Rinses

The cuprous chloride component of copper and its alloys are insoluble and cannot be removed by washing in water alone. If the artifact is placed in a 5% solution of sodium sesquicarbonate, the hydroxyl ions of the alkaline solution react chemically with the insoluble cuprous chloride to form cuprous oxide and neutralize any hydrochloric acid by products formed. Successive rinses continue until the chlorides are removed. The object is then rinsed in several baths of deionized water until the pH of the last bath is neutral.

This has been the standard treatment for fragile cupreous artifacts with chloride contamination and for artifacts that have a patina that is desirable to preserve. However, in practice, conservators found that it often enhanced the patina, making it much bluer in appearance. In other examples, it considerably darkened or blackened the patina.

Recently, Weisser (1987:106) stated:

Although initially the sodium sesquicarbonate treatment seems to be ideal, since you do not need to remove the outer corrosion layers while the cuprous chloride is removed, it has been found to have a number of disadvantages. First, the treatment may require well over a year before all the cuprous chloride has been converted. This fact makes other drawbacks more serious. It has been shown that sodium sesquicarbonate (a double carbonate) forms a complex ion with copper and therefore preferentially removes copper from the remaining metal (Weiser, 1975). This can be potentially structurally damaging over a prolonged period. It has also been shown that a mixture of carbonates, including chalconatrite, a blue-green hydrated sodium copper carbonate forms over the patina and also seems to replace other copper salts within the patina (Horie and Vint 1982). This creates a color change from malachite green to blue-green, which in many cases is undesirable. In the objects the author has examined the blue-green color can be found in cross section from the outer corrosion crust extending down to the metal substratum.

and Weiser (1987:108) concluded:

The stabilization of actively corroding archaeological bronzes remains a difficult problem for conservators. At the present time no known treatment can be called ideal. A sodium carbonate pre-treatment in conjunction with a standard treatment with benzotriazole offers one more option to the conservator who is faced with difficulties in stabilizing bronzes. Although successful stabilization has been achieved with this treatment where others have failed, it should be used with caution until the problems observed have been more thoroughly investigated. Bronzes which cannot be stabilized by this treatment should be stored or displayed in a low relative humidity environment. In fact it is recommended that all bronzes be kept in a low relative humidity environment if possible, since the long-term effectiveness of 'bronze disease' treatments has not been proven.

Weiser suggests that if previous treatments with BTA have not been successful, then treat with 5% w/v of sodium carbonate in distilled water. The sodium carbonate removes the cuprous chlorides and neutralizes the hydrochloric acid in the pits. Sodium carbonate, unlike sodium sesquicarbonate, which is a double carbonate and acts as a complexing agent with copper, reacts relatively slowly with copper metal. Still, in some cases, slight alterations in the color of the patina can occur.

Benzotriazole

The use of benzotriazole (BTA) has become a standard part of any conservation treatment of a cupreous metal, following any stabilization process and preceding any final sealant. The artifact requiring treatment is immersed in 1% BTA for 24 hours. For artifacts from a freshwater site, it may be the only treatment required; it being used to prevent any future corrosion or discoloration of the patina. The BTA is usually dissolved in water, but ethanol can be used. See Green (1975), Hamilton (1976), Merk (1981), Sease (1978) and Walker (1979) for additional information. BTA forms an insoluble, complex compound with cupric ions. Precipitation of this insoluble complex over the cuprous chloride forms a barrier against any moisture that could activate the cuprous chlorides responsible for bronze disease. The treatment does not remove the cuprous chloride from the artifact, but merely forms a barrier between the cuprous chloride and the moisture in the atmosphere. For

artifacts heavily contaminated with chloride, the treatment may have to be combined with one of the processes described above. Treatment by this method alone is not always successful but it should be part of any treatment of copper or copper bearing alloys. BTA is a suspected carcinogen and contact with the skin should be avoided and the powder should not be inhaled.

Electrolytic Reduction Cleaning

Electrolytic reduction of cupreous metals is the best and most efficient method of removing corrosion layers and any chlorides from the object and is carried out in the same manner as described for iron. The alkaline electrolytes, 2% sodium hydroxide or 5% sodium carbonate or 5% formic acid can be used. If formic acid is chosen, stainless steel must be used for the anode, otherwise mild steel is used. In contrast to iron, electrolytic cleaning of cupreous metals is of short duration.

Alkaline Dithionite

This treatment was devised for consolidating mineralized silver. Since then, it has been found to be effective on cupreous objects. See a complete description under Silver. The treatment destroys the patina, but it effectively removes the bulk of the total chlorides in the shortest period of time.

Final Treatment and Sealant

Following electrolytic or chemical cleaning the objects are put through a series of hot rinses in deionized water. Because copper tarnishes in water, Pearson (1974:302), recommends washing in several baths of denatured ethanol. If a water rinse is used any tarnish can be removed with 5% formic acid or by polishing with a wet paste of sodium bicarbonate (baking soda).

After rinsing, copper objects should be dehydrated in acetone and sprayed with a protective coating of clear acrylic. Krylon Clear Acrylic Spray #1301, which is Acryloid B-72 in toluene, is recommended for ease of application, durability, and availability. For additional protection BTA can be mixed with Acryloid B-72 or polyvinyl acetate and brushed on the artifact. Microcrystalline wax can be used, but in most cases has no special advantage over acrylics.

Copper Stripping Formulas

10% Silver Nitrate

1 part Ammonium Hydroxide
1 part Chloroform
3 parts Isopropanol

Mix and use soon. Does not keep for days.
Dip and wipe off, polish with baking soda.