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Conservation of Ethnographic Metal Objects

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ABSTRACT: The recent conservation literature has paid particular attention to the deterioration and conservation of archaeological iron, in particular from underwater sites. There is little published information available on the treatment of the metal and metal composite collections housed in ethnographic museums and in open air museums. This paper describes the author's experiences in conserving these materials. It commences with an overview of the general conservation treatments used, including examination, storage and exhibition and report writing. It then discusses in detail the conservation treatments used for treating iron, copper, silver, gold, lead, tin and their alloys, also composite materials. The final section looks at outdoor sites.

[KEY WORDS: ETHNOGRAPHIC METAL OBJECTS, OUTDOOR METAL OBJECTS, CONSERVATION, RESTORATION, EXAMINATION, STORAGE, EXHIBITION, IRON, COPPER, SILVER, GOLD, LEAD, TIN, ALLOYS, COMPOSITE MATERIALS]

1. INTRODUCTION

Ethnographic metal objects would, by definition, include all those metal objects made and utilised by man. This would, of course, cover many different types of metals and their alloys, and every range and size of metal object, from a pin to a steam locomotive. Since it would be impossible to cover all of these even in a single text book, the subjects discussed here are restricted to the conservation of tools and equipment used in activities such as farming and cottage industries, which constitute many objects in ethnographic museums.

The metals discussed are restricted to iron, copper, silver, lead and their basic alloys, and the objects limited to those used by everyday workers. The fine metal work of the upper classes and nobility is not examined. Further, archaeological objects in origin, which cause specific conservation problems are not discussed. Rather I examine those that have either been handed down from generation to generation, lost or buried (but not underground or underwater), or kept by such institutions as museums. Information will also be provided on the conservation of metal objects, both large and small, of composite materials, those which operate by mechanical means and on objects displayed both indoors and outdoors.

The conservation literature pertaining to the conservation of metal objects is
limited, particularly if those of an archaeological origin are excluded. It is significant that much research has been conducted into the deterioration and conservation of archaeological metal objects over the past decade, in particular those from underwater sites. However, the information available for non-archaeological metal objects is restricted to the general conservation publications, such as those by Plenderleith and Werner [1971], and Guldbeck [1976], or to the conservation handouts provided for small museums [WEST AUSTRALIAN MUSEUM 1981; CCI 1984]. For this reason much of the following information is based more on experience of the author rather than the conservation literature.

2. CONSERVATION OF METALS—GENERAL APPROACH

For every metal object there are a number of conservation procedures that need to be carried out. These include examination and documentation of the object with details of its provenance, method of manufacture, its condition and, where possible, the reasons for its condition. This is necessary to provide information that will enable a proposal to be made for conservation treatment.

A wide range of conservation treatments are available for metal objects. These will be discussed briefly in this section, with more details being provided below.

2.1 Examination

The range of examination techniques include:

1. visual examination—often with the aid of a probe;
2. microscopy—including stereo and compound, through to the scanning electron microscope;
3. radiography—including the use of X-rays, γ-rays;
4. analysis of the base metal—using spot tests through to techniques such as SEM, XRF, AAS;
5. analysis of corrosion products—also using spot tests, the SEM, XRF and XRD, (the latter two techniques have been developed in Japan to allow non-destructive analysis of whole objects); and
6. photography—using both black and white and colour, and the additional range of photographic techniques, such as I.R. and U.V., where necessary.

Most of these techniques are routine in the conservation laboratory and so will not be discussed further. However, the chemical spot tests used at the Canberra College of Advanced Education, Conservation Training Program, are a combination of a number of different systems, and, as they have been found to work well in practice, are detailed in Appendix 1.

It is normal for each conservation laboratory to have one or more standard “Examination and Treatment” forms for detailing all the information obtained by the techniques listed above, followed by a proposal for treatment. Following agree-
ment between the conservator and the curator/custodian, the object is then treated and a full report of the treatment provided (see section 2.3).

2.2 Basic Conservation Treatments

Following the detailed examination of the metal object, and the determination of the reasons for its deterioration, a proposal for treatment is prepared. This must take into account a number of important factors. In particular:

(1) Are the corrosion products on the object, active or passive? If the former they will have either to be removed or stabilized, and if the latter a decision may be made on aesthetic grounds as to whether they should be removed;

(2) Do the objects contain other material of an historical/ethnographic significance? This may include soil from a weapon recovered from a battle field; evidence of use of the object; original coatings such as paint, grease and oil. Should these materials be removed, and if so why? and if they remain will their presence be a potential source of further corrosion to the metal object? For example, grease can be protective for many years but in time, owing to oxidation, will deteriorate and may then cause the metal object it is protecting to corrode;

(3) Is the object currently in sound mechanical working order, and is there a requirement for it to "work" following treatment? This is particularly relevant to motor vehicles and engines. Should a motor vehicle be put into running order and then run on a regular basis with the knowledge that in the long term, components of the engine will wear and need replacement?; and

(4) Will the metal object be displayed or stored indoors or outdoors? This may determine the protective coatings applied to the surface (see section 2.2.8).

The treatments themselves fall into a number of different categories. It should be basic conservation policy that the simplest treatment, or the treatment that affects the object the least should be used first. More drastic techniques will be applied only if absolutely necessary. In order of procedure the conservation treatments would include:

(1) dirt, grease and paint removal;
(2) mechanical cleaning;
(3) chemical cleaning;
(4) electrochemical and electrolytic reduction;
(5) washing and drying;
(6) repair of damaged objects or replacement of missing pieces if this is justified;
(7) polishing, where this is required—usually for aesthetic purposes;
(8) surface coating; and
(9) additional inhibition against further corrosion.

2.2.1 Dirt, Grease and Paint Removal

In order that later conservation processes can function effectively, it is
necessary to first remove all dirt and grease from the surface of a metal object. For this purpose a combination of aqueous and non-aqueous solvents are available, depending on the material to be removed. Light dirt is best removed with an aqueous soap solution containing 1–2% v/v of a non-ionic detergent, such as Lissapol (I.C.I). Light grease, such as that from handling, can be removed using ethanol or acetone, whereas heavy grease may require a solvent, such as white spirit, petroleum spirit or toluene, etc.

Old paint—if it needs removal—can be done using a 2% w/v solution of sodium hydroxide. (This cannot be used for metal objects made from or plated with aluminium or zinc, as these metals are attacked by sodium hydroxide.) This will also remove any grease on the metal surface. Thorough washing is then required (or the use of a dilute acid, such as citric acid) to remove and neutralize the alkali.

A range of commercial paint strippers is available, most of which are based on methylene chloride. These should be tested first on a small area to determine the most effective method of paint removal.

2.2.2 Mechanical Cleaning

Mechanical cleaning covers a wide range of techniques, from gentle picking away with a dental probe of a corrosion product through to aggressive sand blasting. The technique used depends on the material to be removed and the condition of the base metal.

If the corrosion products are readily removed then, as stated above, a wooden or metal probe or scalpel can be used. The next stage is the use of dental drills, vibrotail, compressed-air driven vibrating pen, through abrasive cleaners (a wide range from talc powder and jewelers rouge through course pumice powders). Next, brushes from soft bristle, through fibre glass to wire can be used, in the latter case taking care that the metal wires of the brush are similar to the metal of the object, i.e. steel wire for iron alloys and brass wire for copper alloys. A further range of cutting, chipping and hammering processes are available if required.

Ultra-sonic cleaning can be gentle or aggressive depending on the frequency of the system. Although most commonly used for cleaning jewelry, it has also been used for a range of ethnographic objects. The most convenient system uses an ultra-sonic probe rather than the bath, which allows the cleaning of any size or shape of object.

The most aggressive system is the use of mechanical abrasion, by either dry or wet blasting techniques [North 1979]. Dry sand blasting can be carried out using only the correct equipment and in a specific location. (The latter is particularly important, as it can be a serious health hazard.) This process will remove all surface contaminants down to ‘white metal’. However, it leaves a finely etched surface which is highly susceptible to further corrosion. It is essential, therefore, that any surfaces cleaned by this process be coated immediately following sand blasting.

A much more controllable dry cleaning process is that using an air abrasive
unit. These use a range of powders (from fine round glass beads to sharp angular and course alumina) and air pressures which allow careful cleaning of small areas of corrosion. They are particularly useful for cleaning metal components adjacent to another material, where chemical cleaning, for example, is not feasible. Again, this air abrasive system will leave a highly reactive surface that will require coating immediately. However, preliminary experiments at the Canberra College of Advanced Education have shown that metal surfaces freshly cleaned by chemicals are more reactive to further corrosion than surfaces cleaned by mechanical abrasion. An alternative to dry cleaning is wet sand blasting, which, although safer from a health point of view, is not as efficient and also leaves a wet—clean surface which must then be dewatered and coated immediately to avoid recorrosion.

2.2.3 Chemical Cleaning

The most common chemical cleaners are sequestering agents, acids and, occasionally, alkalis. The most common sequestering agent is ethylenediaminetetraacetic acid (EDTA), and the di-sodium salt (pH approx. 4.5) or the tetra-sodium salt (pH approx. 11) is used depending on the pH requirement of the solution, and the metal to be cleaned. Acids, such as hydrochloric and phosphoric, are much too aggressive for museum metal objects, and more ‘gentle’ acids, such as citric acid, are preferable. The use of inhibitors to prevent any chemical attack of the base metal during cleaning is very important. This is discussed below for individual metals.

The question is invariably asked, “How long should a metal object be treated?” Although this can be answered simply by, “As long as is necessary to clean it”, during the chemical cleaning process there must be regular brushing of the metal surface to remove solubilized corrosion products (which hinder further action of the chemical), and a change of the chemical once its cleaning action has become exhausted. The corrosion products may be removed from a metal object by simple dipping (e.g., silver dip, see section 3.3.2), or it may take several days to remove all traces of corrosion.

Care should be paid to the procedures used, to avoid overcleaning. This is an aesthetical problem and requires careful consultation with the owner/custodian of the object to determine exactly what level of cleaning is required.

2.2.4 Electrochemical and Electrolytic Reduction

These processes involve making the object the cathode in either a galvanic reduction cell or an impressed direct current system, so that the corrosion product on the surface can be reduced. The electrochemical systems are now rarely used as it is difficult to control them, and electrolytic reduction is the most common technique for stabilising metal objects and reducing their corrosion products. This process is particularly useful for metal objects that contain aggressive ions, such as chloride ions, and the conservation of archaeological objects literature has many references to this process [PLeNDERLEITH and WERNER 1971; CLARKE and BLACKSHAW 1982;
Fig. 1. Concreted cast iron cannon as recovered. Jettisoned by Captain Cook on the Great Barrier Reef, Australia, during his first voyage of discovery in 1770.

Fig. 2. Cast iron cannon following stabilisation by electrolytic reduction. Note the well preserved markings for a cast iron object submerged under the sea for over 200 years.
Fig. 3. Early 19th century carronade that was not stabilised after recovery from the sea. It has completely disintegrated.

Although archaeological objects are not covered specifically in this paper, electrolytic reduction is still a viable method for removing corrosion products, and in particular aggressive chloride ions from a metal object. Again, as this is a standard technique the reader is referred to the basic conservation literature for details.

There are, however, a number of important points that have to be considered when carrying out electrolytic reduction. The electrolysis is usually carried out at a d.c. cell voltage of 2 - 6V, and a current density of 2 - 100 mA/cm² [Clarke and Blackshaw 1982]. In fact it is not appropriate to use a specific current density as this would necessitate the accurate measurement of the surface area of a metal object, and I would defy anyone to measure accurately the surface area of a graphitized iron object, for example. The best procedure is to adjust the voltage control until bubbles of hydrogen gas are just evolved from the surface of the metal object as cathode. Then, depending on the nature of the object, in particular as to whether it is sound or very friable, then either reduce the voltage to just below the hydrogen evolution potential, or if hydrogen evolution is to be used for mechanical cleaning of the surface, increase the voltage accordingly. As the resistance to current flow will change in time it will be necessary to vary the voltage to keep the correct conditions of hydrogen evolution.

The most common electrolytes are sodium hydroxide or sodium carbonate solutions, and stainless steel or mild steel is appropriate for the anode material. To produce a good current throwing power and even current distribution, careful placement of anodes around the object is important.

It is normal to measure the chloride content of the electrolyte to determine
both the efficiency and completion of the removal of chloride from the object. As the rate of chloride extraction depends on the rate of diffusion of chloride ions through the corrosion layers, then a graph of quantity of chloride released vs. square root of the electrolysis time will give the best indication of when to replenish the electrolyte. In this case the curve will suddenly level off, indicating that the chloride ion concentration in the electrolyte is the same as in the corrosion layer. The process is repeated until the final electrolyte chloride concentration is less than 200 ppm, which has been found from experience to be a safe residual level and will not cause further corrosion of the metal.

It has often been debated whether metal corrosion products are reduced down to the base metal or merely to a lower oxidised state during electrolysis. It is claimed that silver corrosion products can be reduced to silver [Corrosion 1977], whereas iron rust can only be reduced to magnetite (Fe$_3$O$_4$) [Clarke and Blackshaw 1982]. Irrespective of the process, the reduced corrosion products are not very adherent to the base metal, and can usually be removed by brushing.

There are many more details of electrolysis that need to be known if treatments are to be carried out effectively and efficiently. As indicated at the beginning of this section careful reading of the most up-to-date literature is important in order to obtain the latest information.

2.2.5 Washing and Drying

Following any form of chemical or electrolysis treatment it is necessary to wash the metal object to remove all chemical traces. It may be necessary to first neutralise a strong acid or base, but then this is invariably followed by thorough washing. During washing it is important that the object does not corrode further, and an iron object, for example, will rapidly start to re-rust if left for any period of time in water alone. The use of inhibitors is important in such cases during washing to prevent re-corrosion occurring. Although heating wash solutions is also recommended [Plenderleith and Werner 1971], this should be done with caution, as some metals will begin to reoxidise, in particular copper, if exposed to hot water.

Following the completion of washing, checked by both measurement of pH and chloride ion content where applicable, it is next necessary to dewater the object and dry it as fast as possible in order to again avoid “flash rusting”. If small, the object can be dewatered in a number of successive baths of ethanol or acetone. The number of solvent washes will depend on the extent of corrosion of the metal surface, the greater the corrosion and subsequent pitting (or porosity) of the surface, the more solvent washing is required to ensure the complete removal of all traces of the aqueous washing procedure.

Large objects, on the other hand, cannot be dipped in a solvent, and in this case commercial water displacing solvents are applied by brush or spray to remove excess water and to allow the object to dry without re-corrosion. Care must be taken in selecting dewatering fluids, as some contain anti-corrosion coatings which
may have to be removed at a later stage.

Drying can be carried out by natural air drying, forced cool or hot air drying, or by heating. Care should be taken when using heat because even though it will increase the evaporation rate of solvents and any remaining water, it can also increase oxidation rates.

2.2.6 Restoration

Broken or damaged metal objects may be restored if necessary. Where appropriate, conventional metal working techniques, such as welding, bronzing or soldering, and the fabrication of missing pieces by machining etc., can be done. The former have to be done with care as they are likely to cause some alteration to the metal surface, melting lacquer or paint systems, or changing patinas, which would be unethical. In some cases, however, this may have to be the compromise between making a sound repair or doing nothing, which may leave the object in a potentially dangerous situation.

The alternative is to use adhesives and fillers to repair and infill broken metal objects, and consolidants for deteriorated surface layers. There are a range of such materials available, which should have the following basic properties:

1) must adhere well to the metal surfaces;
2) must penetrate well into the object, particularly if used as a consolidant;
3) set preferably with no change in volume (e.g., no shrinkage);
4) provide a stable barrier against atmospheric corrosion;
5) have good spreading qualities;
6) be chemically stable;
7) be inert to the metal object;
8) be easy to apply and remove—in the latter case particularly with time; and
9) not change the appearance of the object.

Adhesives that have been used include the epoxy resins, of which there is a wide range of grades available. The most common are the Araldites (CIBA-Geigy), such as Araldite AY 103, plus Hardener HY 956 or 951 [TUTTLE 1982]. Ablebond 342-1 is claimed to be a better alternative epoxy resin to Araldite, as it is more light stable [TUTTLE 1982].

Cyanoacrylic resins have also been used, but with little success as they do not have good load bearing capacity, which is usually important with metals. Nitrocellulose adhesives, such as HMG, on the otherhand, have been found to be satisfactory for restoring thin metal vessels [LANE 1972].

It is essential for a good repair using adhesives, that the surfaces of the break are clean from dirt, grease and corrosion products. The choice of adhesive will depend on the metal, the surfaces to be joined, and the load bearing requirement of the join. It may be necessary in some cases to insert reinforcing pins in the join. Organ has pointed out that the epoxy adhesives do not adhere well to copper alloys, possibly owing to the presence of copper ions affecting the curing of the adhesive
A range of fillers is also available for filling gaps in a metal object. Once the ethical/aesthetical aspects have been resolved the choice will again depend on each individual object. It is particularly important that fillers do not shrink during curing, and that they adhere well to the sides of the fill. Polyester resin, with or without pigments, and also fibre glass reinforcement have been used with success [Sekino 1965], as has pigmented Araldite 502 plus Hardener HY 956 filled with fumed silica, and also an epoxy 2 part putty, Araldite K58.

Consolidation of friable surfaces has been carried out using waxes, in particular microcrystalline and paraffin waxes [Organ 1963]; polyvinyl acetate [Bhowmik 1968]; and Paraloid B-72 (a copolymer of methyl acrylate and ethyl methacrylate). The use of soluble nylon, common some years ago, is no longer recommended owing to the long term crosslinking of the nylon film, which makes it irreversible [Sease 1981].

As corrosion products on metals are polar, and the metal underneath is non-polar, it is necessary for good adhesion of the consolidant to the corrosion products, that the consolidant is also polar [Rosenqvist 1963].

Experiments are currently being carried out at the Canberra College of Advanced Education Training Program to study the effectiveness of the consolidation of corroded wrought iron using Paraloid B-72, microcrystalline wax and polyvinyl acetate.

2.2.7 Metal Polishing

It is a matter of aesthetics that we polish some metal objects before they go on exhibition. This polishing is not necessary from the point of view of preserving the object, and in fact it is due to regular polishing over the years that the surfaces of metal objects, in particular those of silver or plated metal, have been worn away. However, as we do not like to see tarnished silver, copper or brass on display it is necessary to polish the object. This procedure may be carried out at this stage in the conservation treatment of the metal object, it may, on the other hand, be the only process used as it is possible to clean, remove corrosion products and polish a metal surface in one process.

Most of the commercial polishes contain an abrasive, and as mentioned earlier, continued use will cause damage to the metal surface. The most common ones are Brasso for copper alloys, Silvo for silver objects, and there are also pewter and steel polishes. These contain an abrasive in white spirit, usually with other additives, such as ammonia. In general they are considered too abrasive for use on museum objects, and efforts should be made locally, as in Canada [C.C.I 1984], to find materials that are less abrasive. There is no point in listing recommended products at this time as each country will have different materials, but in Canada, for example, the recommended polishes are Never-Dull Magic Wadding and jewellers’ cloth (consisting of an outer flannelette for polishing and an inner flannel impregnated with jewellers rouge—a fine abrasive of iron oxide) [C.C.I 1984]. In Australia,
North, for example, has compared the effectiveness of nine polishes and one chemical cleaner in removing the tarnish from silver [North 1980]. Similar experiments should be carried out elsewhere to determine the most suitable local products.

Some polishes claim to have anti-tarnish properties, and this is usually due to the presence of silicons in the polish producing a polymeric silicone film barrier on the metal surface. Although providing initial anti-tarnish properties, they will break down in time, often causing a streaking effect, and, more important, when the object is recleaned an abrasive will be required to remove the silicone film, otherwise chemical cleaners, for example, will not be effective. Also, other coating systems, such as waxes and lacquers, will not take well to a silicone-coated surface.

2.2.8 Surface Coating

In order to provide a barrier against the atmosphere, thereby preventing further tarnishing or corrosion, most metal objects are coated. There are a range of coating materials available, depending on the metal to be coated, the type of surface finish required, and whether the object is to be displayed indoors or outdoors.

For indoor purpose, the common coating systems are either wax or lacquers. In the former case the use of Renaissance Wax [Pleinderleith and Werner 1971; C.C.I 1984], a mixture of polyethylene wax and microcrystalline wax (25 parts by weight of polyethylene wax, 25 parts by weight of microcrystalline wax in 230 parts by weight of white spirit [West Australian Museum 1981]), is most common. This can be applied to give either a matt or glossy finish. For copper alloys, an inhibitor, benzotriazole (BTA), can be added to give better protection [Lafontaine 1980].

The common indoor lacquers are the nitrocellulose lacquers, Frigilene (which if applied correctly does not affect the surface finish and is used in particular for silver) and Ercalene (which provides a glossy finish) [Pleinderleith and Werner 1971]. For copper alloys, in particular, Incralac (an acrylic lacquer of Paraloid B-44 in toluene, also containing the BTA inhibitor) [Sease 1981] is the most commonly used coating system. It has also been recommended for iron alloys. There have, however, been recent examples where Incralac applied several years ago is now becoming very difficult to remove, particularly if used outdoors.

Whenever lacquers are applied it is always better to apply a number of thin coats (using the appropriate thinners) rather than one thick coat, and, in order, of preference the best coats are obtained by dipping, spray coating, and brush coating the object.

For outdoor display of metal objects, which are usually fairly substantial, such as machinery and large agricultural implements, there are a wide range of commercial coating systems available [Kilminster 1979]. Again it is not appropriate to provide a list of paint systems, as their availability will vary from country to country. Where information is required it is advisable to contact the senior chemist of a major paint manufacturing company who should be able to provide a specific paint
system for the objects displayed outdoors.

2.2.9 Inhibition

In addition to the use of surface coatings, inhibitors are sometimes used to assist in the prevention of further corrosion of a metal object in storage or on display. The most common form of inhibitors are vapour phase inhibitors (VPI), which are essentially alkaline volatile inhibitors, such as cyclohexylamine carbonate or nitrite. In high humidities they volatilize and settle on anodic sites on the metal surface, inhibiting further corrosion. The VPI can be in the form of a powder or crystal, or impregnated into wrapping paper.

2.3 Report Writing

Following completion of the conservation of the metal object, a detailed report must be produced. This should include:

1. chemicals used, their temperatures and compositions including by weight, by volume etc.;
2. physical and chemical measurements, such as pH, conductivity, cell voltages;
3. results of examinations, such as XRD, XRF, SEM, radiography, spot test analysis;
4. treatment times;
5. photographs taken before, during and after treatment;
6. any particular problems, in particular failures with any of the conservation and restoration processes;
7. trade names, chemical types and sources of materials used;
8. conclusions, including comments as to the success of the treatment, problems which future workers may be able to overcome, and recommendations for future research if required; and
9. recommendations for storage and display.

2.4 Storage and Display

It is a waste of time and money if metal objects are not stored or displayed in a stable environment following conservation treatment. Obviously, outdoor objects are a different problem and this will be discussed further below. The following general guidelines are provided for the storage and display of metal objects [JOHNSON and HORGAN 1979; STOLOW 1979; BERTRAM 1982].

2.4.1 Storage and Display Environment

If metal objects alone (i.e., with no associated materials, such as wood) are to be stored or displayed, then the recommended relative humidity is 30%; preferably lower [JOHNSON and HORGAN 1979], to avoid corrosion problems, with a constant temperature of 20±2°C. Unfortunately, it is rare that metal objects do not contain other materials, and therefore the compromise environment of 50±3% R.H.
and $20^\circ \pm 2^\circ C$ is more usual [THOMSON 1978].

The air should also be clean, otherwise air pollutants, such as sulphur oxides, can produce an acid environment, and particulate matter can settle out on metal objects, creating localised corrosion cells with resultant pitting [THOMSON 1978].

2.4.2 Lighting

Although not normally susceptible to damage by high illumination and ultra violet (U.V.) radiation levels, if a metal object is lacquered or if associated with light sensitive materials then it will be necessary to control the illumination and U.V. levels [THOMSON 1978]. The recommendations are for very sensitive materials 50 lux illumination and 30 $\mu$W/lumen U.V. radiation ($1500 \mu$W/m$^2$); for sensitive materials 150 lux and 80 $\mu$W/lumen (12,000 $\mu$W/m$^2$); and if no sensitive material is present the levels should not need to exceed 300 lux and 200 $\mu$W/lumen (60,000 $\mu$W/m$^2$). Of course, special raking lighting may be needed for high-lighting purposes, and the like.

2.4.3 Insect, Mould and Rodent Control

Again, metal objects are not normally affected by attack from insects, fungi and rodents, unless they contain organic components. Mould growth can occur on metal objects, which could cause staining or etching of the surface. However, if the relative humidity levels are controlled to those recommended above there should be no mould growth problems.

If organic materials are present then the procedures required for controlling insects, mould and rodents need to be applied [STOLOW 1979; PEARSON 1985a].

2.4.4 Handling of Objects

A lot of damage to metal objects can be caused by poor handling. Objects can be dropped, causing breakage or damage, but more common are the finger prints left by curatorial and display staff (assuming conservators know better). Hands contain moisture, grease and salt, which if left on the surface of an object will in time cause staining and etching of the metal surface. All metal objects during and following treatment must therefore be handled with gloves.

2.4.5 Materials of Construction of Storage and Exhibition Units

During the storage and exhibition of metal objects it is essential that the materials of construction of the units do not exude harmful chemicals in either the short or long term.

A number of materials have been tested, revealing the following problems [ODDY 1975; PADFIELD et al. 1982].

(1) Polyvinyl acetate emulsions, which are the basis of many wood glues, cause severe corrosion of lead or pewter objects, they can also tarnish copper and silver. Adhesives containing ammonia can cause tarnishing of lead, silver and particularly copper, brass and bronze;
(2) Plastic dust excluders and edging strips can give off harmful vapours, such as sulphur, which will cause tarnishing of metals;

(3) Paints must be allowed to cure and dry out well before exhibition or storage units are used;

(4) Some fabrics give off harmful vapours, usually produced by the dyeing agent. Beware of fire-proofing agents, these can also release harmful vapours; and

(5) Some woods, particularly chipboard, give off harmful vapours such as formaldehyde. This can easily be detected in a storage or display unit by the strong, sharp odour produced. The application of paint films is not always sufficient to prevent the slow release of harmful vapours.

If chipboards have to be used, because of economics, then they should either be formaldehyde free (difficult to obtain) or treated with a solution of urea in water (a mixture of 50 g of urea to 75 ml of water brushed on to each m² of wood surface [ZENICHI 1975].)

Materials that are considered safe to use include [PADFIELD et al. 1982]:

- Metals
- Polycarbonates
- Glass
- Polystyrene
- Ceramics
- Polyester fibres
- Inorganic pigments
- Cotton
- Polyethylene
- Linen
- Acrylic polymers (solutions rather than emulsions).

The important thing here is to TEST ALL MATERIALS BEFORE USE. Oddy recommends heating the material under test with samples of polished metal (copper, silver etc.) in a humidified atmosphere at 60°C in an oven [ODDY 1975]. If tarnishing is to occur it will happen within a few hours. The material is considered safe if there is no tarnishing after 28 days.

In order to support metal objects, particularly those on exhibition, it is important that the correct support materials are used. The following, which should NEVER be used, include drawing pins, nails, staples, adhesive tapes. These are all likely to cause damage to the object, with pins and nails rusting in particular from galvanic corrosion if in contact with a dissimilar metal, and adhesives becoming very difficult to remove with time. If pins have to be used then they must be stainless steel (e.g., insect pins). Objects that need to be elevated for exhibition are best supported on shaped pieces of Perspex, or bracketed shelves attached to the wall of the case. Do not support objects with nylon wire. Under the influence of light, heat and with time the nylon can deteriorate and might break. Heavy metal objects should be supported on a solid base.
3. CONSERVATION OF INDIVIDUAL METALS AND THEIR ALLOYS

The preceding information although perhaps rather general does indicate the wide range of treatments available for conserving and restoring metal objects. The most up to date publication covering the deterioration and conservation of metals, is that by Stambolov [1985].

In the following sections the information provided will be based on conservation procedures that have been used for a number of years and which have yielded satisfactory results. This is not to say that they are the best techniques or the only techniques, and metal conservators should establish their own evaluation programs to determine which procedures best suit their particular metal conservation requirements. The information will be limited to small indoor objects, with a final section being devoted to outdoor objects.

3.1 Iron and Its Alloys

Iron is very rarely found in a pure state, normally being alloyed with carbon to produce, in order of increasing carbon content, wrought iron, steel, malleable iron and cast iron. It has also been alloyed with other elements, in particular with nickel and chromium to produce stainless steels.

The corrosion of iron alloys depends on the environment to which the object is exposed. Table 1 lists the typical corrosion products encountered on iron.

### Table 1. Common corrosion products found on iron alloys.

<table>
<thead>
<tr>
<th>Corrosion Product</th>
<th>Formula</th>
<th>Colour</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous oxide</td>
<td>FeO</td>
<td>Black</td>
<td>Air</td>
</tr>
<tr>
<td>Magnetite*</td>
<td>Fe₃O₄</td>
<td>Black</td>
<td>Moist air</td>
</tr>
<tr>
<td>Ferric oxide (hematite)*</td>
<td>Fe₃O₄</td>
<td>Reddish-brown-black</td>
<td>Air/water</td>
</tr>
<tr>
<td>Ferrous hydroxide*</td>
<td>Fe(OH)₂</td>
<td>Pale green</td>
<td>Air/water</td>
</tr>
<tr>
<td>Limonite*</td>
<td>FeO(OH)</td>
<td>Brown</td>
<td>Air/water</td>
</tr>
<tr>
<td>Lepidocrocite*</td>
<td>γ-FeO(OH)</td>
<td>Brown</td>
<td>Air/water</td>
</tr>
<tr>
<td>Geothite*</td>
<td>α-FeO(OH)</td>
<td>Blackish-brown</td>
<td>Air/water</td>
</tr>
<tr>
<td>Ferrous sulphate</td>
<td>FeSO₄·H₂O</td>
<td>Off white</td>
<td>Polluted air/water</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>FeCl₂</td>
<td>Green-yellow</td>
<td>Marine/polluted air</td>
</tr>
<tr>
<td>Ferrous oxychloride</td>
<td>FeOCl</td>
<td>Brown</td>
<td>Marine</td>
</tr>
<tr>
<td>Ferrous sulphide</td>
<td>FeS</td>
<td>Black-brown</td>
<td>Polluted air/marine</td>
</tr>
</tbody>
</table>

* A combination of one or several of these corrosion products constitutes what is known as rust, very often being complicated by the addition of chlorides, sulphates and sulphides.

The iron object must first be checked to determine its condition and particularly for signs of chloride corrosion. This is often evidenced by droplets of yellow moisture, called “sweating”, on the surface of the object (Fig. 4), and can readily be confirmed by the use of the silver nitrate spot test for chloride ions (Appendix 1).
Fig. 4(a). Typical concreted wrought iron anchor and chain as recovered from the sea.

Fig. 4(b). The wood grain appearance of corroded wrought iron. Beads of moisture (too small to be seen on this photograph) indicate that the anchor is still corroding.
3.1.1 Removal of Dirt and Grease

The methods described in section 2.2.1 are appropriate, in particular the use of 2% w/v sodium hydroxide solution, as iron is immune to corrosion in this solution.

3.1.2 Removal of Corrosion Products

Heavy corrosion should be removed by mechanical means (section 2.2.2), whereas it is safer to remove light corrosion by the use of chemicals. Two systems that have been found satisfactory are:

(a) Solution of 10% w/v citric acid, 4% w/v thiourea (as inhibitor), 86% w/v distilled/deionized water; and

(b) Solution of 10% w/v citric acid buffered to pH 4 with ammonium hydroxide.

The aim of the inhibitor [WALKER 1982] is to prevent corrosion of the base metal during the removal of the corrosion products. Solution (a) is more aggressive than solution (b), and care must be taken with the former during long treatment times, as the influence of the inhibitor can wear off and may need replenishing.

Either of these solutions can be made into a poultice by making up a 20% w/v mixture with carboxy-methyl cellulose. This is applied to localised corrosion, con-

Figs. 5(a)/(b). 19th century iron padlock with brass keyhole cover, before (left) and after (right) chemical cleaning. The brass was masked with lacquer to prevent corrosion during derusting of the iron.
fining the acid treatment by means of the carboxy-methyl cellulose gel. The gel must be kept covered with plastic at all times to prevent drying out, which would cause differential aeration corrosion problems.

The other means of removing small areas of iron corrosion, particularly if surrounded by another medium such as wood or leather, is to use the air abrasive, the choice of air pressure and powder type and flow rate being determined by the type of corrosion to be removed. Figs. 5–8 show before and after photographs of a variety of different metal objects that have been derusted by chemical and mechanical processes.

Figs. 6(a)/(b). Arabian dagger, before (top) and after (bottom) derusting, using chemical and mechanical processes.
Figs. 7(a)/(b). Japanese entrenching tool (1939-45), before (top) and after (bottom) cleaning. Careful cleaning is required to retain the soil remaining on the tool from the battle field.
Figs. 8(a)/(b). "Harbas" insecticide tin case (early 20th century), before (top) and after (bottom) derusting by acid treatment.
3.1.3 Electrolysis

Particularly if chlorides are present, the iron object will require stabilising by electrolysis. A typical set up would use stainless steel or mild steel anodes and an electrolyte of 2% w/v sodium hydroxide solution. For cast iron, particularly if graphitised, it is important that the cell voltage be kept below the hydrogen evolution potential. A voltage of 2 volts is recommended initially, with care being taken to lower this once reduction has commenced and hydrogen gas starts being evolved. Higher voltages can be tolerated for wrought iron. In fact, hydrogen evolution is encouraged to assist in the removal of corrosion products from crevices in the metal surface. As discussed in section 2.2.4, the chloride ion concentration of the electrolyte has to be monitored to determine the rate and completion of chloride ion removal.

3.1.4 Washing and Drying

During the washing of iron objects to remove previous treatment chemicals it is essential that no further corrosion takes place. A suitable inhibited wash solution is 1,000 ppm (1 g/l) of chromate ion in distilled or deionised water. This has a pH of approximately 8.4, and monitoring of the pH will indicate when the washing is complete.

Finally the wash solution is removed by the use of several baths of acetone or ethanol, or if the object is too large, by the use of a commercial dewatering fluid, and the object allowed to dry. Forced drying can be used if required.

3.1.5 Inhibition

The previous treatments will normally leave an iron object with a dull grey finish. For aesthetic reasons, and also to provide an extra protection against further corrosion, the metal can be treated with an inhibitor, namely 3% w/v solution of tannic acid in water or ethanol, either by immersion or brush-on application. This reacts with the iron to form dark blue/black iron tannates which provide protection to the metal surface. (Fig. 9).

A further means of inhibition is by use of a vapour phase inhibitor (VPI). For iron, a dish of VPI powder (e.g., cyclohexylamine nitrite) placed in the storage or display unit will help prevent further corrosion of exposed iron.

3.1.6 Coating

For clear coatings which provide a natural finish to the object, either Frigilene, Incralac or Paraloid B-72 have been found to be satisfactory.

An alternative method, in particular for heavily corroded iron objects is immersion of the object in molten microcrystalline wax. The white wax, with a hardness of approximately 16, and a melting point of approximately 80°C, is melted and the preheated object immersed until all air bubbles cease to evolve from the surface. The wax is then allowed to cool with the object still submerged, since it is during
Figs. 9(a)/(b). Cast iron pot lid, before (top) and after (bottom) derusting by acid and treatment with tannic acid inhibitor.
this cooling period that the wax penetrates into the object. Finally, just before the wax solidifies, the object is removed and excess wax removed from the surface with white spirit.

3.2 Copper and Its Alloys

The main alloys of copper are brass (essentially copper/zinc) and bronze (copper/tin). However, there are a large number of variations of these alloys containing a range of other alloying elements that have been used over the centuries.

The major corrosion products normally found on copper alloys are given in Table 2. Not included in this table are the corrosion products that might be produced on the alloying elements, such as zinc, tin, lead, etc.

<table>
<thead>
<tr>
<th>Corrosion Product</th>
<th>Formula</th>
<th>Colour</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuprous oxide</td>
<td>Cu$_2$O</td>
<td>Red</td>
<td>Buried/air/marine</td>
</tr>
<tr>
<td>Cupric oxide</td>
<td>CuO</td>
<td>Black</td>
<td>Buried/air/marine</td>
</tr>
<tr>
<td>Basic copper carbonate</td>
<td>CuCO$_3$·Cu(OH)$_2$</td>
<td>Dark green</td>
<td>Buried/air</td>
</tr>
<tr>
<td>Basic copper carbonate</td>
<td>2CuCO$_3$·Cu(OH)$_2$</td>
<td>Blue</td>
<td>Buried/air</td>
</tr>
<tr>
<td>Cuprous chloride</td>
<td>CuCl</td>
<td>White</td>
<td>Buried/marine</td>
</tr>
<tr>
<td>Basic copper chloride</td>
<td>CuCl$_2$·3Cu(OH)$_2$</td>
<td>Yellow-green</td>
<td>Buried/marine</td>
</tr>
<tr>
<td>Copper sulphide</td>
<td>Cu$_2$S</td>
<td>Black</td>
<td>Buried/marine</td>
</tr>
<tr>
<td>Copper sulphide</td>
<td>CuS</td>
<td>Black</td>
<td>Buried/marine</td>
</tr>
<tr>
<td>Basic copper sulphate</td>
<td>CuSO$_4$·3Cu(OH)$_2$</td>
<td>Green</td>
<td>Industrial air</td>
</tr>
<tr>
<td>Basic copper nitrate</td>
<td>Cu(NO$_3$)$_2$·3Cu(OH)$_2$</td>
<td>Blue-green</td>
<td>Industrial air</td>
</tr>
<tr>
<td>Basic copper phosphate</td>
<td>Cu$_3$(PO$_4$)$_2$·Cu(OH)$_2$</td>
<td>Blue</td>
<td>Buried in contact with bone</td>
</tr>
</tbody>
</table>

An important cause of corrosion with all copper alloys is the presence of chloride ions, that cause the infamous bronze disease [PLENDERLEITH and WERNER 1971]. The corrosion reactions that occur are well documented and will not be discussed here [MACLEOD 1981].

A further important form of corrosion experienced with copper alloys is due to a galvanic couple being formed between different phases in the alloy. Phases high in zinc (in brass), for example, will corrode preferentially in an aggressive environment leading to a corrosion process known as dezincification, and for bronze the tin-rich phase will be leached out by destannification.

In both processes the surface is left high in copper content and care has to be taken with both the conservation—should these surface layers be removed—and any surface analysis that might be taken of the object.

3.2.1 Removal of Dirt and Grease

Organic solvents are preferred for cleaning and degreasing copper alloys. The use of alkali baths is to be avoided. The removal of paint using a methylene
Fig. 10(a). Victorian brass candlestick as received covered in paint (before treatment).

Fig. 10(b). Victorian brass candlestick. Paint was removed using methylene chloride paint stripper.
chloride paint stripper is shown in Fig. 10.

3.2.2 Removal of Corrosion Products

Again, mechanical techniques as outlined in section 2.2.2 are applied where appropriate, and most metal conservators have experienced the many hours spent mechanically removing the corrosion scale from a bronze artefact.

For chemical cleaning a number of processes are available and the following have been found satisfactory. Solutions (a) and (b) indicated in section 3.1.2, as used for cleaning iron objects, Figs. 11 (a) and (b) show a copper boiler before and after cleaning; and solution (c) which consists of 1.5% w/v sodium hydroxide, 15% w/v sodium potassium tartrate (Rochelle salt), and 83.5% w/v water. This, however, produces a dark deposit on the metal surface and is not very popular.

Merk [1978, 1981] has studied a series of reagents used for stripping bronzes, with and without the use of benzotriazole as corrosion inhibitor. She concluded that none of the uninhibited solutions (alkaline glycerol, alkaline Rochelle salt, Calgon [sodium hexametaphosphate], citric acid and buffered citric acid) were effective in removing corrosion products without also etching the base metal. When benzotriazole (BTA) was added as an inhibitor, it was most effective for Calgon, less effective for alkaline Rochelle salt and alkaline glycerol, and not effective for citric acid solution.

It is obvious that care must be taken with these stripping solutions, which should be used for the minimum period of time to prevent etching of the base metal. Much more research is required on the use of inhibitors for the chemical cleaning of metal objects.

Where there are small spots of corrosion, they can be removed either by cotton swab, using a 1-2% v/v of sulphuric acid, or a carboxy methyl cellulose poultice made up with the stripping agents similar to that used for iron. Alternatively, careful use of an air abrasive unit might be appropriate.

3.2.3 Electrolysis

Electrolysis of copper alloys must be carried out with caution, as during this process the corrosion products will be reduced and will end up as a sludge that is easily removed from the metal surface. This, as with chemical cleaning, cannot be used if the patina on the object (e.g., patinated Chinese bronze) has to be retained.

Electrolysis is carried out where it is important that surface detail of an object is revealed. The normal process is similar to that for iron objects (section 3.1.3), with care being taken with voltage control, which may be as high as 6-12 volts.

This process is continued until all the corrosion products have been reduced and chloride ions (if present) removed.

3.2.4 Washing and Drying

There is no need to use inhibited wash solutions for copper alloys as they will not retarnish at room temperature. Washing is therefore carried out in distilled or
Fig. 11(a). Victorian copper boiler as received.

Fig. 11(b). Victorian copper boiler, cleaned using inhibited citric acid solution.
deionised water until there is no change in pH.

3.2.5 Treatment for Bronze Disease

If bronze disease is suspected, evidenced by areas of soft grey/green corrosion products (Fig. 12), then this should be confirmed with the spot test for chloride ions (see Appendix 1). If present, the chlorides must be removed either by chemical stripping or electrolysis, or stabilised so that the cyclic corrosion process of bronze disease is broken. This can be achieved in a number of ways. The simplest is to create a dry (less than 25% RH) atmosphere by the use of a desiccant such as silica gel. Moisture is required for bronze disease to proceed and an object can be stabilised by this method for a long period of time. Unfortunately, if then exposed to a high relative humidity the bronze disease will reactivate.

A method used for some years has been that based on silver oxide [PLENDERLEITH and WERNER 1971]. The affected areas are excavated and the whole then plugged with silver oxide-ethanol paste which reacts with the chloride to form stable silver chloride. Unfortunately this is an extremely tedious process and can only be applied to known areas of bronze disease. For an object with a heavy corrosion crust the bronze disease may not be noticeable on the surface, and if undetected could not be treated and would continue to attack the base metal.

The common process is based on the use of the inhibitor, benzotriazole (BTA) [MACLEOD 1981; MERK 1978, 1981]. This is applied to the object either in a 3% w/v solution in ethanol or in water. The object should preferably be placed in a BTA solution under vacuum for 24 hours. It is then tested to determine the effectiveness of the treatment by exposing the object overnight to a relative humidity of

Fig. 12. Bronze spearhead (Cyprus, c. 1800 B.C.). The damage caused by bronze disease is clearly visible.
Figs. 13(a)/(b). H.M.A.T. Duntroon Plaque (1942). The corrosion caused by the remnants of previous polishes can be seen, when the badge was removed from the plaque.
approximately 80%. If no new blisters of bronze disease erupt, the treatment is considered successful. Although not fully understood, the BTA is believed to stop bronze disease by complexing with copper ions and forming a polymeric film on the surface of the object. This, in effect, binds up the copper ions making them no longer available for attack by chloride ions. The literature should be studied for more exact details [MACLEOD 1981; MERK 1978, 1981].

3.2.6 Polishing

It is quite common for copper alloys, in particular brass and bronze, to be polished following conservation. The polishes detailed in section 2.2.7 are suitable, with care being taken to remove any excess polish with ethanol. Damage caused by continual polishing can be seen in Fig. 13.

3.2.7 Coating

The most common coating systems for copper alloys are either a wax paste containing BTA [LAFONTAINE 1980] or an acrylic lacquer, Incralac, also containing BTA [SEASE 1978]. The comments in section 2.2.8 concerning methods of application of lacquers, and also the possible problems of irreversibility of Incralac, should be noted.

3.3 Silver and Its Alloys

Silver is used either in its pure form as a plating metal, particularly as electroplate (e.g., Electroplated Britannia Metal or Electroplated Nickel Silver), or as an alloy, the most common being Sterling Silver (925 parts silver and 75 parts copper). The most common problems with silver objects, or objects containing silver, is the dark tarnish, essentially silver sulphide, that forms, even in reasonably clean environments (Table 3).

<table>
<thead>
<tr>
<th>Corrosion Product</th>
<th>Formula</th>
<th>Colour</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver sulphide</td>
<td>Ag₂S</td>
<td>Grey-black</td>
<td>Buried/polluted air</td>
</tr>
<tr>
<td>Silver chloride</td>
<td>AgCl</td>
<td>White-grey</td>
<td>Buried/polluted air</td>
</tr>
</tbody>
</table>

Most silver objects that require conservation do not have a heavy corrosion crust and are usually relatively easy to clean. Care should be taken due to the corrosion process of surface enrichment, whereby the copper in sterling silver, for example, may have been leached out leaving the surface of the object rich in silver.

3.3.1 Removal of Dirt and Grease

The use of a soap solution or organic solvent (section 2.2.1) is all that is normally required to remove dirt and grease from the metal surface.
3.3.2 Removal of Corrosion Products

Mechanical methods are rarely required for removing corrosion products from silver, particularly as the tarnish films are so thin. The most common method is to use a silver dip which can be obtained either commercially, or made up in the laboratory (at a much lower cost). It consists basically of a dilute acid (e.g., sulphuric, formic or phosphoric acid), a wetting agent and a sequestering agent [NORTH 1980; STAMBOLOV 1985]. For example:

(a) 1 ml conc. sulphuric acid
  7.5 g thiourea
  0.5 ml Lissapol
  Make up to 100 ml;
(b) 0.5 ml conc. formic acid
  8.5 g thiourea
  0.5 ml Lissapol
  Make up to 100 ml; and
(c) 8 ml, 85% phosphoric acid
  7 g thiourea
  0.5 ml Lissapol
  Make up to 100 ml

Figs. 14(a)/(b). E.P.B.M. glass holder (Victorian), before (left) and after (right) cleaning, using sulphuric acid based silver dip.
Do not use silver dip based on hydrochloric acid. It is also important to remember that the cleaning solution should be used as a dip. If a silver object is left in solution for more than a few minutes the metal surface will become etched and will then require polishing. Care should also be taken not to reuse old silver dip, as the dissolved silver ions in solution may tend to plate out on sterling silver or the base metal of silver plate (Figs. 14 and 15). Chemical cleaning should not be used for silver objects which have been deliberately oxidized to create a dark surface finish, as this will be removed.

Figs. 15(a)/(b). E.P.N.S. Epergne (Victorian), before (top) and after (bottom) cleaning, using sulphuric acid based silver dip.
3.3.3 Electrolysis

A heavily corroded silver object can be cleaned by electrolysis, and again a similar set up as used for iron or copper can be used. An alternative electrolyte to sodium hydroxide is a 5% v/v solution of formic acid.

Consolidative reduction [PLENDERLEITH and WERNER 1971], which has been used in the past for treating very deteriorated silver objects, is no longer used as results have not been satisfactory.

3.3.4 Washing and Drying

It is important that only deionised or distilled water is used for washing silver objects following removal of corrosion products. Household detergents etc., should never be added to the wash solution, as they may cause retarnishing of the silver. Inhibitors are not required during washing as silver will not readily recorrode in "pure water".

3.3.5 Polishing

It is common for silver to have a polished surface, and if the previous surface is polished and the silver dip has been used only as a dip, then the surface should remain polished. If, on the other hand, the surface is etched, then a silver polish is required, as discussed in secton 2.2.7. Care should be made in the choice of polish, using the least abrasive cleaner available. Again, removal of excess polish is carried out using ethanol. Great care, however, should be taken not to remove any black oxidized areas which are part of the design of the silver object.

3.3.6 Coating

Coating silver to prevent further corrosion can be difficult. If carried out by dipping or spraying then the result can be successful, however, if by brush application, there may be gaps (holidays) left in the film, through which corrosion may reoccur, and some time later the surface may gain a streaky appearance. The other problem is to achieve a finish whereby the metal surface does not appear to be coated. The major problem is to avoid producing a rainbow effect.

The lacquers most commonly used for silver are Frigilene and Paraloid B-72.

3.3.7 Inhibition

In order to prevent retarnishing of silver during storage and exhibition, it is normal to use some form of inhibitor. Silver can be stored in "silver bags", which are cloth bags impregnated either with fine particles of silver which preferentially remove any corrosive atmospheric chemicals, or with a vapour phase inhibitor. Again these are commercial products and should be tested before use.

3.4 Gold and Its Alloys

Pure gold has the unique property that it does not corrode in most buried or above ground environments. However, it is normally alloyed with base metals, such as silver, copper or occasionally iron, to produce metals of different properties and different colours. In a corrosive environment the base metal will tend to corrode and tarnishing of the surface will occur. Gold is also used in the form of leaf or as a thin layer in gilt metal or rolled gold. In this case the problem will be the corrosion of the base metal causing the gold layer to lift off. Scott [1983] has discussed the deterioration of gold alloys by tarnishing, dissolution of anodic constituents, stress corrosion, cracking and embrittlement, and by changes due to order-disorder transformations. He points out that the corrosion of gold alloys is more common than normally thought.

3.4.1 Removal of Dirt and Grease

Gold alloys should not require more than the aqueous cleaning treatment to remove dirt and grease (section 2.2.1).

3.4.2 Removal of Corrosion Products

The corrosion products will depend on the alloying element, and will normally be copper or silver. Copper corrosion products may be removed with 10% v/v ammonia solution or the inhibited citric acid solution (section 3.1.2), and silver corrosion products in one of the silver dip solutions (section 3.3.2). An alternative for removing silver sulphide is a 5% w/v solution of ammonium thiosulphate [SCOTT 1983].

Gold leaf, particularly if pure gold, is readily cleaned with a 5% v/v solution of ammonia.

3.4.3 Washing and Drying

The usual deionised water followed by acetone is recommended for washing and drying gold alloys. Care must be taken with layered gold to remove any contaminant from between the gold and base metal.

3.4.4 Polishing

It should not be necessary to polish gold. If it is carried out the mildest polish should be used, as gold is very soft and scratches easily.

3.4.5 Coating

Gold alloys should normally not require coating. However, if they have a high base metal content it may be advisable to use Frigilene or Paraloid B-72.
3.5 Lead, Tin and their Alloys

Lead may be either alone or alloyed, usually with tin, to make pewter (e.g., 80% tin and 20% lead). Tin is rarely found in the pure state. It is either as tin plate on steel, as pewter, or as leadless pewter, (e.g., 93% tin, 5% antimony and 2% copper), which replaced lead pewter in the 19th century. The major corrosion products found on lead, tin and their alloys are given in Table 4.

The major corrosion products on lead are usually lead carbonate, and on tin, tin oxide (which may occur as blisters). Lead and pewter objects do not often require any cleaning, as they build up an attractive patination which would be damaged by cleaning processes.

Table 4. Common corrosion products found on lead and tin alloys.

<table>
<thead>
<tr>
<th>Corrosion Product</th>
<th>Formula</th>
<th>Colour</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEAD:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead oxide</td>
<td>PbO</td>
<td>Yellow</td>
<td>Air</td>
</tr>
<tr>
<td>Lead dioxide</td>
<td>PbO₂</td>
<td>Black</td>
<td>Polluted air/buried/marine</td>
</tr>
<tr>
<td>Lead carbonate</td>
<td>PbCO₃</td>
<td>Colourless</td>
<td>Water</td>
</tr>
<tr>
<td>Lead chloride</td>
<td>PbCl₂</td>
<td>White</td>
<td>Polluted air/marine</td>
</tr>
<tr>
<td>TIN:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stannous oxide</td>
<td>SnO</td>
<td>Black</td>
<td>Buried/marine/air</td>
</tr>
<tr>
<td>Stannic oxide</td>
<td>SnO₂</td>
<td>White</td>
<td>Buried/marine/air</td>
</tr>
</tbody>
</table>

3.5.1 Removal of Dirt and Grease

Care must be taken in any cleaning of lead and tin alloys not to cause damage to the surface. Lead, in particular, is a soft metal and is easily scratched. Any brushing in the aqueous and organic solvents (section 2.2.1) should be carried out with care. Lead can be corroded by distilled water [PLENDERLEITH and WERNER 1971], and therefore any aqueous treatments should be kept to a minimum.

3.5.2 Removal of Corrosion Products

Again, mechanical cleaning methods have to be used with caution. Guldbeck [1976] recommends the use of a fine abrasive powder in oil or ethanol to remove corrosion products.

Acid cleaning, using acetic or nitric acid, is not recommended. Although removing corrosion products they also attack the base metal. The process that has been successful is a 5% w/v solution of the di-sodium salt of ethylenediaminetetraacetic acid (EDTA) (pH approx. 4.5). Here again, over-cleaning must be avoided, to prevent damage to the metal.
3.5.3 Electrolysis

The usual electrolytes are 5% w/v sodium hydroxide or 10% v/v sulphuric acid, with stainless steel anodes. The voltage is controlled so that a steady stream of hydrogen is evolved from the metal surface, which assists with the removal of corrosion crusts. For lead, the objects must not be left in the alkaline electrolyte without the current being switched on, as corrosion of the lead may occur. In sulphuric acid it is recommended that at the end of electrolysis the current is reversed for a short period, to form a protective layer of lead peroxide on the surface.

Consolidative reduction has also been used for lead and pewter objects [Pleinderleith and Werner 1971; Corrosion 1977]. This uses either a very low voltage (and hence current), i.e., well below the hydrogen evolution potential, or a partially rectified alternating current system, where the object is made alternatively the anode and cathode. The same electrolyte and anode system for normal electrolysis can be used here.

3.5.4 Washing and Drying

Boiled distilled water is often used to remove chemicals from lead or tin alloys. This can be followed by a brief dip in a dilute sulphuric acid solution to produce a protective lead sulphate layer (for lead alloys) on the surface.

3.5.5 Coating

It is not normal to polish lead or tin alloys. Therefore after conservation the next procedure is the application of a protective coating. The most common system is the wax paste, detailed in section 2.2.8.

3.5.6 Surface Inhibition

Although inhibitors (e.g., 4,4-diaminodicyclohexylmethane) are available for the further protection of lead and tin alloys [Grz et al. 1976], it is also essential that lead alloys are kept away from organic acid vapours. Acetate vapours from some timbers and also adhesives will attack lead alloys (section 2.4.5). This must be avoided. It is therefore advisable to store such objects in metal containers or sealed in polythene bags.

3.6 Composite Materials

The most difficult type of object to conserve is one which consists of a number of different materials. These can be metal/organic or metal/different metal. If the components can be separated the task is relatively simple. But if not each process must be carefully examined to ensure that there is no damage caused to either component during treatment (Fig. 16).

Among metals there are a number of metal combinations, such as Sheffield plate (sterling silver plate on a base metal, usually copper), silver plate (pure silver on a base metal), tin plate (tin on steel), galvanized iron (zinc on steel), plated nickel
and plated chromium (both on steel). In each case in a corrosive environment the one metal will become anodic and corrode, and in doing so protect the other metal as cathode. For example, zinc is anodic to iron and tin is cathodic to iron. This will then indicate what condition is to be expected with a plated object. (In some cases the plate will have corroded badly, in others the base metal.) Care must therefore be taken during any conservation process to avoid loss of either the plate or base metal.

The process used for iron and copper alloys (section 3.1 and 3.2), in particular, that based on inhibited citric acid, has been found satisfactory in removing corrosion products from plated metals. Thorough washing is important (wash solution depends on the metals involved) to remove chemicals that may remain between the two metal surfaces. The same applies to the removal of water.

Any of the lacquers, such as Frigilene, Incralac or Paraloid B-72, are suitable for coating a plated metal object. Waxes are not recommended owing to the problems of achieving good coverage of the crevices between the metals.
4. METAL RESTORATION

The techniques of metal restoration, as discussed earlier in section 2.2.6, cover welding, soldering, the fabrication of missing metal pieces, and the use of adhesives and consolidants. In this section an example will be given of the restoration of a pair of bronze candleholders with the use of adhesives (Figs. 17–20). The other metal restoration techniques listed above will not be discussed, as they are well known techniques relying on the skills of the metal worker.

The bronze candleholders (Japanese Edo Period, late 18th century) are each in the form of a crane holding a lotus blossom candle holder which fits into a socket in the crane's beak. The crane is standing on a tortoise. On one crane the bracket to support the candleholder is missing, and on the other a leg is broken. Fig. 17 shows the crane with the broken leg, the bracket in the beak of the crane is missing from the second crane.

The problem with the broken leg was, that in addition to being out of alignment, there was a gap of approximately 2 mm between the two pieces. Although it was possible to reposition the two pieces, this could not be done without exerting considerable vertical pressure because the whole object had been slightly twisted.
Fig. 17. Bronze candleholder in the form of a crane standing on a tortoise. A lotus blossom candleholder sits in a bracket held in the crane's beak, (Japanese Edo Period, late 18th century).

Figs. 18(a)/(b). Leg of crane, before and after restoration.
Fig. 19. A dental wax dam is formed around the bracket in order to obtain a silicone rubber mould.

Figs. 20(a)/(b). Head of the crane before and after the fitting of the new bracket.
when the leg was broken. This tension in the join meant that epoxy resin adhesives, using a very thin layer of adhesive, were not successful. It was decided not to pin the joint, so as to cause as little further mechanical damage as possible. The gap in the joint was filled using Araldite K58 Epoxy Putty (CIBA-Geigy). Equal parts of the resin and hardener were weighed, mixed together, and applied to the gap. In order to get good bonding to the metal surfaces it was necessary to use Araldite 5 Minute, 2 part Epoxy resin (CIBA-Geigy), again in a 50:50 mixture of resin and hardener. The putty was adhered into the gap, the break realigned, and then clamped for 24 hours. Finally, the gap fill was inpainted (which was easier than trying to tint the resin) using ivory black and raw umber pigments in Liquitex Matt Medium. Additional matting was achieved with the aid of fumed silica. Fig. 18 shows the break before and after restoration.

To obtain a new bracket for the second crane, a cast was made of the bracket from the first crane. A dam of dental wax was placed round the bracket and melted onto the metal surface, using a heated spatula (Fig. 19). A mold was made using Silastic ERTV Silicone Rubber (Dow-Corning) (10 parts of rubber to 1 part of curing agent). After setting, the wax dam was removed, and the mold carefully prised away from the bracket.

To provide a bracket with enough mechanical strength to support the candle holder, it was decided to use an epoxy resin for casting the new bracket. Araldite Epoxy Resin 956, plus hardener (5:1) was prepared and pigmented with the same pigments of ivory black and raw umber, matted with fumed silica, as were used for the beak. This provided a satisfactory cast of the bracket, which was then fixed into the beak of the crane using Araldite Epoxy Putty K58. The head of the crane, before and after the fabrication of the new bracket, is shown in Fig. 20. The result is a bracket that would support the candle holder but which was not distinguishable from the rest of the crane.

5. CONSERVATION OF OUTDOOR METAL OBJECTS

Objects are placed in an outdoor situation for a variety of reasons. They are either too large for indoor display, they need an outdoor environment for their setting such as with an open-air museum, they are working objects or sometimes mistakenly, they are considered immune to deterioration owing to their size or mass. The problems are that any object, inorganic or organic, if displayed or stored outdoors (and often such items are in a storage/display situation) will deteriorate much quicker than if in a stable environment, e.g., indoors, or even if sheltered under a roof. Such a shelter is better than exposure to the influence of sun, wind, rain, snow, and frost and the effects of air pollution and bird droppings, which can cause a lot of damage to objects. But shelters can be expensive, and it may therefore be necessary to display a number of objects outdoors. If this is done consciously, then deterioration can be kept to a minimum.

The most common metals in outdoor objects are iron and copper alloys. Used
in machinery, agricultural implements, motor vehicles and the like, they are also often associated with organic materials, such as wood, leather and canvas. Obviously, the conservation of the organic materials is as important as the metal components.

The major problems with metal objects is that when exposed, particularly to rain and air pollutants (including salts), a number of forms of corrosion occur which would not be a problem indoors [PEARSON 1985b].

Dissimilar metals in contact and in the presence of water will corrode owing to their galvanic couple. One becomes the anode (and corroding) and the other the cathode (being protected). In the iron-copper couple iron would corrode and in doing so would protect the copper.

Crevices or junctions and joints on the metal structure would tend to harbour water from rain or condensation. Here, differential aeration cells will be set up, with areas high in oxygen becoming cathodic, and deep inside the crevice, becoming anodic and corroding. By a similar process, the settling of particulate matter from air pollution or from dust can lead to pitting corrosion underneath the particles in the presence of moisture.

Air pollution itself can cause chemical attack, particularly in industrial environments. Sulphur oxides, with resultant sulphuric acid, are probably the biggest danger.

It is important, therefore, that all metal objects are not only treated for conservation purposes, but that they be protected against the above-mentioned forms of deterioration.

Some treatments for metal objects described in the previous sections can also be used for outdoor metal objects. However, as these are invariably large items, industrial type techniques are more common. For example, wire brushes, sand blasting and steam cleaning would be more common techniques to remove grease, dirt and corrosion products. The removal of grease, however, should be done with caution. Grease is an excellent protector of metal against corrosion, providing it is not too old. It may, in time, have oxidised, become hard and non-protective, and may also generate harmful deterioration products.

The use of sand blasting systems has been discussed in section 2.2.2. This will normally be carried out by contractors, and is best done away from the museum.

Advice will be required on the paint systems and other protective measures used for objects normally kept outdoors. Are the traditional lead-based primers, followed by an undercoat and then a topcoat, sufficient protection? The ethical aspect often has to be considered, i.e., trying to retain as much as possible of an original coating system with all its maintenance problems, compared with replacing it with a new system offering much better protection.

If and when a new system is required, advice from the senior chemist of a major paint manufacturing company is important to provide the best paint system for the metal(s) to be treated in the environment to which it will be subjected. Paint salesmen do not always have the technical know-how to provide the best in-
formation. The method of application of paint systems is important, and it may be cheaper in the long term to employ a professional rather than rely on untrained museum staff.

Following conservation, every outdoor object requires a maintenance schedule [PEARSON 1985b; GAYLE, LOOK and WAITE 1980]. It must be inspected on a regular basis, cleaned, and checked for deterioration. If it is a working object it may need to be “started up”, if this is museum policy.

Consideration must also be given to control of insects, mould growth, birds (if a nuisance) and rodents. Wooden components may need to be treated with a fungicide/insecticide, but the choice of treatment must take into account the fact that visitors may touch the object [TILBROOKE 1979].

Many metal items, such as vehicles, rest on wheels, and it is important that these are supported at the axles. In addition to taking weight off the wheel bearings and the tires—whether wood, wood/iron, or rubber—they also provide a means of installing an insect barrier (e.g., for termites) through the jacks that are used.

Metal objects should, wherever possible, never be placed directly on the ground, but separated to provide air space. Contact with the ground, in particular soil or grass, will lead to corrosion. If the object has to be placed on the ground then concrete pads are better than soil.

Objects on open exhibition are very susceptible to being touched or climbed on by the public. This may be intentional, e.g., children may be encouraged to climb on a vehicle, however, it will, in the long-term, create conservation problems, particularly if gravel surrounds the object, which, if picked up on shoes, can scratch the metal surface. These objects are also open to vandalism, so some form of security may be required.

It can be seen, therefore, that metal objects displayed or stored outdoors are a particular problem. They require good protection, in particular, as regards paint systems that are used initially to coat the object, or later for routine maintenance [GAYLE, LOOK and WAITE 1980; TILBROOKE 1979]. They will also required regular cleaning to remove atmospheric pollutants and damage caused by the public or vandals. Regular inspection and good security is essential to avoid serious loss or damage.

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Photographs of Figs. 1 and 2 were offered from the D.S.L.
APPENDIX 1

Inorganic Spot Tests for Metal Objects

The aim of these tests is to identify metal cations and the main anions associated with their scale corrosion products, by the use of semi-micro qualitative analysis. They have been developed from a number of sources by the Technical Officer, Conservation of Cultural Materials Program, Canberra College of Advanced Education.

1. Metal Ions (Cations)

Method A (Analysis using Merck Test Strips)*

1) Materials required
   Merck test strips are available for the following ions, Cu⁺/Cu²⁺, Co²⁺, Fe²⁺, Al³⁺, Ca²⁺, Ni²⁺, Zn²⁺, CrO₄²⁻, NO₃⁻, NO₂⁻, SO₃²⁻.
   Metal surfaces must be cleaned using acetone before commencing the test.

2) Tests
   All test strips may be applied directly to metal surfaces after being wetted with distilled water. Colour development (indicating metal presence) will be noted after about 20 seconds contact. However, so far it has been noted that:
   a) Zn²⁺ test strip will not function correctly when testing brasses. This is due to interference from Cu²⁺ and other ions.
   b) Colour development of the Ni²⁺ test strips is quite slow, with colour intensity somewhat lacking. For improved development, wet the strip with 0.1 M HCl and apply to the metal surface with a slight rubbing motion for about 20 seconds.

Ni²⁺ test strips can be used with the electrolysis technique used in Method B (see later), replacing the moistened filter paper with a test strip moistened with saturated NaCl solution. Electrolysis should be continued for approximately 5 seconds. Colour development will be:
   Ni²⁺: Pink/Red

The Ni²⁺ test strip can also be used to detect Fe²⁺, Cu²⁺ and Au²⁺ ions. The same procedure is followed and the colour development will be:
   Fe²⁺: Brown
   Cu²⁺: Green
   Au⁺: Yellow

Method B

1) Materials required
   - 9V battery
   - Leads with alligator clips
   - Metal tweezers
   - Filter paper cut into small wedge shapes
   - Disposable pipettes and bulbs
   - Specific chemicals mentioned for each test.

* MERCK, E., Frankfurter Str. 250, Postfach 4119, 6100 Dormstadt 1, Federal Republic of Germany.
2) Preparation
This method consists of applying a small voltage across the metal object to be tested, electrolytically removing a small sample onto a piece of filter paper moistened with an appropriate acid. The filter paper is then treated with a reagent that develops a distinctive colour if the metal is present.

A diagram of one possible configuration is shown below [Laver 1978]. Note that the positive terminal is connected to the metal (care must be taken not to scratch) and the negative terminal to the filter paper.

![Diagram](image)

**Fig. 21.** The electrolysis apparatus [Laver 1978].

Before any tests are commenced metal surfaces must be cleaned of dirt, grease and fingerprints, using acetone.

3) Tests

- **Nickel:** Soak filter paper in $1M$ HCl and electrolyse for approximately 15 seconds. Add 1 drop of Dimethylglyoxime in 1% Ethanol to paper. Red colour will indicate Ni$^{2+}$.

- **Chromium:** Soak filter paper in $0.5M$ HNO$_3$ and electrolyse for approximately 15 seconds. Add 1 drop saturated solution of Diphenylcarbazide in Ethanol. Violet colour will indicate Cr$^{2+}$.

- **Tin:** Soak filter paper in $1.0M$ HCl and electrolyse for approximately 30 seconds. Add 2 drops saturated (aq.) Cacotheline solution. Red/Purple colour indicates Sn$^{2+}$.

- **Aluminium:** Soak filter paper in $0.1M$ HCl and electrolyse for approximately 2 seconds. Add 1 drop of Alizarin S solution. Red colour indicates Al$^{3+}$.

- **Zinc:** Soak filter paper in $1M$ H$_2$SO$_4$ and electrolyse for approximately 5 seconds. Mix 1 drop of 10% (aq.) Ammonium Thiocyanate with 1 drop of 10% (aq.) Mercuric Chloride on a watch glass. Dip in filter paper and white needle-shaped crystals will form if zinc is present.

- **Copper:** Soak filter paper in $0.1M$ HCl and electrolyse for approximately 15 seconds. Add 1 drop of 0.1% Rubeanic Acid in Ethanol to paper. Green/Gray colour will indicate Cu$^{2+}$.

- **Iron:** Soak filter paper in $0.1M$ HCl and electrolyse for approximately 15 seconds. Add 2 drops of 5% (aq.) Potassium Ferricyanide solution. Blue colour will include Fe$^{2+}$/Fe$^{3+}$.

- **Lead:** Soak filter paper in $0.5M$ HNO$_3$ and electrolyse for approximately 5 seconds. Add 2 drops of 10% (aq.) Potassium Iodide solution to paper. Yellow colour will indicate Pb$^{2+}$.

- **Silver:** Soak filter paper in $0.1M$ HNO$_3$ and electrolyse for approximately 1 se-
cond. Add 1 drop of 0.5% p-Dimethylaminobenzylrhodamine solution in Ethanol to paper. Pink/Red colour will indicate Ag⁺. 10% w/w Dichromic Acid can also be used as the indicator reagent here. Dark red will indicate sterling silver. Bright blood red will indicate pure silver.

**Antimony:** Soak filter paper in 0.1M HCl, electrolyse for approximately 15 seconds. Add 1 drop of 0.01% (aq.) Rhodamine B solution to paper. Violet colour will indicate Sb³⁺.

**Gold:** Soak filter paper in NaCl (saturated solution in water). Electrolyse for approximately 15 seconds, some darkening will probably be evident if Cu is present. Leave the paper on the spot until slightly dried out so that Au is well into the paper. Dip into a SnCl₂/HCl mixture (20% SnCl₂ in 15% HCl). Au causes a black colour immediately with no interference from Cu or Ag.

2. **Non-Metallic Ions (Anions)**

If in solution, these salts can be rapidly identified by the spot tests described below. If as solids, the salts must first be dissolved.

- **Sulphate:** Dissolve the solid in 1M HNO₃. A white precipitate formed upon the addition of 10% Barium Chloride solution indicates SO₄²⁻.
- **Chloride:** Dissolve the solid in 1M HNO₃. A white precipitate formed upon the addition of 0.5M Silver Nitrate solution indicates Cl⁻.
- **Carbonate:** Carbonates are generally insoluble in water. Addition of a few drops of 1M HCl causes fizzing (evolution of CO₂), and dissolves the carbonate.
- **Sulphide:** Sulphides are generally insoluble in water. Digest a small sample in conc. HCl, add a little 0.1M CH₃COOH (acetic acid) and 10% Lead Acetate solution. A black precipitate indicates sulphides.