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The problem of protecting bronze in outdoor exposures

Abstract

This chapter defines the problem of protecting bronze art and ornamentation in outdoor exposures according to engineering, conservation, and conservation research points of view. The discussion includes a brief overview of atmospheric corrosion of bronze.

1.1. Introduction

Outdoor bronze sculpture and ornamentation are a seamless part of our urban landscape. Without the imposition of museum walls, these objects are a vital part of our everyday experience, subtly influencing the way we appreciate our artistic and cultural heritage. Hidden to the commuter and passerby, however, a daily micro-drama is being played out on the metal surface: materials struggling to maintain their identity against the forces of nature. And so the sustained presence of bronze sculpture and ornamentation in our environment is anything but effortless. In fact, the maintenance of outdoor bronze art and ornamentation requires an enormous amount of consideration and energy on the part of the caretakers of this heritage. It is to this effort that the present research is addressed.

According to surveys by the public organization SOS! (Save Outdoor Sculpture!), tens of thousands of outdoor bronze monuments in the United States are in need of attention [1]. This represents only a small portion of bronze sculpture and ornamentation on an international scale that require preservation. Besides vandalism and unintentional damage by the public, pollution in the environment, especially acid rain, has been linked to detrimental and disfiguring corrosion on bronzes globally [2,3,4,5,6,7]. That this poses a serious threat to our artistic patrimony is without question. The most common approach to these problems is to apply a coating, the most important class of which is clear, organic coatings. While many traditional coatings, such as wax, are adequate in certain situations, decreasing funding to institutions responsible for the maintenance of
outdoor sculpture instills a pressing need for new, low maintenance coating solutions.

The research presented in this dissertation approaches the problem of protective organic coatings for outdoor bronzes in terms of coating design and system failure. These concepts are considered within the framework of current practices and needs in the conservation field. In this study, new and old coating systems have been tested on various model substrates in simulated accelerated weathering and natural outdoor weathering conditions. The model samples were evaluated by visual and chemical means. Results of this research may lay the groundwork for field trials and optimization of some new coatings for practical use by conservators of outdoor sculpture. Ultimately, it is hoped that this work will be a guide to conservators in the development of new strategies for the protection of outdoor bronze sculpture and ornamentation.

1.2. The effect of outdoor environments on bronzes

By the third millennium BC it was discovered that addition of certain ores, specifically tin and arsenic, to naturally occurring copper not only hardens the metal, but minimizes the release of oxygen bubbles during casting and allows difficult castings to succeed. Stretching from the Bronze Age to the present, this amazing and valuable material has been associated not only with functional tools and vessels but with artwork. Due to developing metallurgical technology and changes in the availability of different metals over the centuries, many compositions of bronze alloys have historically been used to produce artwork. It is therefore difficult to classify bronze as one material, but bronzes do have significant properties in common, foremost of which is the predominance of copper—and the noble behavior of copper—in the alloy composition. In the world of art and ornamentation, besides relatively pure copper materials, common types of bronzes in the 19th century include copper-lead-tin-zinc alloys, and, increasingly in the 20th century, silicon bronze alloys. This study utilizes a copper-lead-tin-zinc bronze that is broadly representative of 19th century alloys.

It should be recognized that not only techniques of alloying and casting have changed over time, but also the impact of outdoor exposure for bronze objects has changed dramatically since the industrial revolution. The major factors in environmental exposure before this era consisted of oxygen, water, and, near oceans, chloride salts. Exposure of copper alloys to air immediately results in the formation of an oxide layer. Alloying alters the oxidation rate of copper, generally slowing it in the case of tin addition, and speeding up oxidation in the case of nickel addition. A slow-growing, natural oxide film is normally thin, smooth, and compact, and may protect the metal surface to a fair degree from non-aggressive environments. The oxidized bronze surface may appear golden to reddish to blackish brown, depending on the alloy composition, and is commonly referred to in artistic circles as a patina. Green copper carbonate minerals have only rarely been reported in patinas from natural atmospheric exposure. Exposure to chlorides, on the other hand, readily causes the localized formation of various
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green colored copper minerals and is known to have a marked destabilizing effect on copper alloy patinas [8,9,10,11,12,13,14,15].

Since the advent of urban-industrial environments, outdoor exposure of materials has entailed contact with corrosive pollutants in the atmosphere, such as sulfur dioxide, a by-product of burning of fossil fuels. In recent decades, the urban environment has been associated with so-called acid rain, a precipitation cocktail of sulfates, nitrogen oxides, and ozone, as well as more minor quantities of ammonia, ammonium sulfate, other organics, and soot [7,16]. Records indicate that sulfur dioxide emissions in Europe and the United States peaked in the 1970s and have since been declining; in Europe nitrates and ozone concentration continue to increase, while a general decrease in these emissions has occurred in the United States since the 1980s [16,17]. In general, however, levels of SO₂ and NOₓ emissions remain high today throughout the world, and there are indications that the current political climate in the United States will reverse this trend and allow increased emissions again. Chlorides have also been found to be a significant contaminant in urban environments, a major source of them being the steadily increasing winter salting practices [17,18].

Although the complex reaction mechanisms between metal surfaces and acid rain remain incompletely understood, the basics of this process may be summarized. Acidity is introduced to the metal/patina surface via condensation and/or rain deposition, forming a layer of water that contains conductive salts, including corrosive species. It is also known that hydrolysis and oxidation of SO₂ and NOₓ occur in the atmosphere, yielding sulfuric and nitric acids directly on the bronze surface. The acidity of modern precipitation is normally less than pH 4.0. As the precipitation brew evaporates on the metal surface and from within the patina, the mixture becomes increasingly concentrated, and, by extension, increasingly acidic. In combination with oxidizing pollutants, the acid precipitation induces corrosion at significant rates at the metal surface [19]. During extended wetting/washing cycles and wind exposure, there is a high potential for dissolution of the metal along with erosion, dissolution, and migration of select components of the patina. New corrosion minerals are precipitated in pits, on the surface, and underneath existing minerals. In this way a patina that is generally porous, permeable, and soluble to different degrees in the environment forms and reforms. This process thus effectively disarms the metal’s natural ability to form a protective mineral layer [5,7,20,21].

The question of whether patinas are protective is complex. The corrodibility of the metal surface in any one environment depends upon multiple factors, including alloy composition, manufacture and exposure history. Compared to copper roof material, Weil relates the apparently greater corrodibility of many cast bronze monuments directly to a cast vs. a wrought structure, rather than to alloying [21]. In particular, the quality of the bronze casting is of crucial importance, since inhomogeneous and porous casting greatly increases susceptibility to corrosion. The patinated surface itself introduces additional factors into the complex electrochemistry of environmental interactions. These factors include the chemical stability, solubility, and hygroscopic behavior of the patina salts in the environment, as well as the physical structure of the patina.
Important physical properties of the patina layer include the density, porosity, homogeneity, and coverage [3,5,17,22].

Studies and general observations have established that bronze corrosion patinas created by acid rain are not only disfiguring in terms of loss of detail and a unified surface, but are also unstable. The dominant corrosion minerals found in the patinas of outdoor copper and its alloys are: cuprous oxide (cuprite); copper hydroxy sulfates, primarily brochantite and antlerite; and copper hydroxy chlorides, primarily paratacamite and atacamite [18,22]. While the copper sulfates render bronze surfaces light green overall or in patches, complex cycles of wind, rain washing, and particulate deposition often result in unsightly black crusting and streaking over the surface. The existence of black copper sulfides in the dark crusts has not been established, although it is often assumed.

The formation of raised black areas adjacent to green areas on outdoor bronzes suggests to some corrosion scientists that carbonaceous and other particulate material in the black areas play a crucial role in terms of creating local cathodic protection, which accelerates dissolution and corrosion in the green areas [2,17,21]. A study of bronze corrosion on the Capitoline Hill in Rome showed that there was a large difference in the relatively low corrosion rates observed in compact green, green-brown, or black areas on bronzes vs. relatively high rates in porous, pale white-green areas. These researchers concluded that the pale green corrosion crust does not significantly contribute to the corrosion resistance of metal [23]. In addition, chloride corrosion is most often visible as severe light green pitting or pockmarking overall. Corrosion rates are normally quite high in this type of pitting corrosion. Chloride salt layers have also been shown to exist underneath the sulfate patina [20].

The manufacture of bronze artworks since the 19th century has usually included the production of an artificial patina on the metal surface through the application of chemicals to obtain certain coloristic effects [13,24]. These mineral patinas vary greatly in nature, have generally not been investigated, and may or may not have protective qualities. For more detailed discussions of bronze corrosion in outdoor settings, see excellent treatments of this subject in the literature [2,5,16,17,18,22,25].

1.3. The engineering problem

The problem of bronze and copper alloy corrosion in the outdoor environment is at base defined by the electrochemical conversion of metal into metal ions. For an engineer, the problem is fundamentally a metallurgical one: how to limit the rate of overall and localized corrosion of the pure metal, whether this involves bridge ornamentation, a roof, or a car. That is, corrosion is primarily a structural problem, as in the case of intergranular corrosion of metals, which weakens the integral fabric of the material. Corrosion of metal surfaces, particularly in the form of pitting, has structural as well as aesthetic repercussions.
Aesthetic issues have importance commercially for consumer goods like cars, but these issues are mostly limited to maintaining a new appearance.

One approach to achieving corrosion resistance in outdoor environments is through protective organic coatings. The industrial importance of protective coatings has given rise to the field of coating science, to which the paint and automotive industries have devoted much energy. The following is a brief outline of some principles and current thinking in this field [17,26,27,28,29,30,31].

### 1.3.1. Surface preparation and coating adhesion

It is an axiom in the coatings industry that good surface preparation is the essential starting point for good coating performance. This means a clean surface, as well as one with good wetting and adhesive properties for the intended coating. It is well known that contaminants such as oil, dirt, or corrosion products on the metal surface compromise coating adhesion. In addition, both dirt and corrosion minerals on the metal surface are hygroscopic. Residual corrosion salts at a coating/metal interface are an important source of soluble salts in solutions that may form in this region once moisture penetrates through the coating; the salts may then initiate corrosion beneath the coating. Scrupulous washing and degreasing may remove these contaminants; in cases of corroded surfaces, industrial practice recommends removal of a layer of metal through an abrasive procedure such as sandblasting.

In order to achieve sufficient wetting during application of a coating, the surface tension of the coating must be lower than that of the metal surface. Cleaning of the metal raises the surface tension so that good wetting can occur. Good wetting leads to good contact and spreading, resulting in superior adhesion and film quality. Roughening of the surface increases surface area and may improve adhesion of the coating, although a too-rough surface may leave voids underneath a coating with imperfect wetting characteristics [32]. Blasting techniques employed for cleaning off corrosion layers also have the potential to leave behind stresses and deformations in the metal to various degrees. These stresses may also induce corrosion. As always, a balance must be struck. Chemical means of surface preparation also exist and include: etching with acidic mediums; reaction with chemicals such as chromates and phosphates, the salts of which may passivate the surface; cathodic protection by a zinc primer film; treatment with adhesion promoters such as silanes; and treatment with corrosion inhibitors such as benzotriazole. These are all important industrial practices.

Good adhesion of a coating to the metal is of course a fundamental aspect of protection of the underlying metal surface from contact with corrosive media. Adhesion has often been differentiated as dry or wet adhesion [33,34]. Dry adhesion may be defined as a net phenomenon, equal to the force necessary to detach a defined area of coating under standard room conditions. Wet adhesion may be defined more particularly as the force necessary for water to displace the coating at the metal interface. This displacement is dependent on the dominant type of bonding here, i.e., strong chemical bonding or relatively weak physical bonding. Poor wet adhesion is significant in all instances of moisture, oxygen, and
salt penetration to the metal/coating interface. This is, of course, the case with all organic coatings, which are permeable to water and oxygen to some degree, and are imperfect structures that may become damaged or deteriorated [35]. It should be remembered that although we can attempt to optimize adhesion in a system, chance events that occur during coating application, such as dirt deposition, air bubble formation, or change in humidity, can compromise good adhesion as well as affect measured adhesion values.

The displacement forces involved in wet adhesion are difficult to measure directly. Dry adhesion is thus a starting point for assessment of an intact coating system with the potential for corrosion protection. Adhesion is also dynamic, i.e., may change over time depending upon extraneous forces within the system, such as stress and the presence of moisture. Measurement of dry adhesion after weathering provides an indication of disruption of coating to metal adhesive forces that may have taken place, and thus indirectly reflects wet adhesion properties of a system [36].

1.3.2. Coating quality and durability

Good coating quality, i.e., the relative lack of defects, is another essential building block in the corrosion protection of a coating system. Coating defects not only affect aesthetic appearance, but also mitigate performance in aggressive environments. This is obvious in the case of gross defects, such as bubble holes and cracks. Another clear example is pinholing, a common defect that may arise from solvent popping/air entrapment during coating application. These small air holes allow air and moisture ingress and may result in local corrosion pits. The defect commonly known as orange peel is a phenomenon arising from poor flow compared to relatively fast solvent evaporation characteristics. This sets up tensions that result in a bumpy surface upon drying, which may be clearly seen in reflected light. The orange peel surface translates to thickness variation on a micro-scale. This fluctuation has important bearing on performance since it will set up local differences in permeability as well as in electrochemical and osmotic pressure gradients. Other common coating defects include seeds and cratering: little wells and dimples created by specks of dust and other contaminants on the surface during coating application. These present similar problems in terms of local thickness fluctuation [27].

In order to achieve good coating quality, scrupulous practices and technical skill are of utmost importance. Nevertheless, normal spray and brush application of coatings inevitably results in a range of defects. Multiple, thin layers of coatings, applied at right angles if possible, are usually recommended to offset defects. A thin wax topcoat may be quite beneficial in this respect, while not appreciably adding to overall thickness. However, operators must be careful that layers do not exaggerate thickness variations nor leave residues that can lead to interlayer delamination. Layering may also aggravate residual stresses built up during film formation, and may be associated with adhesion loss and/or cracking and crazing [37,38]. It is interesting to speculate whether orange peel may also be associated with stress-related loss of adhesion or cohesion.
Assuming that a coating is applied in an optimal manner, coatings vary greatly in terms of their inherent protective properties and stability in outdoor environments. Several coating properties that are desirable for good outdoor durability include: 1) good ultraviolet light (UV) resistance, 2) sufficient flexibility to withstand thermal stresses, 3) chemical compatibility with the metal surface in order to achieve good adhesion and good chemical resistance to the environment, and 4) relatively low oxygen and water permeability. In the first case, superior UV protection may be provided foremost by pigments; for clear coatings, UV protection is provided by innate chemical saturation as well as UV absorbers and hindered amine light stabilizers. Minimum flexibility is not a well defined quantity, but some flexibility should be built into the chemical and/or physical structure of coatings in order to avoid stress build up during application and service, which may result in debonding and cracking. Chemical compatibility with the metal may be promoted, for example, by the inclusion of polar hydroxyl and carboxyl groups in a polymer that are attracted to the oxides and hydroxides on the metal surface. These same groups may increase water permeability, however, through a solvency effect. Low permeability, which is perhaps most important, is best achieved in a coating by high density, such as in crosslinked polymers. Ideally, crosslink density should be as homogeneous as possible. However, very high crosslink density may also contribute to stress buildup in the film.

Unfortunately, it is not easy or even possible to engineer all desirable qualities into one coating material. It is more feasible to design a coating system that combines desirable qualities, such as in 3-part systems where the primer coating promotes good adhesion to the metal, the middle coat provides durability and other desired qualities, and a top coat aids in low permeability [39]. This common industrial approach was utilized in the research design of the National Gallery of Art’s project.

1.4. The conservation problem: current attitudes, practices, and research

1.4.1. Aesthetics vs. protection

Every outdoor bronze work of art is a unique case scenario, with its own history in terms of materials, manufacture, and outdoor exposure. Artists, art historians, connoisseurs, and conservators have developed keen sensitivity to the uniqueness of each work of art, and yet no consensus exists about what limits are acceptable for the changes in appearance that inevitably occur in outdoor settings. Here we enter the domain of aesthetics, where the ground shifts with changing tastes in different societies and different eras. This is not the territory of the scientist or, theoretically, the conservator, although decisions regarding conservation treatments that intimately involve aesthetics inevitably fall to the conservator. Ideally, treatment and aesthetic decisions for works of art go hand in hand, and should be arrived at jointly by conservators, curators, the artist (if alive),
and art custodians. This does happen, but a lack of consensus about the aesthetics of outdoor sculpture continues to fuel controversy surrounding treatment options [40].

A camp of opinion still exists that supports non-intervention. This is a disputed approach, especially given the obvious effects of man-made pollution on copper alloys. In many cases, the entire form of an artwork may become obscured under a veil of contrasting streaks and dots as corrosion progresses in outdoor environments. In a sense, this is nature’s graffiti, clearly overwriting the artist’s intent. Indeed, in the vast majority of these cases, such changes, which may penetrate quite deeply into the metal, are completely unforeseen by the artist.

In less aggressive environmental conditions, the overall surface texture and coloration of a work may corrode evenly, and change may be viewed in some circles as an acceptable course of events. On the other hand, an historical view of outdoor bronzes, such as that presented by P.D. Weil, asserts that any value ascribed to matte green, mineralized outdoor bronze surfaces is misplaced, unless that surface was purposely created by an artist, as it may be on some modern sculptures. Weil maintains that, artistically and aesthetically, the original lustrous, semi-translucent browns and green-browns that are natural to bronzes should be prized and protected by proper maintenance [41]. Furthermore, we must consider changes in appearance that inevitably result from protective treatments themselves, such as color changes from repatination, darkening from saturating coatings, and shininess from some synthetic polymer coatings.

Realistically, the rates of loss suffered by bronzes in outdoor urban environments in terms of surface texture and detail are unacceptable by any standards. This is because exposure to even mildly polluted outdoor urban environments subjects these materials to chemical and electrochemical instability, i.e., progressive deterioration. Therefore, the conservation approach to metal objects in outdoor exposures should more properly be based on a different set of criteria than that relied upon for objects protected in indoor museums. Traditional notions of non-invasive or minimal intervention may have to be abandoned, or in any case redefined, if objects are to be properly protected and preserved.

Ultimately, decisions concerning surface preparation, coating choice, and maintenance planning will be based on subjective as well as objective criteria. With curatorial and scientific input, conservators must find a difficult middle ground of an aesthetically acceptable option that does not compromise the object in terms of stability in the harsh setting of outdoor urban environments. It seems obvious that it is unrealistic to expect that one solution may exist to universally satisfy the aesthetic requirements and protective function of coatings for outdoor bronzes. Yet, these expectations are often encountered in the field. The coupling of corrosion science, polymer science, and interfacial chemistry, along with aesthetics, renders the subject of coatings for outdoor bronze sculpture and ornamentation complex and difficult to approach for conservators and scientists alike. Nevertheless, it is hoped that a combined approach may help practitioners to identify and reach a better understanding of the relative importance of various factors in outdoor coating appearance and durability appropriate to individual situations.
1.4.2. Current methods in the treatment of outdoor bronze

Conservation applications may be distinguished from industrial applications by aesthetic considerations, as discussed above, and perhaps more importantly by physical and chemical differences. While industrial coatings are designed for fresh metal surfaces that are stripped, sandblasted, and primed, the surfaces of artworks and historical objects generally cannot be prepared in this fashion without unacceptable damage. Thus, conservation applications are handicapped from the outset by typically requiring coatings to perform on inhomogeneous, contaminated and naturally or artificially corroded surfaces.

Because of this handicap, it is difficult to draw up a list of desirable properties of coatings for outdoor bronzes, since the requirements vary with each individual work of art. In general, coatings should be durable within a proposed maintenance period, and should have a viable and safe method for removal once they start to fail, i.e., must be reversible by some method. Although it is desirable not to alter the original surface of an object, this is a controversial point, since the original surface is not strictly retrievable once oxidation and corrosion occur. In order to retain---or regain---original appearance and surface detail as much as possible, clear coatings are usually applied relatively thinly; they should thus be UV stable and capable of providing protection well below the usual manufacturer's recommended thickness. It should be noted that pigmented coatings are increasingly tolerated for use over existing corrosion crusts; for this application, conservators most often prefer to tint clear coatings themselves. The following discussion outlines current approaches and methods in the conservation of outdoor bronze [41,42,43].

1.4.2.1. Cleaning

Approaches to cleaning already weathered objects before coating vary greatly among practitioners, both historically and geographically. This stems from available resources and differing aesthetic approaches, as well as an incomplete understanding of the relative stability of the surface and corrosion patina, both before and after treatments. In the United States, the most common method for cleaning weathered bronze and copper alloys entails washing with an aqueous detergent, usually followed by light to heavy scrubbing with bristle brushes or nylon pads to remove loose corrosion, plus degreasing in an organic solvent. Steam cleaning and/or solvent cleaning are often necessary to remove old wax and other organic coatings, which may be deeply embedded.

More aggressive cleaning is also common and may include abrasion with bronze wool or a form of air-abrasive blasting to remove all or a portion of the corrosion patina [44]. One blasting medium currently favored by North American professionals is ground walnut shells. This method is usually employed so that the loose and pale green corrosion are removed, leaving behind a dark green mineral surface [45]. Other blasting media in use in similar manners include low- to high-pressure water [46], ground maize, and wheat starch. Less favored at this time, but still in use internationally, are low pressure, fine mesh glass beads, which are normally used to clean down to the metal surface [47]. Other media that have been
proposed for blasting but have found little application and development include CO\textsubscript{2}, ice blasting, plastic beads, and baking soda [47,48]. The use of poultices and alkali cleaning agents to remove old green and black patinas has also been reported [49]. Recently, reports and studies of laser cleaning of corroded bronze may be found in the literature [50].

After cleaning procedures, the surface is often re-colored through application of chemicals, i.e., the work is repatinated, as previously mentioned. It is known, for example, that application of an ammonium sulfide solution to an existing green patina adjusts the color to a darker, more yellow-brown. Potassium permanganate, applied with heat, turns a green patina to dark brown or even black. These techniques chemically alter the surface; they have arisen out of foundry practices for the most part, and have not been examined as a chemical component of the coating system.

1.4.2.2. Coating

Coating technologies in current use in conservation have generally been borrowed from traditional and industrial applications without accompanying research into adaptation and optimization of materials and methods. There is, however, well-voiced accord among conservators that these materials and techniques often fail to meet the full range of requirements and conditions encountered in the field.

Traditional coatings that continue to be popular for use on outdoor bronzes include: (1) oils, such as lemon oil, paraffin oil, linseed oil and castor oil; and (2) tinted or clear natural waxes, such as carnauba and beeswax mixtures [51]. These types of coating treatments easily saturate existing patinas, causing darkening. Drying oils are reported to last up to one year and are increasingly insoluble with age. Waxes require frequent maintenance, ideally about every six months, and vary widely in makeup and formulation. Commercial paste waxes favored on outdoor sculpture, such as Butcher’s Paste Wax, are basically natural wax mixtures with high carnauba content and some synthetic wax and solvent added. Carnauba is a vegetable wax that imparts desirable hardness and luster to the wax. The natural waxes, particularly animal waxes, may contain some free acids which can potentially attack the metal surface, and are also subject to acid hydrolysis at the ester group [18,52,53].

Many wax recipes favored by professional conservators in North America and elsewhere since the 1980s are based on microcrystalline waxes. These synthetic waxes are straight chain, cyclic, and branched products that are refined from petroleum. The small crystal structure inherent in these materials allows the wax to approach an amorphous state. Individual conservators often make up their own wax formulation based on microcrystalline wax, and typically mix in other synthetic wax ingredients, such as polyethylene wax, to achieve a relatively high melting point while retaining good application properties.

Typically, wax coatings are either brushed or sprayed on and buffed. In either case, the wax may be applied either hot, i.e., after heating of the metal surface, or cold. Hot waxing allows the wax to penetrate more deeply into the
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surface, especially in cases of high porosity or existing patinas. In both cases, but particularly hot waxing, conservators have ample experience that shows wax coatings are not entirely reversible [54,55,56]. Wax residue is inevitably left behind to some degree, and complicates future treatments that are incompatible with wax. This has also been demonstrated in some analytical studies [18,52]. However, waxes remain the coatings of choice in many situations. This is due in large part to their accessibility and ease of use. While waxing application is often perceived to require only minimal training, this is also a controversial point. Adding pigments to wax, particularly earth browns, is a very common practice, mainly for aesthetic reasons.

Cellulose nitrate, sold as an Agateen product, continues to have some popularity although it has been commonly observed to have poor outdoor durability. By far the most widely used modern coating material on outdoor bronzes is an acrylic lacquer coating called Incralac®.* The International Copper Research Association (INCRA) developed this unpatented coating in 1964 for general use on copper alloys. It is also common to use pigmented acrylic inpaints in conjunction with acrylic coatings to unify color variations in an existing corrosion patina [57].

Incralac has been reported to generally last two to three years on outdoor bronzes, and up to nine years with topcoats of wax and regular maintenance [58,59]. The most common problem associated with Incralac in normal application is orange peel [60]. The shiny appearance of Incralac, which is often felt to be undesirable, can be moderated by the addition of matting agents and/or wax topcoats. Other problems commonly noted with Incralac may include eventual embrittlement of the film, resulting in delamination and spalling.

Of great concern with Incralac are inconsistent reports of difficulty with its removal over time. There has been one report of yellowing and crosslinking of an Incralac film over a gilded bronze statue [61]. However, many conservators say they have not experienced this problem. Related to this perceived problem, conservation professionals have sometimes voiced concern about batch inconsistency. It is unclear whether scattered reports of reversibility problems with Incralac coatings are inherent in the polymer or are related to particular conditions of its use, such as application over certain artificial patinas, inclusion of pigments in the coating, and use over other metals such as gold or iron. This will be explored during further discussions, particularly in Chapter 5.

There is one final point of consensus among conservation professionals: the need for adequate maintenance planning along with any treatment of outdoor bronzes [42]. The lack of planning and funding in place or earmarked for future maintenance may well dictate the type of coating that is appropriate for consideration. In addition, the inconsistent hiring of professionals and workers to maintain an individual work may compromise adequate coating maintenance. There is a great need in this field to educate local government appointees or hired architectural firms, who are often responsible for decisions about maintenance.

* Hereafter referred to simply as Incralac.
regarding the importance of having local advisory committees with conservators to aid in planning of care for outdoor monuments. Such committees are necessary also to ensure that proper bidding and hiring procedures are adhered to, so that well trained professionals with proper credentials are given the responsibility to treat outdoor works, which is often not the case.

1.5. The research problem

1.5.1. History of the National Gallery of Art research

In November 1994, in preparation for launching this research project, relevant issues and conditions governing the conservation application of protective coatings for outdoor sculpture were brought into focus at an international meeting organized by the National Gallery of Art in Washington, DC. The meeting included conservators, scientists, and representatives of Save Outdoor Sculpture! (SOS!). Several issues were highlighted in this forum, as well as in subsequent consultations with leading figures in the fields of outdoor sculpture conservation, corrosion, and coating science.

Themes that echoed throughout these discussions may be summarized as follows. While high maintenance coatings such as annually maintained waxes are reasonably successful in many applications, there exists a very real need to develop low maintenance coatings, i.e., coatings with improved durability and corrosion protection. Furthermore, volatile organic compounds (VOC) laws, Occupational Safety and Health Administration (OSHA) restrictions on solvent use, and safety issues of public exposure to harmful substances, increasingly affect conservation treatments, especially in terms of the removal of old coatings. It is thus worthwhile to look to industry for new, more durable coatings or coating systems. It is also important to devise a method for testing of coatings that has general validity for outdoor sculpture. It was generally acknowledged that the limited research on coatings for outdoor metal sculpture and ornamentation has been inconclusive and gives little basis for forming coating strategies.

At the same time, continued research into wax and acrylic resin coatings such as Incralac is valuable to better understand the necessary conditions for their optimization. These common coatings remain the standards against which new coatings can be assessed. It is clear that evaluation of coatings prior to this research project has most often been based on visual inspection of samples following accelerated testing, so that reasons for coatings failures are unknown.

1.5.2. Aims and design of the National Gallery of Art research

Research priorities and problems were identified from the above discussions and from a review of current literature. The ultimate goal of the National Gallery's research project was to impartially evaluate a series of model systems and to develop recommendations for better coatings and coating methods
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based on a materials science approach. To this end, the investigation aimed at identifying reasons why protective organic coatings work and fail on pristine and patinated bronze surfaces, as well as designing improved coating systems for possible trial in the field. The study paid particular attention to the interplay of adhesion, thickness, coating quality, and pretreatment with the corrosion inhibitor BTA in overall performance. Other factors, such as coating composition, were also considered.

With the aim of identifying and testing new coating systems with high performance potential for the conservation of outdoor bronzes, both old and new materials, and issues of surface preparation and removability were considered. The specific selection of coatings and substrates arose from the belief that the successful development of new coating strategies in conservation will ultimately arise from a tailored design approach that includes the combination of materials into one coating system to achieve desired properties, and the selection of materials based on an understanding of physical and chemical interactions between the particular bronze substrate at hand and the selected coating. Therefore, different types of model coatings were chosen, and each was varied by surface preparations, additives and combination with other coatings. The different coating systems were then examined on different types of copper alloy substrates.

The research project was divided into two phases. In Phase I [62], a total of twenty-nine coating systems were weathered on two types of substrates: polished, cast bronze and 50-year-old copper roof. These are referred to throughout as “Phase I samples.” In Phase II [63], five of the coating systems deemed most viable were chosen for further study in a new round of weathering on an expanded range of substrates (“Phase II samples”). Methods used in this phase sought to repeat as well as to clarify results of Phase I. Weathering in Phases I and II was both natural, on the roof of the National Gallery of Art, and accelerated in the laboratory using UV exposure and an acid rain-type solution, coupled with cyclic, broad range exposures of temperature and humidity. This type of accelerated weathering was modeled on methods used in the automotive industry. Experimental details and results are presented for each phase of the research in their respective chapters.

The results described in the following chapters provide information which may help to select and tailor real coating systems, as well as roughly predict their relative performance. In particular, measurements of thickness and adhesion properties of the samples provide useful data, and warnings, about coating properties and imperfections resulting from application methods. Broad correlation of these results with visual and chemical analyses of bulk coatings and a variety of interfacial surfaces from weathered, model coating systems provides insight into the complex mechanisms involved in coating failure on outdoor bronzes.

1.5.2.1. Choice of substrate

No one substrate can represent a general situation encountered in outdoor bronze conservation. This is true in terms of the metal alloy composition, as
discussed above, as well as its manufacture and condition. For experimental purposes, however, it is of utmost importance to limit and define important variables that occur in the field as much as possible. For this reason, model systems must be designed that offer reasonable correlation to the actual world as well as enough control over variables to allow conclusions to be made from the study.

The model systems designed for use in Phase I of the study consisted of two types of substrates, which were chosen to represent typical and, at the same time, extremes of surface conditions. One model substrate was a polished, cast bronze alloy of Cu (85%), Pb (5%), Sn (5%), Zn (5%). This alloy composition is fairly representative of 19th century bronze alloys and is a good general example of bronze as encountered in monuments found in North America [18]. The substrate was cast in a mould in order to reproduce a normal level of material stresses and microstructure characteristics. This type of manufacture carries a high degree of imperfections which could not be eliminated, such as a certain level of porosity. Samples, which appeared extraordinarily porous were rejected, but due to the cost of the bronze, most material was utilized in the study, imperfections included. The relatively large size of the samples allowed averaging of results across the surfaces.

The bronze plaques were polished to mirror finish in the foundry. Although this is a less typical finish for outdoor monuments, the polished surface offered certain experimental advantages. First, the polished surface allowed an even base from which to judge the coating appearance and performance. Second, this surface preparation allowed coating thickness measurement with reasonable accuracy, as well as the possibility of adhesion testing and delamination for interfacial examination. A polished surface is probably the least forgiving in terms of coating application and performance, since adhesion is difficult and initial corrosion potential is high. In the field, these disadvantages are in fact often encountered. Experimentally, these are aids to quicker differentiation of coating performance.

The copper roof substrate was chosen as an excellent example of a natural, brochantite patina. These patinas cannot be reproduced exactly in a laboratory, either compositionally or morphologically, but are very similar to those formed on bronzes in terms of the corrosion products and impurities [22]. In addition, the patina formed on pure copper is relatively even, which is necessary for experimental purposes.

In Phase II, this repertoire of substrates was expanded to include an artificially patinated cast bronze, and a walnut shell-blasted copper roof patina. The chemical patina was chosen to represent a typical foundry patina. The cleaned copper roof patina was included as a typical substrate produced by conservation treatment as favored at the present time. By studying a small number of coatings on four representative substrates, Phase II of the research focused on the importance of substrate preparation and substrate composition in the choice of a protective coating.
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1.5.2.2. Choice of coatings

In addition to coating materials in current use, new materials that appeared to meet general conservation criteria were chosen for study. Both thermoset and thermoplastic polymeric materials were considered, since mechanical means of coating removal remain viable, if underdeveloped, options for coatings that cannot be dissolved. Wax and Incralac coatings included in the study serve as benchmarks, and were varied with different surface preparations in order to test their effect. The wax coating chosen for this study is broadly representative of microcrystalline wax preparations that are used by conservators. This choice was also based on results of a preliminary study by Stromberg, which indicated that two microcrystalline wax mixtures typically used in the United States had superior performance characteristics in outdoor weathering on bronze compared to two natural wax mixtures [64]. The wax was also used as a topcoat in some systems in order to gauge its effect on overall performance and aesthetic qualities. Topcoats of wax are typically used over Incralac.

New model coating systems were designed according to coatings industry principles of three-part systems, in which an adhesion-promoting layer is first applied, followed by a main and topcoat. The design of coating systems for outdoor bronzes with optimal adhesion characteristics to the bronze/corrosion patina substrate was considered essential for maximizing the protection a coating can afford. The main coat of model systems was chosen with consideration of impermeability, durability, removability, and appropriate physical and aesthetic properties. Coupling agents, corrosion inhibitors, such as benzotriazole, and other appropriate materials were considered for the adhesion-promoting layer.

1.6. Conclusion

It should be recognized that a “safe” coating choice for all outdoor bronze situations will necessarily remain the elusive wish of conservators and caretakers of art. A more realistic approach to the complex problem of protecting outdoor bronzes should include a basic understanding of the complexity of environmental and metallurgical phenomena in aggressive chemical environments, coupled with thought, expertise, research, and, above all, decision-making appropriate for each individual work of art. It is hoped that the research methodology presented here will serve as an aid in understanding and pinpointing “weak links” in coated bronze systems in outdoor exposures, and thus in making informed decisions about appropriate coating strategies.
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