BronzeShield™

A Durable, Selectively Removable Clearcoat for the Protection of Bronze

TECHNICAL BULLETIN

MATERIAL DEVELOPMENT

Summary

BronzeShield™ was formulated to protect outdoor sculptures with durability and easy removability as key priorities.

Bronze is especially susceptible to deterioration caused by atmospheric corrosion. Therefore, delaying corrosion is one of the most important aspects of surface preservation. To do that, barrier coatings are often used.

The development of a selectively removable coating for the protection of bronze has been a focus of research at North Dakota State University's Department of Coatings and Polymeric Materials since 1999 and has resulted in the invention of a new polymer.[1,2,3]

Elinor Specialty Coatings licensed this patent-pending technology and further developed the polymer to produce BronzeShield™ in 2011.[4] Through this research, Elinor developed a modified polyester-urethane clear coat that is both protective and removable while maintaining rigorous environmental standards well below stringent California low-VOC laws.

A zero-VOC non-toxic remover was also formulated to selectively remove the clear BronzeShield™ without damaging the bronze surface or patina.

This combination coating-remover eliminates the need for harmful solvents (e.g. Toluene or Xylenes) or aggressive physical/mechanical means (e.g. sandblasting or wire brushing).

Product development timeline:

1999-2004: Laboratory development at NDSU focused on polymer synthesis by Shedlosky, Bierwagen, Webster and Houvinen

2004-2010: Technology dormant

2010-2011: Elinor Specialty Coatings starts laboratory testing to evaluate feasibility and testing to downselect material candidates

2011-2012: BronzeShield™ formulation, scale up and pre-production runs

2012-2013: Conservators/end users evaluation for feedback gathering ("Field tests")

2013: Commercial sales

Motivation for Product Development: Bronze Sculptures as Substrates

When sculptures are placed outdoors, they take on an integral place in our surroundings. When taken outside museum walls, sculptures become accessible to the public. However, the sculptures are also exposed to numerous pollutants and hostile environments. For the most part, outdoor sculptures are left to exist as best they can in their environment. Upkeep of outdoor sculpture is often difficult as funds for maintenance are limited and access to the sculpture may be difficult.

Corrosion is often accepted by those who do not understand its consequences. Outdoor sculptures exposed to chemical pollution, in fact, suffer irrevocable changes from corrosion. This corrosion can result in the loss of the original patina, and prolonged deterioration results in the loss of sculptural detail. Although it is impossible to completely stop the deterioration of an outdoor sculpture, conservation measures can significantly prolong its life. Coatings are often used to help protect bronzes from outdoor corrosion.

For corrosion to occur, the copper ions need to migrate through the cuprite layer. The corrosion resistance of the copper alloys is improved when the ionic conductivity of the layer is reduced with divalent or trivalent cations. With the addition of aluminum, zinc, tin and nickel to a copper alloy, the corrosion film becomes doped and the corrosion rate decreases.[5,6]

Typically, copper and its alloys corrode at negligible rates in unpolluted air and water because they form a protective cuprite (Cu_2O) layer when exposed to oxygen. The copper oxide patina is virtually insoluble in water and, thus, provides good protection. However, the pollution of the industrial revolution changed the way outdoor copper reacts with the environment. When modern acidic conditions occur, the copper metal will be attacked and the destructive action of the environment occurs by an electrolytic reaction.

The ideal coating for the preservation of bronze sculpture needs to be durable to protect the underlying metal surface from outdoor weathering for a long period of time while it remains removable without the need of damaging or changing the visible appearance of the sculpture when the time for maintenance comes.

The ethics of conservation appears to run counter to normal coating design. For a coating scientist, *durable* means coatings with good adhesion, usually cross-linked, and this means *irreversibility*. The current practice for conservators seems to be applying only coatings that are removable by solvents, as non-removable coatings have been interpreted as "adversely (affecting) cultural property or its future."[7] This practice limits the materials that may be used on a sculpture to thermoplastic, solvent soluble coatings.

In addition to removability, there are a number of other factors that need to be addressed when developing a coating for the protection of bronzes. A survey was conducted by NDSU to obtain a broad opinion of both practical information about the techniques and materials used to maintain outdoor sculptures and the future needs of the conservation community relating to coatings for outdoor bronzes.

Within the survey, conservators were asked to rank specific properties from very important to not important. It was determined that *weather resistance, appearance* and *removability* were the three most important features, followed by *longevity, safety* and *ease of application*.[8]

The seemingly contradictory properties of removability and durability stand at odds with each other in coating design. To achieve good protection of a metal from a coating system, one needs adhesion and chemical stability to external stresses. But when looking for removability, these properties must be decreased.

The development of BronzeShield™, and before that the polymer development at NDSU, attempted to combine this combination of incompatible requirements by adding a weak link within the coating that can be activated within an externally imposed set of conditions that is unlikely to occur in natural outdoor exposure.

Synthesizing a Selectively Removable Polyester

Developing a coating system that was sufficiently durable and selectively removable required considerable effort. Several different theories of polymer science and chemistry were investigated, with varying degrees of success. BronzeShield® is the result of a series of testing that downselected the material candidates in the best performing system that satisfied the guiding principle for the development.

One of the monomers used in the polymer synthesis has a particular structure that allows selective neutralization in a particular environment. Because of the hindered status of this reactive group, it is unlikely to react during the polymerization, and therefore does not need to be protected during the synthesis.

Once the polyester is synthesized and the coating cross-linked, this site can be neutralized and the polymer becomes water soluble.

In the case of developing a removable coating, the polymer would not be neutralized until it is time to remove the coating; in fact an alkaline environment is not likely to occur in nature. The means by which this occurs is the base catalyzed hydrolysis reaction, as seen in *Figure 1.*

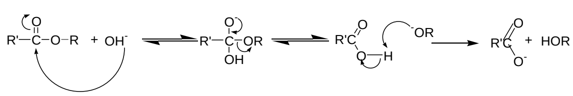

Figure 1. Base-catalyzed hydrolysis reaction.

Formulating an ultra-low VOC product and its zero-VOC remover

During commercial development, BronzeShield™ was formulated to meet stringent environmental requirements. The scaled-up two-part formula (Part 1 Resin and Part 2 Catalyst combined) has an ultra-low VOC of 56g/l. The primary solvent is Ter-Butyl Acetate, which has a characteristic odor.

The zero-VOC non-toxic remover is formulated to contain alkaline components which activate the cross-linked polymer, swell it and make it water soluble. The remover has no odor and can be applied in situ.

Coating testing

Application

BronzeShield™ is formulated in two parts to be mixed in 1:1 ratio by volume. It can be applied using common paint air guns and thicknesses of 1-3 mils were achieved with multiple layers.

In our laboratory testing, the coatings were applied in triplicate samples to both polished and patinated bronze using a Gardco Automatic Drawdown Machine. Because the patinated samples were very porous, it was necessary to coat these samples twice to achieve the same thickness as the polished samples. The coating was allowed to fully cure before the second topcoat was applied. Before artificial weathering, the edges of the samples were taped to reduce edge effects.

Removability Evaluation

Each coating that was developed was exposed to the remover for 15-30 minutes. *Figure 3* is a photograph of the panels undergoing this treatment. Some panels in the photo were lightly abraded with a plastic scraper and rinsed with deionized water but most of the coatings were removed using only a paper towel and rinsed with tap water. Each panel was evaluated visually to see if the all the coating was removed after the exposure to the remover and water rinse (not shown).

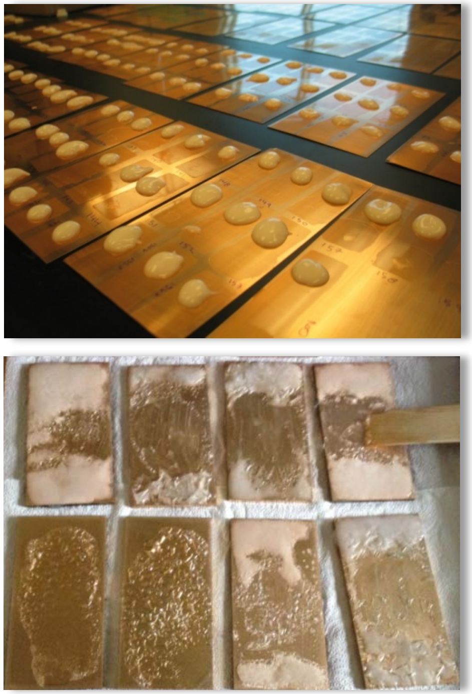

Figure 3. BronzeShield™ samples being tested for removability.

Coating Exposure: Accelerated Weathering

The best performer formulations were cast on patinated and polished samples. All of the coatings were allowed to cure at room temperature and left in air for two weeks before weathering commenced. Before weathering the edges of the samples were taped to reduce edge effects.

The samples were cycled weekly between an ultraviolet weathering chamber and a fog/humidity chamber in accordance with ASTM D 5894-96 Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal, (Alternating Exposures in a Fog/Dry Cabinet and a UV/Condensation Cabinet). This weathering protocol begins with 7 days exposure in the Prohesion® chamber in an environment that cycled between one hour of salt fog at 25°C and one hour of no fog at 35°C.

The weathering was then followed by 7 days in a QUV® chamber which cycles between four hours of exposure to 340 nm UV-A light at 50°C (this temperature was changed from the recommended 60°C, because many of the coatings tested would have been above their glass transition temperature), alternated with 4 hours of condensation at 50°C. The electrolyte used for weathering was diluted Harrison solution (0.35 wt. % $(NH_4)_2SO_4$ and 0.05 wt. % NaCl in H_2O) to emulate acid rain.

Results

Figure 4 and *Figure 5* show the behavior of BronzeShield™ on polished and patinated bronze, while *Figure 6* and *Figure 7* show the behavior of non-removable Incralac.

Note that the patinated bronze panel of *Figure 5* BronzeShield™ revealed a preexisting surface defect that caused the discoloration in the middle of the panel. The defect was on the metal surface and the coating outer surface was intact after the 4 weeks of exposure.

Using these test samples, the visual weathering performances of BronzeShield™ and Incralac appear equivalent:

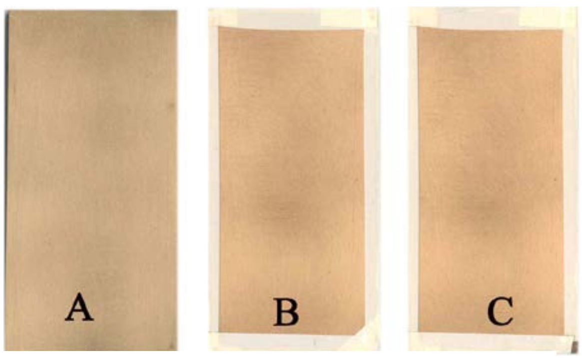

Figure 4. BronzeShield™: Accelerated weathering on polished bronze.
A) initial B) 2 weeks C) 4 weeks

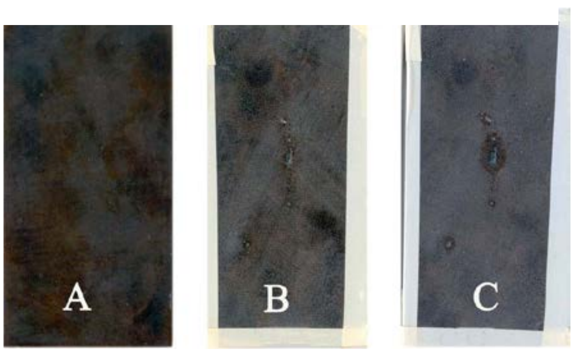

Figure 5. BronzeShield™: Accelerated weathering on patinated bronze.
A) initial B) 2 weeks C) 4 weeks

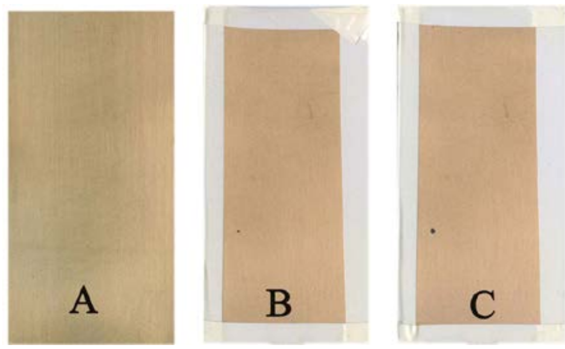

Figure 6. Incralac: Accelerated weathering on polished bronze.
A) initial B) 2 weeks C) 4 weeks

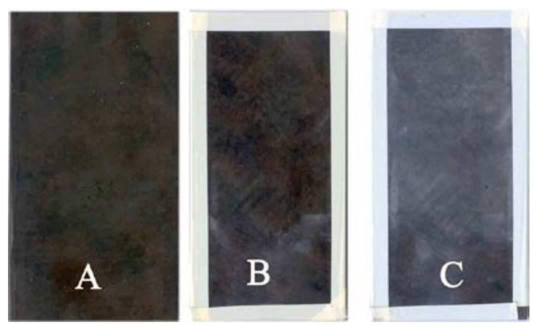

Figure 7. Incralac: Accelerated weathering on patinated bronze.
A) initial B) 2 weeks C) 4 weeks

After four weeks of accelerated weathering the removability of BronzeShield™ was tested, and the coating was completely removed after 45 minutes of exposure to the remover.

Removability vs Weathering Time

A separate set of panels were subjected to the removability test by exposing them to the remover after different hours of accelerated weathering exposure. The coating remained removable although the time necessary for the removal increases with exposure time. This aspect is being investigated further.

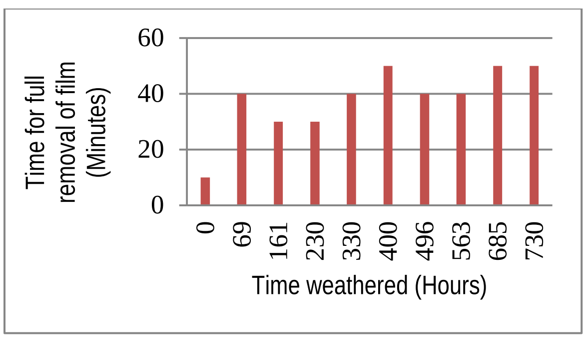

Figure 8. Coating removability versus exposure time.

Conclusions

Elinor Specialty Coatings developed a durable, selectively removable clear coat that is viable for protecting a bronze sculpture. The accelerated weathering confirmed that BronzeShield™ is as protective as its commercial benchmark and, in addition, maintained its removability after exposure.

We believe that the research on BronzeShield™ will contribute to the knowledge base regarding coatings for bronze sculptures, coatings and material science in general, but most of all it provides one more material option to conservators.[9]

Elinor Specialty Coatings continues to research how BronzeShield™ is affected by prolonged environmental exposure through accelerated and real-time weathering (e.g. salt fog for sea environment simulation, extreme UV exposure, water immersion, graffiti and human handling).

BronzeShield™ research related to interaction with modern patinas, acrylics and waxes is also ongoing.

Additional additives will be considered as the product is evaluated by potential users.

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For additional product safety and health information or Material Safety Data Sheets, please visit our website: www.bronzeshield.net

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References

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[9] Tara Shedlosky, Gordon Bierwagen, Dean Webster & Andrew Huovinen, Protective Coating for Metals, US Patent Application 60/674, 220 filed April 20, 2005. Eur. Patent Office 05760218.7 (2005)