Master in Conservation and Restoration of Cultural Heritage, specialisation Metal

RESEARCH PROPOSAL FOR MASTER THESIS

“Coatings on bronze and visual alteration of the surface. Researching an adequate coating system for archaeological bronzes utilised for microscopic investigation.”

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INTRODUCTION

The conservation of archaeological bronzes has always been a topic of interest in the conservation field, as they form a vast and important part of our worldwide cultural heritage. Bronze is an alloy where copper is the major component in combination with tin and it has been largely used in the ancient world. Ancient bronzes which survived over time need special care when they are being excavated. Upon excavation, these bronzes can undergo a fast and destructive deterioration process. In particular, the so called *bronze disease* represents a harmful threat. In order to protect fragile bronzes subjected to this kind of degradation process, research on the most proper treatment methods has been carried out in the last decades. The necessity to stabilize the objects and stop corrosion has lead to the use of corrosion inhibitors in combination with protective coatings.
Coatings protect the metal against weathering and external damaging agents. For this reason, lacquers and waxes are largely used by conservators as they serve as a preventive measure to avoid damage. The protection of bronzes is therefore an important topic in the conservation research, in which new coatings with good protective and optical properties are always being investigated.
The study of coatings for bronze is also the central topic of my own investigation, which is part of a research which is being carried out at the RCE[1] based in Amsterdam. In this context I am cooperating with Ir. Janneke Nienhuis who is investigating the effectiveness and mechanism of the corrosion inhibitor Benzotriazole (BTA) on archaeological bronzes. BTA seems to be effective and has found vast application in the conservation practice, but research still needs to be done in order to deeply understand its effectiveness and mechanism. This compound is always applied to bronzes in combination with a protective coating; this is done both for safety reasons and to give more stability to the BTA film.
In this context, I will make a contribution to this field of research by investigating different coatings. In particular, my aim is to find an adequate coating system for bronzes which have to be used for research purposes. Such coatings need to meet specific requirements as they do not have to alter the metal substrate when the bronzes are being investigated.

DEFINING THE RESEARCH PROBLEM

In the conservation practice, BTA is applied in solution with ethanol to the bronze which is afterwards protected with a coating. For her own research, Janneke Nienhuis is investigating the mechanism of BTA on a collection of very small and fragile bronzes excavated at Zevenbergen. She adopted the following treatment method: a 3% (w/v) Benzotriazole solution in ethanol has been applied to the bronze surface. Afterwards, ethyl-2-cyanoacrylate[2] has been applied as a coating layer. Being the objects very small, the treatment has been carried out using a small dentist tool.
In her research, Janneke Nienhuis is now facing the problem that the cyanoacrylate layer causes a considerable optical disturbance on the surface of the bronzes when they are observed under the SEM and the HIROX microscopes. This visual alteration is hindering the research as the metal surface can not be clearly seen and interpretation of the observed phenomena can be altered. In the photos in Appendix I, it is shown how the surface of one of the bronzes treated by Janneke Nienhuis is subjected to disturbing optical effects potentially causing bias in the interpretation of the surface phenomena.

[1] Rijksdienst voor het Cultureel Erfgoed. (English: Cultural Heritage Agency of the Netherlands).
[2] The trade name is Three Bonds Europe S.A.

In particular, the investigation is hindered by the glossiness of the coating; when the bronzes are observed under the microscope, light is reflected on the coating layer hence making observation difficult (photo 1-3). Furthermore, the cyanoacrylate layer appears to be fairly thick and it is not homogeneously transparent. Due to a cloudy milky effect, it is problematic to see through the coating layer (photo 2 and 4). Grains, presumably of cyanoacrylate, are also observed (photo 3). Furthermore, shrinkage cracks are visible, especially under the SEM microscope (photo 1, 4 and 5). Such cracks create a disturbance and are a sign of a non proper setting of the coating.
For the research to progress it is essential to be able to detect all the possible surface phenomena. These are now difficult to monitor as the surface is greatly altered by the coating layer. In this context, my research takes place in an attempt to better understand the nature of this disturbance and to provide a more proper way of coating bronzes when they have to be observed under the microscope.

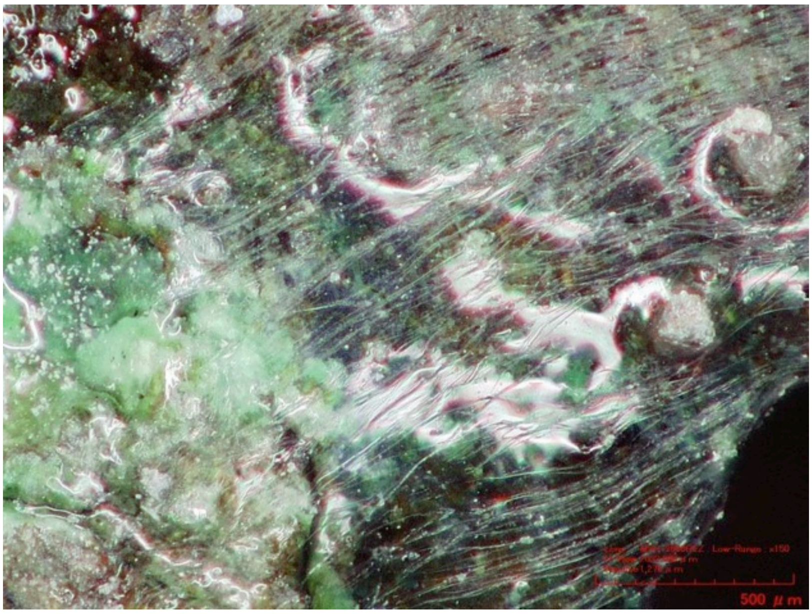

Photo 1. Photo taken with a HIROX microscope. Gloss and shrinkage cracks.

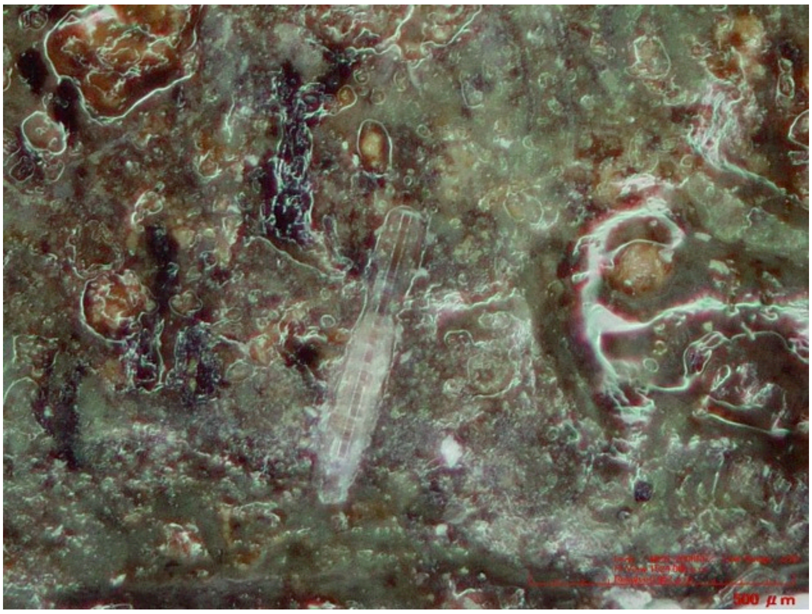

Photo 2. Photo taken with a HIROX microscope. Gloss and cloudy milky effect.

Photo 3. Photo taken with **a** HIROX microscope. Gloss and grains of cyanoacrylate.

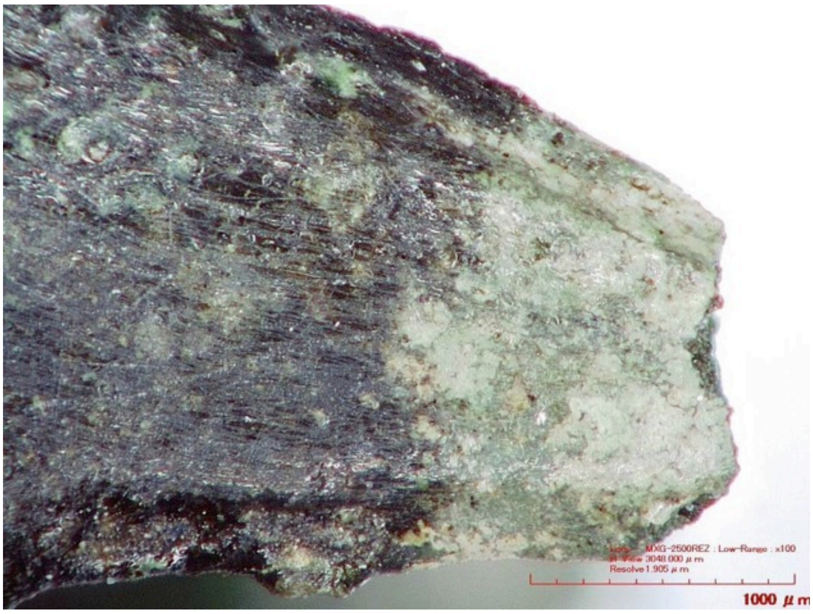

Photo 4. Photo taken with a HIROX microscope. Shrinkage cracks and cloudy milky effect.

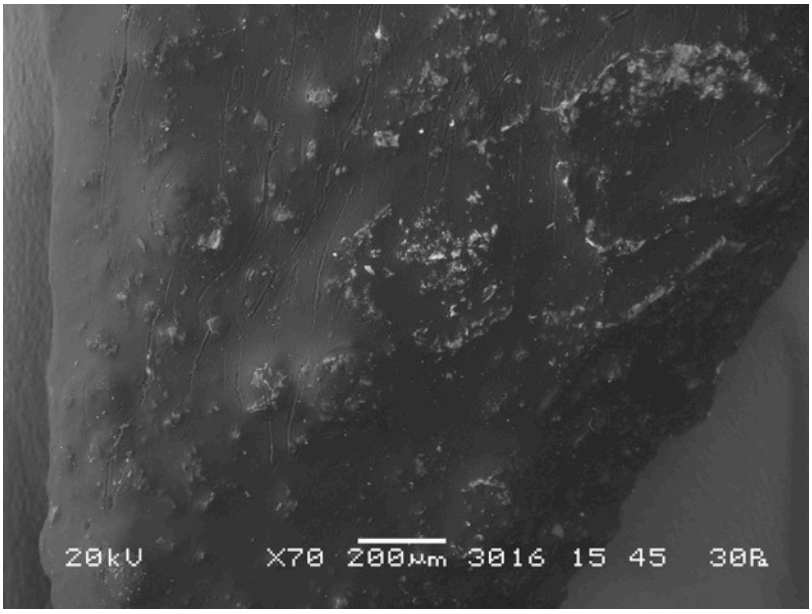

Photo 5. Photo taken with a SEM microscope. Shrinkage cracks.

RESEARCH QUESTIONS

The main aim of my research is to provide, by means of a systematic approach, a solution to the problem defined above. My main objectives are to understand the causes of optical disturbance caused by the cyanoacrylate layer and to find an alternative proper coating system for bronzes when they have to be used for research purposes. My research questions can be therefore formulated as following:

1. What causes the optical surface disturbance on the bronzes treated with ethyl-2-cyanoacrylate?

2. What is the degree of optical surface disturbance when other types of coatings are used?

   - Is there a difference when using a acryl lacquer or a wax?
   - Is there a difference when using two different solvents for the acryl lacquers, namely one with a slower and one with a faster evaporating rate?
   - What is the degree of disturbance when a matting agent like aerogel silica particles is added to the acryl lacquers to lower the surface gloss?

3. What is the degree of optical disturbance when the coatings are applied to bronze corroded substrates? Furthermore, does BTA crystallize and therefore also contribute to making the observation of the surface under the microscope difficult?

RELEVANCE OF THE RESEARCH

The research on conservation of bronze is still open nowadays trying to seek the best coating methods and trying to better understand the working mechanism of corrosion inhibitors. The specificity of my research in this context is of importance for two main reasons. Firstly, I will provide both theoretical and practical information about coatings and their application. More specifically, my aim is to provide a small database in which the properties of coatings on different substrates are given after observation under the microscopes. Furthermore, I will try to better understand why the coating chosen by the RCE is not satisfactory when used in the context of microscopic investigation. All the obtained information will help the progress of the actual research as a more efficient coating can be chosen in the future.
Secondly, my research underlines the importance of multidisciplinarity in conservation research. It is this interdisciplinarity which enables the knowledge in conservation to go further. However, when conservation science and conservation practice come together, problems could arise when there is lack of exchange of knowledge between conservators and conservation scientists. The final aim of my research is to create a bond between the two fields in order to implement knowledge on both sides.
In this context I will carry out my own research using methods and materials normally used by conservators, to avoid discrepancy between the theoretical research and the standard practice. I will therefore select methods and materials which reflect the actual visions, missions and practical uses adopted by conservators nowadays.

LITERATURE REVIEW

In the bibliographic research carried out so far no significant information on the specific topic of optical disturbance caused by coatings on bronzes in the context of microscopic investigation was found. At the contrary, much has been much published about the general topic of coatings. Coatings have been largely studied for their optical, physical and chemical properties. *Material for Conservation* (Horie 2010) and *Organic Coatings* (Wicks 2007) offer insight both on the properties of coatings and on their practical application. In particular, much has been written about coatings for bronze. *Copper and Bronze in Art* (Scott 2002) and *Coatings strategies for the protection of outdoor bronze art and ornament* (Brostoff 2003) are fundamental texts which offer good insight on the topic. Especially the publication of Scott represents a guidance as all the aspects of bronze conservation are taken into account, including the use of coatings in combination with BTA, the application of which is partly connected to my own research. Next to the mentioned key publications, research of coatings is constantly renewed and comparisons of different coating systems are always being published. All these publications focus however on the problem of coating resistance and performance against weathering, and not on the specific problem of coatings hindering observation under the microscope. The text *Microstructural characterization of materials* (Brandon and Kaplan 2001) offers an insight on different aspects of microscopy. However, also here, the problem of hindrance of surface observation caused specifically by coatings is not treated.
Being the application of coatings in combination with BTA a side track of my research, publications on this subject are also of important. Key publications on the use of BTA are *A preliminary note on the use of Benzotriazole for stabilizing Bronze objects* (Madsen 1967*)*, the already mentioned *Copper and Bronze in Art* (Scott 2002) and *Coatings strategies for the protection of outdoor bronze art and ornament* (Brostoff 2003). In the case of BTA treatments, the use of a coating in combination with this compound is recommended for different reasons. It is known that BTA tends to crystallize and therefore the metal surface has to be rinsed off after treatment.[3] My attention focuses on whether crystallisation plays a role in disturbing the investigation under the microscope in the case it occurs. Also about this specific subject no information was found in the literature.
I will therefore address my research on the subjects where there is a lack of information in the literature in an attempt to systematically create a database in which coatings on different substrates are being studied specifically for their optical properties at a microscopic level.

EXPERIMENTAL

❖ <u>Step 1</u>
I will first test 5 different coatings on metal test plates which provide an equal and neutral substrates for all the coatings. Cyanoacrylate will be also tested in order to have a direct comparison. The aim is to obtain a thin, well adhered, pinhole and bubble free layer of colourless transparent coatings which enables objective observation under the microscope. The selection of coating is the following:

- Two acryl polymer coatings:
  - Paraloid B- 48N
  - Ethyl- 2- Cyanoacrylate

[3] Scott 2002: 380.

- Two waxes:
  - Polyethylene wax
  - Microcrystalline wax
- One Ormocer coating (new coating based on a sol-gel method of manufacture)

❖ <u>Step 2</u>
After the data has been collected, analysis under the microscopes SEM and HIROX is carried out. The optical observed phenomena are being observed. Values from 0 to 5 will be given to characterize the degree of observed phenomena like gloss and clarity. All other possible detected phenomena will be noted.

❖ <u>Step 3</u>
After analysis of the data all the coatings will be compared based on the degree of optical disturbance observed under the microscopes. Value from 0 to 5 are given to characterize the degree of optical disturbance observed.

❖ <u>Step 4</u>
Once the 3 best performing coatings have been defined these will be tested on corroded bronze. After the data has been collected, analysis under the microscopes SEM and HIROX is carried out. The optical observed phenomena are being observed.

❖ <u>Step 5</u>
After analysis of the data all the coatings will be compared. Value from 0 to 5 are given to characterize the degree of optical disturbance observed under the microscope. The values given will also be based on comparison with the photo's of the bronzes treated by Janneke Nienhuis, to which I conventionally give a value of 5.

❖ <u>Step 6</u>
Once the best performing coating of the 3 has been defined, I will finally test this one on corroded bronze previously treated with BTA. For this test, four different application methods are used:

I. Immersion of the bronze in a 3% BTA solution for 24 hours. Afterwards, the surface is rinsed off with ethanol in order to remove eventual BTA crystals. The object is then let dry and coated.[4]
II. After immersion of the bronze in a 3% BTA a vacuum is applied until air bubbles stopped emerging from the object. Upon removal, the object is rinsed with ethanol and let dry. The object is then coated.[5]
III. A 3% BTA solution is applied with a brush. The solution let dry for a few hours. Afterward, the object is rinsed with ethanol. The object is then coated.[6]
IV. A 3% BTA solution is applied with a brush. The solution let dry for a few hours and not rinsed. The object is then coated.[7]

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[4] This method is suggested by Scott in: Scott 2002: 380.
[5] This method is suggested by Madsen in: Sease 1978: 81.
[6] Application of BTA by brush is less effective; however, it is a easy and fast application method and it is often used by conservators when a vacuum system is not available.
[7] The application of BTA not followed by rinsing with ethanol is not recommended in the literature because of the risk of BTA crystals remaining on the surface and therefore interesting in the context of my research to monitor crystal formation and its eventual influence on the visual appearance of the coating.

❖ Step 7

The coatings on bronzes treated with BTA are compared based on observed phenomena (see table 14).

ANALYTICAL TECHNIQUES

The analytical techniques that I will use for analysis of the data are HIROX and SEM microscopes. I have chosen for these two techniques as they provide the means for a proper observation of the surface phenomena that I have to monitor. Furthermore, these techniques are used already by the Janneke Nienhuis of the RCE for the bronzes treated with cyanoacrylate. In order to create a consequent and systematic method of observation, I have decided to use the same techniques for my own evaluations.

- HIROX digital microscope: visual analysis of the surface, observation of the optical surface phenomena.
- SEM scanning electron microscope: visual analysis of the surface, observation of surface phenomena at a higher magnification.
- SEM/EDS: elemental detection (for detection of aerogel silica particles)

EXPECTED RESULTS

On basis of the information collected so far, I expect all the selected coatings to perform better then cyanoacrylate. Cyanoacrylate is an acrylic resin normally used as an adhesive and not much as a coating. Nevertheless, it is often used in archaeological conservation when the metal is very fragile in order to strengthen the objects. Known as the one second glue because it dries very fast I assume that it is difficult to apply it as a thin regular layer on bronze. It also has a high gloss which create a disturbing effect. I will also test Paraloid B48 N and cyanoacrylate with addition of silica particles, often used to lower the surface gloss of coatings. The high gloss of acryl polymers causes reflection of light on the cyanoacrylate layer, the biggest disturbing factor hindering observation of the bronze surface. Lowering the gloss, the reflection is reduced. Even though I am aware of the fact that the silica particles themselves might cause a disturbance not helping the observation under the microscope, with the SEM/EDS technique it is possible to detect elements; once the silicium elements are detected, accurate observation of the metal substrate may still be possible as the foreigner element is localized on the surface.
Furthermore, I expect BTA to contribute to create surface alteration if it crystallizes; however, I expect crystallization to occur only when the object is not rinsed well after BTA application (see application method number IV above).
It is important to notice that the factor time and the consequent degradation of the coatings can also have an influence in creating a greater optical surface disturbance. In the timeframe of my research is however not possible to observe the samples over a period of time long enough to trace considerable conclusions on this topic.

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