A survey of the types of corrosion inhibitors and protective coatings used for the conservation of metal objects from museum collections in the Mediterranean basin

Vasilike Argyropoulos, Maria Giannoulaki, Giorgos P. Michalakakos, Amalia Siatou
Department of Conservation of Antiquities & Works of Art, Technological Education Institution (TEI) of Athens

Ag. Spyridonos, Aigaleo, 12210, GREECE
Tel: 0030-210-5385459
Fax: 0030-210-5385406
e-mail: bessie@teiath.gr

50 museums were surveyed from Egypt, France, Greece, Italy, Jordan, Malta, Morocco, Spain, Syria, Turkey, including Czech Republic to determine the types of corrosion inhibitors and coatings used by conservators-restorers to protect indoor museum objects made either of copper, iron, silver, or gold alloys. The results found that the most popular corrosion inhibitor for copper alloy objects is benzotriazole. For iron alloy objects, not many conservator-restorers use corrosion inhibitors, except in Europe where tannic acid is the most favoured. Paraloid® B72 is the most popular protective coating for archaeological or historical copper, iron, silver, and gold alloys. The paper provides an analysis of the survey and identifies the areas for further training or research in the Mediterranean basin.

Keywords: survey, inhibitors, coatings, museum collections

1. INTRODUCTION

Under the auspices of the European 6th Framework INCO project PROMET, the consortium collected information from professional conservators-restorers (C-R) on the types of corrosion inhibitors and protective coatings used to protect museum objects made of either copper, iron, silver or gold alloys. A questionnaire was designed in English and was then translated into Arabic, French, Greek, Spanish, including also Czech, and posted on the PROMET Internet portal, www.promet.org.gr. The questionnaire asked general information about the type of collection (i.e., archaeological, historical, or modern), and the conservation methods and practices used for the application of corrosion inhibitors and/or coatings. The opinions of the conservators as to the effectiveness of these methods were also recorded.

To date around 54 responses were collected from conservation professionals from ten (10) countries in the Mediterranean Basin: Egypt, France, Greece, Italy, Jordan, Malta, Morocco, Spain, Syria, Turkey as well as Czech Republic. This paper outlines the statistical assessment of the results of the survey and highlights the problems and needs for further research in this field. The purpose of our research was to understand C-Rs' practices in Mediterranean Basin, and to stimulate discussion for further research and training.

2. DEVELOPMENT OF C-R EDUCATION AND PROFESSION IN THE MEDITERRANEAN BASIN

Apart from the questionnaire, each partner was asked to collect information concerning the level of educational training and professional status of C-Rs in each of the participating countries of PROMET. The aim was to establish the basis for the know-how of professional C-Rs working in museums.

Our survey found that all of the participating countries have a law that protects cultural property, in the most part established sometime during the 20th century. Table 1 lists the level of C-R education and date of establishment. All countries, except for Morocco and Syria, offer C-R education at a University level, but in most cases has only recently been established

Table 1 clearly shows that the C-R profession is quite new for most of the participating countries, and many have only recently established laws protecting the C-R profession.

3. THE QUESTIONNAIRE

The questionnaire was separated in different parts. The first part asks for general information for the institution (e.g., public or private museum), including information on the type of collection and how many C-Rs work at the institution.

Table 1 Level of C-R Education and Professional Status of C-Rs for participating countries of PROMET

Country	C-R Masters/Ph.D.	Date of Est.	Univ. Level 3 or more years	Date of Est.	Professional C-R body	Date of Est.	Law C-R Profession	Date of Est.
Egypt	Y	1975	Y	1988	Y	-	Y	-
France	Y	2005	Y	1973	Y	1992	Y	2002
Greece	N	-	Y	1985	Y	1976	Y	1996
Italy	Y	1990	Y	1990	Y	1985	Y	2000
Jordan	Y	2004	Y	2003	N	-	N	-
Malta	Y	2003	Y	1999	Y	2006	Y	2002
Morocco	N	-	N	-	N	-	Y	1992
Spain	Y	1981	Y	1942	N	-	N	-
Syria	N	-	N	-	N	-	N	-
Turkey	Y	1993	Y	1994	Y	2005	N	-
Czech R.	N	-	Y	2005	Y	1990	Y	1987

Then according to the type of metal, i.e. copper, iron, silver or gold alloys, a general description of the types of objects and types of conservation methods used for these objects, i.e. cleaning, stabilization etc., is given. These two parts provide the background information for the institution and C-Rs' practices.

Our statistical analysis was conducted for the remaining sections, where each institution must list the types of corrosion inhibitors and coatings used for each type of metal alloy to protect the collection. The respondent first provides a category for the response according to the following type of collections: A1 and 2 (Archaeological), H1 and 2 (Historical), and M1 and 2 (Modern), and 1 and 2 refers to stable and active corrosion products respectively. Such categorization was necessary for museums that house mixed collections, and to ascertain if coatings for example are being applied to objects with active or stable corrosion products.

Next, how the surface was prepared prior to application of coating or corrosion inhibitor was also filled in, as well as the method of application and drying of the object. The C-Rs were also asked to fill in the expected life duration of the products, both given by the manufacturer as well as what they have experienced in practice. Furthermore, they also had to describe the frequency with which they applied all the coatings and corrosion inhibitors that they listed in the previous section, and if there is a combination of corrosion inhibitors and/or coatings that they use together. Finally, the C-Rs were also requested to fill in their assessment of the success or failure of the coating systems that they have used in the past.

4. THE RESPONDENTS

All the participating partners of PROMET submitted completed questionnaires from national and regional institutions involved in the conservation field.

To summarize, Czech Republic and Turkey provided responses from one institute, Egypt, France and Malta from two institutes, Syria from three, Jordan, Morocco and Italy from four institutes, Spain from 8 institutes and finally Greece from nineteen institutes.

The partners were asked only to provide one questionnaire per institution – since it was presumed that the same conservation methods or protocols, and thus corrosion inhibitors and/or coatings are being used in a museum. However, for Syria, this is not the case, and depending on their training, C-Rs working for the same museum may in fact have different conservation protocols. Also, revising the list of respondents per country, it can be observed that some countries provided more responses than others. For example, Greece had the most responses, 19, as opposed to Turkey with only one response. In some cases, the partners involved in the project had better access to museums and were able to get more responses than others. In other cases, such as Syria, Jordan, Malta, Morocco etc., there are few or no C-R professionals working in museums. Also, in some countries, like France, most C-R professionals have their own private practices, and treat museum objects in their lab and then return them to the museum. Thus, in this case the C-R professionals may have no knowledge as to the effectiveness of the corrosion inhibitor and/or coating applied. Thus, this questionnaire was not adequately designed for them.

5. STATISTICAL ANALYSIS

Due to the sample size, and to provide a balance to the interpretation of the results, statistical analysis was conducted for three groups, G1: Greece, G2: Europe (Czech Republic, France, Italy, Malta, Spain, and Turkey) and G3: rest of Mediterranean (Egypt, Jordan, Morocco, and Syria). The statistical package SPSS version 12 was used to create according to the three groups, frequency tables, crosstabs, histograms, and piecharts. The information assessed using this method was only for the types of corrosion inhibitors and coatings applied according to each type of metal alloy, copper, iron, silver, and gold.

6. BACKGROUND INFORMATION

Certain background information was not assessed using statistics, but is discussed here, since it leads one to understand the approach taken by C-R professionals at museums.

For Group 1: Greece, the majority of respondents work in museums, mostly with archaeological collections, but also many have historical or both types of collections. The number of C-Rs working on the collection varies from 1 part-time to 25 full-time. The majority of collections have all types of metal alloys. Most C-Rs use either mechanical or chemical cleaning for all types of metals objects. However, C-Rs prefer mechanical cleaning for iron and gold alloys. Electrolytic cleaning/stabilization is not common, expect in one or two cases. Furthermore, most C-Rs in Greece do not conduct dechlorination methods for archaeological iron or copper alloy objects.

For Group 2: Europe, the majority of respondents work in museums, mostly with archaeological collection, but some have historical collections or in one case modern. The number of C-Rs working on the collection varies from 1 part-time to 30 full-time. Again the majority of the C-Rs use either mechanical or chemical cleaning for all types of metal objects. Very few C-Rs in European group use electrolytic methods. However, much more C-Rs in this group than for the group from Greece conduct dechlorination methods for both copper and iron alloy objects.

For Group 3: Mediterranean, the majority of respondents work in museums either with archaeological or mixed collections, archaeological and historical. These museums have either no C-Rs to 12 full-time plus 7 part-time (Egyptian Museum). Again the majority of C-Rs in Mediterranean use either mechanical and/or chemical methods to clean all types of metal objects. Only in two museums the staff applies electrolytic methods, but more importantly no dechlorination methods are used to stabilize copper and iron alloy objects.

7. THE RESULTS – CORROSION INHIBITORS

7.1 Copper Alloys

The majority of respondents from all three groups use 3% benzotriazole in ethanol solution. However, there are some C-Rs that do not use corrosion inhibitors for copper alloy objects. Interestingly, the method in which the corrosion inhibitor is applied varies for the groups as seen in Figure 1. Greek C-Rs prefer to immerse the object in the inhibitor, where as in the rest of the Mediterranean the inhibitor is applied by brush. In Europe, immersion is preferred or a combination of immersion plus brush.

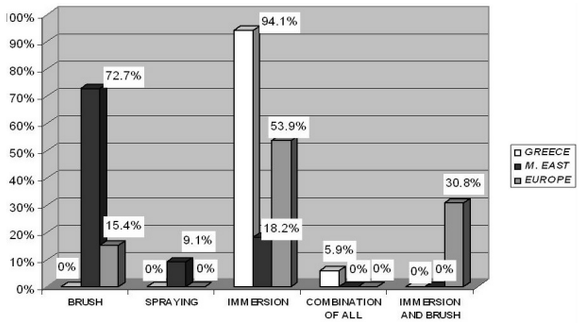

Figure 1 Method of application for BTA in ethanol 3%

7.2 Iron Alloys

In Greece, the majority of respondents do not use a corrosion inhibitor for iron alloys, whereas few use tannic acid. Interestingly, many C-Rs in the Mediterranean use 3-5% benzotriazole in ethanol to stablize iron alloy objects. In Europe, the majority use tannic acid for iron alloys, along with some other types of commercial products.

7.3 Silver Alloys

Very few C-Rs amongst all groups tend to use a corrosion inhibitor for silver alloy objects, but when they do so, it is usually 3% benzotriazole in ethanol.

8. THE RESULTS – COATINGS

Our survey found that for copper, iron, and silver alloys, C-Rs tend to use the same coatings regardless of the type of object (historical or archaeological), and type of corrosion products (stable or active) on the surface. Since most of the respondents had archaeological collections, the results for these pie charts are presented here.

8.1 Copper Alloys – Greece

The majority of C-Rs prefer to use Incralac as a coating for archaeological or historical copper alloy objects as seen in Figure 2.

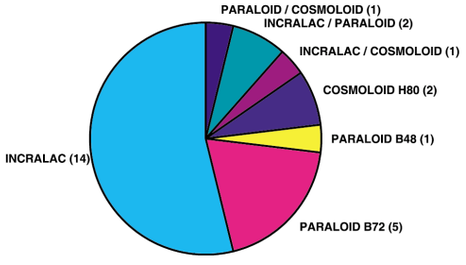

Figure 2 Coatings for copper alloys archaeological objects with stable corrosion products - Greece

8.2 Copper Alloys- Europe

In Europe, the most popular coating for archaeological or historical copper alloy objects is Paraloid B72 as shown in Figure 3.

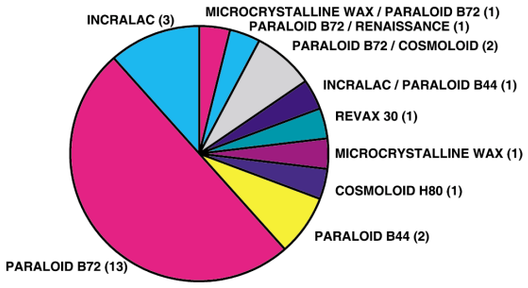

Figure 3 Coatings for copper alloys archaeological objects with stable corrosion products – Europe

8.3 Copper Alloys – Mediterranean

C-Rs from the Mediterranean region use either Paraloid B72 or Cosmoloid wax to protect archaeological or historical copper alloy objects.

8.4 Iron Alloys –Greece

Figure 4 presents the results for the coatings applied for archaeological iron alloys by Greek C-Rs. Again Paraloid B72 is the most popular choice. However, the types of coatings applied to historical iron alloys did differ from the archaeological objects. For historical objects many C-Rs use either Hoppe's oil or Renaissance wax alone, as well as Paraloid B72.

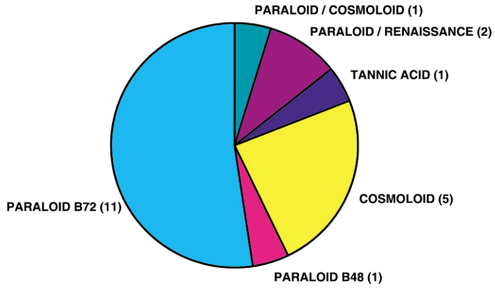

Figure 4 Coatings for iron archaeological objects with stable corrosion products - Greece

8.5 Iron Alloys - Europe

In Europe, the results presented in Figure 5 show essentially the same as for the Greek results.

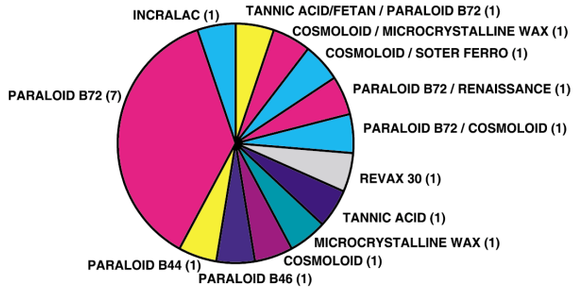

Figure 5 Coatings for iron archaeological objects with stable corrosion products – Europe

8.6 Iron Alloy – Mediterranean

In the Mediterranean group, C-Rs tend to prefer the use of waxes for archaeological iron objects as opposed to other coatings used in Greece or the rest of Europe as shown in Figure 6.

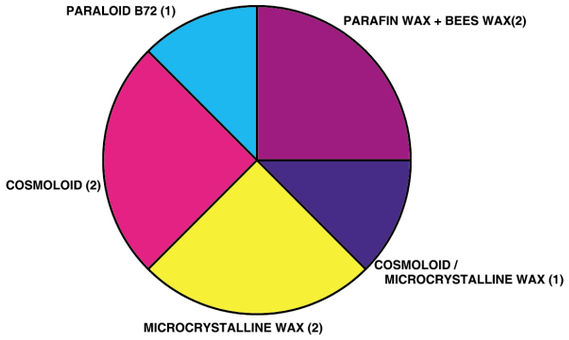

Figure 6 Coatings for iron archaeological objects with stable corrosion products - Mediterranean

8.7 Silver Alloy – Greece

For silver alloy archaeological objects with stable corrosion products, the results shown in Figure 7 indicate that Paraloid B72 or B48 is the most popular coating. For historical objects the same coatings are used, along with Renaissance wax alone.

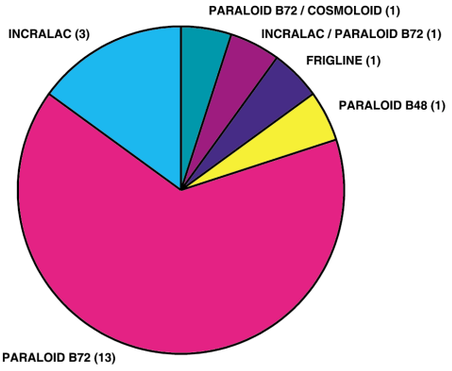

Figure 7 Coatings for silver alloys archaeological objects with stable corrosion products- Greece

8.8 Silver Alloy – Europe

For historical silver objects with stable corrosion products no coatings are used in Europe. However, if there are active corrosion products, some C-Rs use Paraloid B72. Also, some respondents do apply Paraloid B72 on archaeological silver alloy objects.

8.9 Silver Alloy – Mediterranean

The same coatings are used for silver alloy objects, regardless if they are archaeological or historical. Figure 8 shows the results for archaeological silver objects with stable corrosion products.

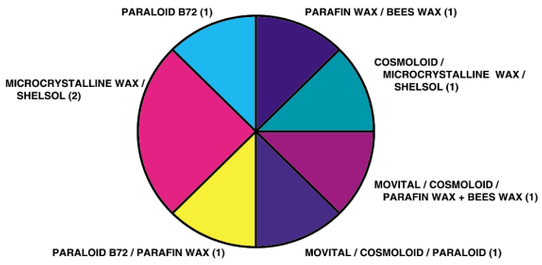

Figure 8 Coatings for silver alloys archaeological objects with stable corrosion products - Mediterranean

8.10 Gold Alloys

Not many C-Rs from any of the groups use coatings for gold alloy objects (archaeological or historical). However, when they do, they prefer either to use Paraloid B72 or B48 alone, Renaissance or Cosmoloid wax alone, or Incralac.

9. DISCUSSION

The results show some very interesting trends in the C-R profession across the Mediterranean Basin.

For copper alloy objects, the most popular corrosion inhibitor is benzotriazole. Nevertheless, the method of application and drying, and the time of immersion tends to vary according to the groups. For iron alloy objects, most C-Rs do not use a corrosion inhibitor, and when they do, it tends to be tannic acid applied with a brush. However, from our Mediterranean group, some use benzotriazole as a corrosion inhibitor for iron objects, which was primarily developed for copper alloys only. For the silver alloy objects, either no corrosion inhibitor is used, or when it is applied it tends to be benzotriazole again.

The reason behind the popular use of benzotriazole is due to its effectiveness as a corrosion inhibitor to stabilize active corrosion of copper alloys, which is well known in the literature [1]. However, this corrosion inhibitor is also known to be toxic. The results also show that for iron alloys, C-Rs are not so familiar with effective types of corrosion inhibitors to apply. For the silver alloys, C-Rs either do not see the need in using a corrosion inhibitor or use benzotriazole to stabilize the copper in the silver alloy metal.

For the coatings, the most popular coating for all copper, iron, or silver alloys is Paraloid B72. However, in Greece, C-Rs prefer to use Incralac more than any other coating for copper alloy objects, and Mediterranean group prefers to use wax for iron alloy objects.

10. CONCLUSIONS

C-Rs tend to use the same corrosion inhibitors and coatings to protect iron, copper, silver, and gold alloy objects throughout the Mediterranean Basin. However, most C-Rs, when needed, do not carry out proper dechlorination methods of copper and/or iron alloy objects prior to using a corrosion inhibitor and/or coating. Furthermore, some of the corrosion inhibitors and/or coatings used by some C-Rs are not suitable for the purposes intended. The most popular corrosion inhibitor and coating used by C-Rs in the Mediterranean basin is benzotriazole and Paraloid B72 respectively.

REFERENCES

[1] Fox, P.G.; Lewis, G.; and Boden, P.J. “Some Chemical Aspects of the Corrosion Inhibition of Copper by Benzotriazole”, Corrosion Science, Vol. 19, pp. 457-467 (1979).