

THE TREATMENT PROCEDURES OF PERSIAN METALLIC OBJECTS COVERED WITH COLORED ENAMELS, 18TH - 20TH CENTURIES AD

Abeer GHARIB, Fatma S. MADKOUR*

¹ Conservation Department, Faculty of Fine Arts, Minia University, 61519, Minia, Egypt

Abstract

This work presents a case study on conservation of highly two deteriorated archaeological silver and copper objects covered with colored enamel. These objects exhibited at the museum of the faculty of applied arts, Helwan University- Egypt and they date back to Qajar dynasty in Persia from 1794 to 1925. The objects suffered from many deterioration phenomena including; corrosion products of copper and silver on the interior surfaces of two objects furthermore, some parts of colored enamel were fragile and some were missing on the exterior surfaces. The aim of the present paper is to study the chemical and the mineralogical composition of the corrosion products of copper and silver, as well as carry out different restoration and treatment processes to the objects. Different analytical and investigation techniques were used including; X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) to study several samples of metals, corrosion products and colored enamel. Restoration treatments processes were carried out on the two objects comprising; mechanical, chemical cleaning and replacement of the missing parts of enamels.

Keywords: Enamels; Qajar dynasty; Mineralogical composition; Corrosion products; Conservation; Cleaning; Replacement.

Introduction

An enameled object is formed by applying of vitreous substance in the form of a dried frit (powdered colored glass), to a metallic surface such as copper, silver or gold. They are then fused at a relatively low temperature about 700-900°C in an enameling oven [1, 2]. Some enameling techniques relied on a framework of metal bands or wires to contain different colored enamels and this technique of using enamel colors was known in Egypt from 1400 BC. [1].

The enamels can show signs of deterioration, induced through the chemical composition of the enamels, humidity, temperature and atmospheric pollution. The implications can be irreversible loss of material, changes in color and transparency of the glass. Through chemical processes, visible corrosion products forming at the surface from the glass or the copper sheet while mechanical stress due to changes in temperature forming cracks in the enamel [3].

* Corresponding author: fatma_madkour@yahoo.com

Different analytical methods are used to identify the chemical and mineralogical composition of ancient metals and enamels. Elemental analysis of metals provides valuable information about the composition of alloys and sometimes may lead to identifying the metals origins, the determination of the original alloys composition is important to know the genuine fineness of the objects. Relative proportion of main elements in objects provides significant information about technology system changes [4].

In this research two metal objects covered with enamel presents some of the most difficult problems that are confronted by conservator. The techniques of preserving these materials have been carefully studied, and various techniques of conservation processes have been reported.

The historical back ground of objects

The painted enamels, was first produced and developed during the Renaissance period in Limoges, France in the 15th century and later transferred into Iran and other parts of the world [5]. Painted Limoges enamels are unique and extraordinary because of their figurative composition and creative achievements. These enamels are made from several layers of translucent or opaque glass powder of different compositions, which were applied and fused in up to ten firing stages onto a thin copper plate. The fabrication of the painted enamels involved the shaping of the copper base, applying counter-enamel and grounding and several layers of colored enamel to create a picture [3].

Two metallic objects covered with enamels which exhibited at the museum of the faculty of applied arts located in Cairo were studied and restored and they date back to Qajar art in Persia during the rule of the Qajar dynasty, from 1794 to 1925. Through this period the enamel working on metals was one of the significant forms of art in Isfahan, Iran [5]. The objects covered with colored enamels (blue, green, rose, black and brown colors). The first object recorded under no. 28 which was made of silver and the other recorded under no. 29 which was made of copper.

They may be were used by smokers as parts of smoking tool (water pipe or narghile) as documented in the museum catalog. The two objects have been decorated with human (portraits) and plant ornaments (Fig. 1).



Fig. 1. Two persian metallic objects covered with colored enamels:
 a- silver object no. 28 covered with different colored enamels (blue, geen, black and rose);
 b - copper object no. 29 covered with different colored enamels (blue, rose, brown and gilded ornaments).

The deterioration phenomena of objects

The two objects consisted of two main materials, the interior surfaces were mad from metals (copper and silver) whereas the ornaments made from colored enamels covered the

exterior surfaces and they are very unique objects. The metal parts of the objects were completed but some of the corrosion became detached, these pieces were kept as samples for analysis.

The surface of silver object showed in some areas brown, black and tarnish. Archaeological silver (which contains a substantial amount of copper) was changes in its microstructure caused by corrosion. The silver – copper alloys tend first to lose copper, leaving behind a surface layer rich in silver, such objects are often completely covered with the corrosion products of copper which is why they can be mistakenly taken for copper materials if it determined only by visual observation [6]. Even pure silver (unalloyed with copper or other elements) that has been exposed to outdoor environment for years may be damaged by aggressive corrosion caused by humid conditions and dissolved salts. The result of reaction with the latter is the formation of silver chloride. The chloride of pure silver is white but if silver was contain impurities it may be grey, brown or tarnished purple [7].

The interior surface of copper object was porous and covered completely with corrosion products with colors of black, green, red and pinkish, and in other areas the copper seemed to have re-deposited on top of the existing red corrosion layer (Fig. 2a and b).



Fig. 2. Different corrosion products in both of two objects (copper and silver)

The enamel ornaments which cover the exterior surfaces of the two objects suffered from many deterioration phenomena including; hairlines cracks (crizzling), detachment of some parts from the gilded ornaments on the rime of object no. 29. Furthermore; flaking of some parts of rose enamel and missing of some parts of enamel in object no. 28 (Figs. 3a and b, 4a and b).

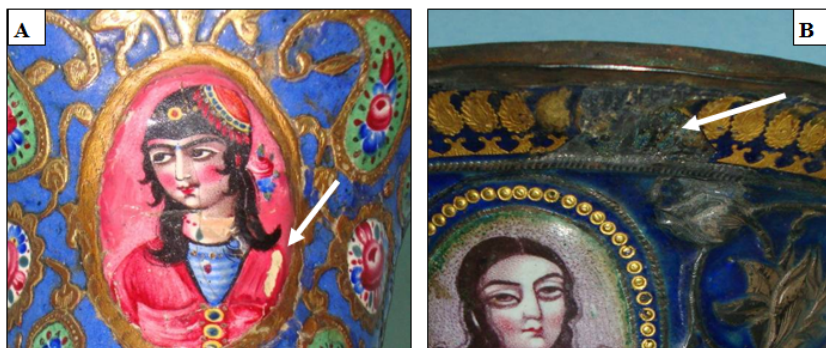


Fig. 3. The flaking of some parts of rose enamel and hairlines cracks in the object no. 28 (a) and the detachment of some parts from the gilded ornaments on the rime of object no. 29 (b).



Fig. 4. Missing parts of colored enamels in object no. 28.

The stability of the enamel depends on its composition and the surrounding environment [1, 2]. The main process of glass and enamel deterioration in the presence of water involves leaching of the alkali ions [8, 9]. The deterioration probably began atmospheric water combining with the alkaline elements (Na^+ or K^+) within the glass (enamel) forming a concentrated alkaline solution of sodium hydroxide or potassium hydroxide (NaOH or KOH) on the surface of the glass which is very hygroscopic. When the NaOH and KOH combined with carbon dioxide (CO_2) in the atmosphere; they form sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3).

Both of two compounds are hygroscopic and can combine with atmospheric water to perpetuate the deterioration process [10]. On the other hand, enamels made up of two different materials (glass and copper or silver) when undergoing temperature changes, will undergo large stresses, where one component will be compressed by the change, whereas the other component is forced apart [3]. These chemical and physical changes result in degradation ranging from a network of fine cracks (crizzling) to larger open cracks, a loss of translucency and flaking. This may be accompanied by corrosion on the metal substrate [2].

Materials and methods

Scanning electron microscopy with energy-dispersive x-ray microanalysis (SEM /EDS) is the most frequently used analytical technique for determining of the composition of metal. Furthermore; it used as non-destructive technique for examination and analysis of ceramic body fabrics and surface finishes such as slips, glazes and enamels [11, 12]. The energy-dispersive system (EDS) is giving qualitative and quantitative information. As well as SEM images provide a characteristic surface morphology and are useful for judging the surface structure of the investigated sample [13, 14]. Microstructure and chemical constitution of the metals, corrosion products, colored enamel samples were examined by scanning electron microscopy (SEM) JEOL, JXA- 840A, Electron Probe Micro Analyzer which coupled with energy dispersive X-ray Spectroscopy (EDS) INCA - Sight.

In order to obtain useful information about the types of corrosion products, different samples have been analyzed by X-ray diffraction analysis which carried out by X-ray diffraction equipment model X' Pert PRO PANALYTICAL, Cu radiation 1.54056 \AA at $45\text{kv}/40\text{mA}$; with used high resolution graphite monochromatic; rotating sample holder and a proportional detector. Measurements carried out on powders of the samples, in the range $0^\circ < 2\theta < 70^\circ$ with a step of 0.02° .

Results and Discussions

Scanning electron microscopy

Microstructure examination by SEM showed that surface of silver object no. 28 at magnification 3000X was patched, porous and bubbly in appearance. The results obtained by EDS showed that the sample contains different mineralogical elements such as 80.42% Ag, 10.44% Cu, 0.26% Zn, 1.25% Cl, 1.62% S and 4% O₂ (Fig. 5).

The sample from copper objects no.29 showed the metal surface was pitted and etched at magnification 3000x whereas EDS analysis of the same location contains the elements 79.30% Cu, 0.26% Sn, 7.51% Cl, 2.89% S and 7.62% O₂ (Fig. 6).

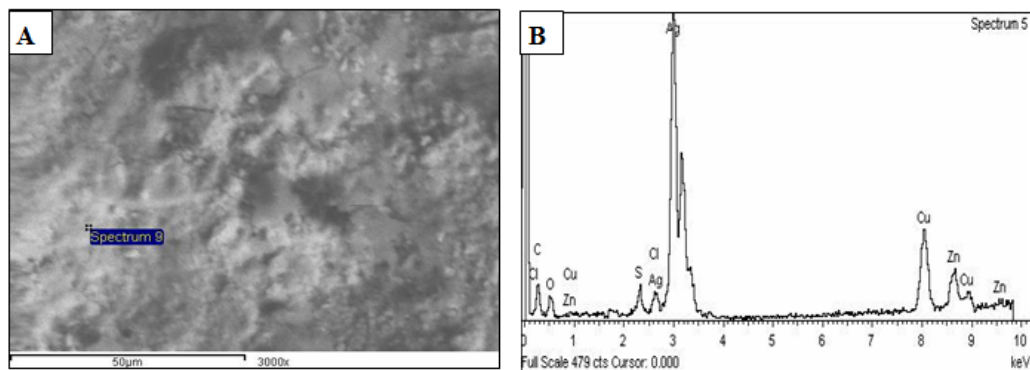


Fig. 5. SEM-EDX analysis:

- a - SEM image at magnification3000x of silver and copper alloy shows the metal surface pitted and porous;
 b - EDX pattern shows the alloy consists of 80.42% Ag, 10.44% Cu, 0.26%Zn, 1.25% Cl, 1.62% S, and 4% O₂.

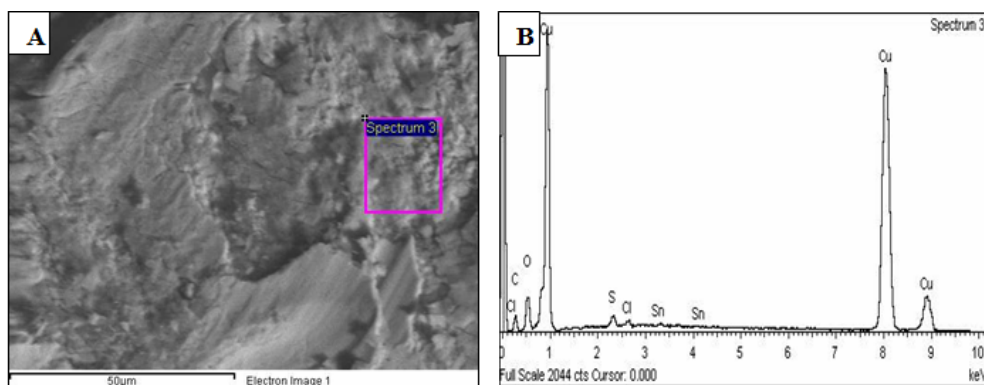


Fig. 6. SEM-EDX analysis:

- a - SEM image at magnification3000x of copper alloy shows the metal surface pitted and etched;
 b - EDX pattern shows the alloy consists of 79.30% Cu, 0.26%Sn, 7.51% Cl, 2.89% S, and 7.62% O₂

The results determined by EDS for green enamel in object no. 28 revealed high proportions of silica (Si), lead (Pb) and potassium (K) with relatively low concentrations of calcium (Ca), sodium (Na). Furthermore; the source of the green color is copper (Cu) (Fig. 7a and b). The presence of lead with a very high amount beside potassium is in agreement with the assumption that lead-potash glass was used for the painted enamel by the 19th century [5].

The results of EDS for blue enamel in object no. 28 showed high percent of calcium and potassium as well as low proportions of silica and aluminum (Al) (Fig. 8a and b). This result is typical agreement with medieval glass with a low chemical stability due to extremely low silica

and alumina contents and high amounts of the network modifiers such as potassium and calcium [15]. The EDS result of blue enamel in object no. 29 revealed many differences compared with EDS result of blue enamel in object no. 28. This enamel contains high concentrations of silica, potassium and lead as well as low percent of sodium. But the source of blue color which applied on the two objects is copper (Fig. 9a and b).

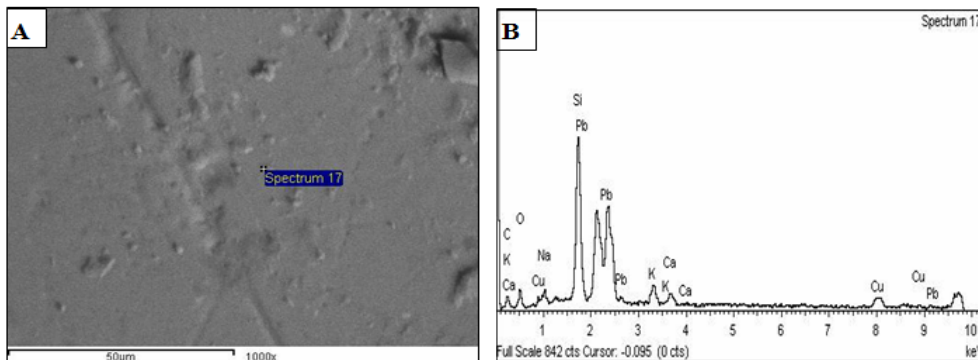


Fig. 7. SEM-EDX analysis:
 a - SEM image at magnification of 1000x of green enamel surface in object no. 28;
 b - EDX results of green enamel in object no. 28.

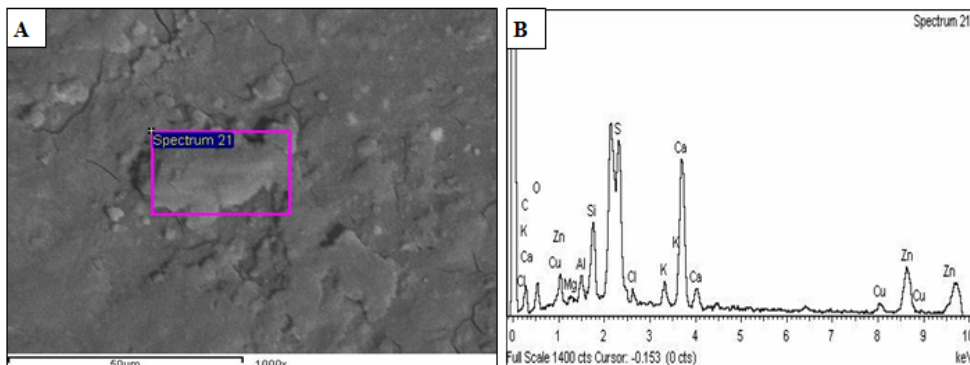


Fig. 8. SEM-EDX analysis: a- SEM image at magnification of 1000x of blue enamel surface in object no. 28;
 b - EDX results of blue enamel in object no. 28.

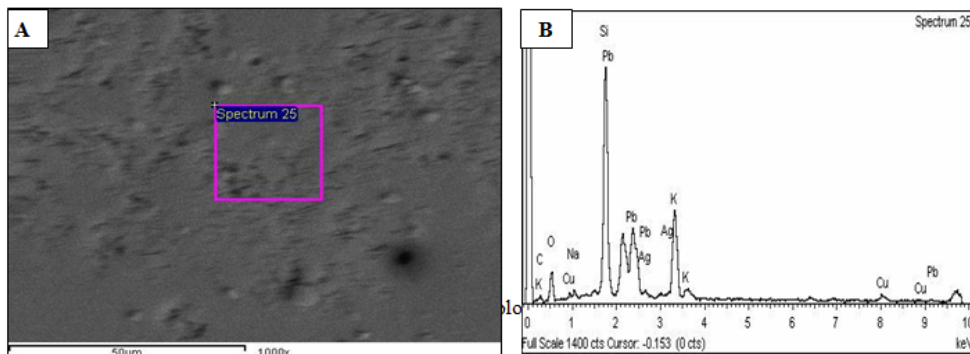


Fig. 9. SEM-EDX analysis: a - SEM image at magnification of 1000x of blue enamel surface in object no. 29;
 b - EDX results of blue enamel in object no. 29.

The EDX results showed that colored enamels have been subjected to high environmental moisture for a long time which caused for leaching of the alkaline elements mainly potassium, sodium and calcium and concentrated them on the surfaces. Through hydrolysis, alkali migrate to the surface as potassium hydroxide or sodium hydroxide and react with carbon dioxide and sulfur dioxide from the atmosphere formed carbonates and sulphates as shown in the EDS result of the blue enamel in object no. 28. As well as this enamel contains high amounts of sulfur and carbon with percent 14.62, and 8.13% respectively. The deterioration of this blue enamel also associated with the enamel composition where it contains low concentrations of silica and alumina with percent 6.79, and 2% respectively furthermore; high amounts of calcium and potassium with percent 46.84, and 4.99% respectively as showed in table (1).

Table 1. EDX results of colored enamels (Green and Blue)

<i>Element %</i>	<i>Green enamel No. 28</i>	<i>Blue enamel No. 28</i>	<i>Blue enamel No. 29</i>
C	2.75	8.13	2.99
O	5.06	7.77	8.05
Mg	-	0.52	-
Al	-	2.01	-
Na	1.50	-	0.79
Si	21.22	6.79	25.53
S	-	14.62	-
Cl	-	2.74	-
K	7.23	4.99	27.01
Ca	5.24	46.84	-
Cu	1.36	0.97	1.25
Ag	-	-	2.59
Pb	55.63	-	31.78
Zn	-	4.61	-
totals	100	100	100

X-ray diffraction (XRD)

The sample from silver object was analyzed by XRD. The obtained results showed that corrosion products consist of silver card no. (04-6783), silver oxide (Ag₂O) card no. (19-1155) as major minerals, in addition to Acaithite silver sulfide (Ag₂S) card no.(14-0075) and Chlorargyrite silver chloride card no. (06-0480) as traces minerals. The sample from copper object showed copper card no. (100399) as a main mineral and Malachite (Cu₂CO₃(OH)₂) card no. (10-0399), Tenorite (CuO) card no. (05-0661), Cuprite (Cu₂O) card no. (05-0667), and Paratacamite (Cu₂(OH)₃Cl) card no.(15-0694) as traces minerals (Figs.10 and 11). The XRD analysis results were detected as listed in table (2).

The investigation of the silver object surface using SEM showed the surface was patched and porous. The EDS and XRD analysis of the object revealed the alloy of the object consists of silver with significant amount of copper and zinc, and the corrosion layers consist of several minerals of corrosion products such as silver oxide, silver sulfide and silver chloride.

Silver-copper alloy is subject to corrosion by reduced sulfur specie. In air of the museum H₂S can result from biodegradation of polymeric materials that contain sulfur [16], silver sulfide form when silver reacts with hydrogen sulfide or with nitrogen sulfide produce by bacteria that reduce the sulfide. Silver is sensitive to tarnishing; which is caused by sulfur compounds, silver object darken with time. Because of human things always contains sodium chloride, handling silver object may bring about chloride pollutants on its surface, sodium chloride reacts with silver and forms silver chloride; which is light – sensitive and will begin darkening with time [17].

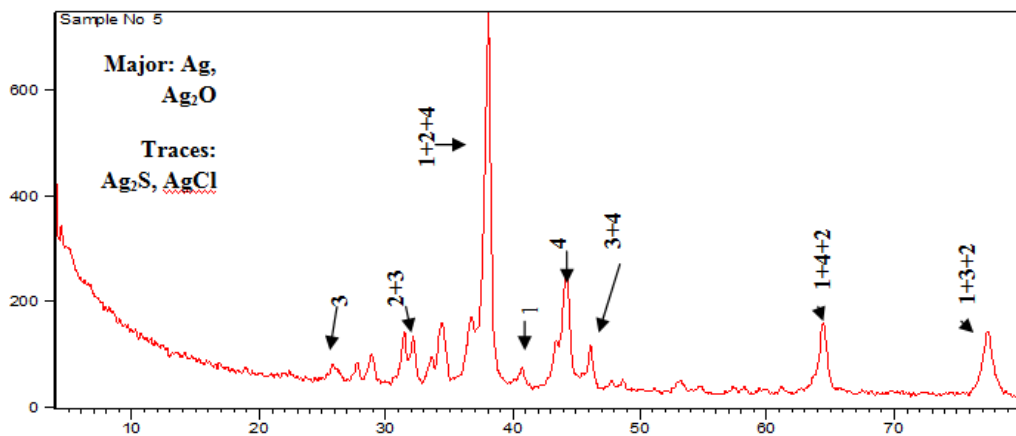


Fig. 10. XRD pattern of the silver sample showed 1(Ag), 2(Ag₂O), 3(Ag₂S), 4(AgCl); the sample consists of silver and silver oxide as major minerals and acanthite, and chlorargyrite as traces

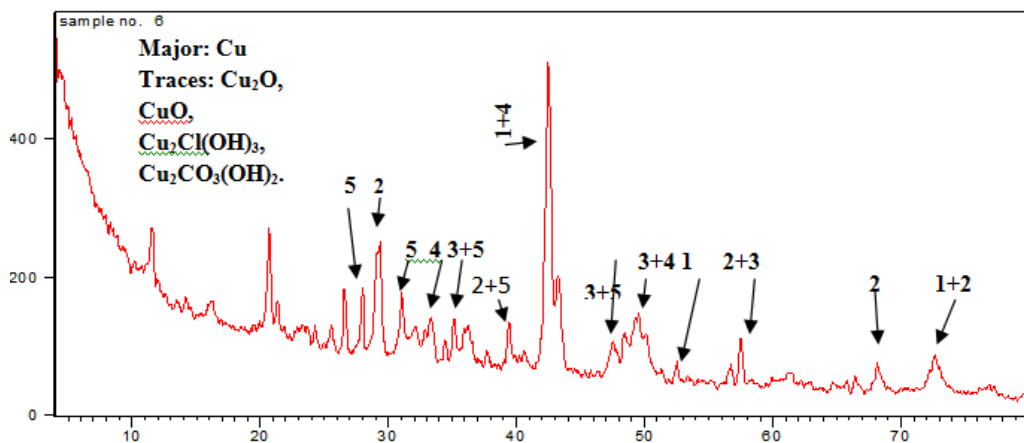


Fig. 11. XRD pattern of the copper showed: 1(Cu), 2(Cu₂O), 3(CuO), 4 (Cu₂Cl(OH)₃), and 5(Cu₂CO₃(OH)₂); the sample consists of Copper as major mineral and Cuprite, Tenorite, Paratacamite, and Malachite as traces

Table 2. The identified minerals of copper and silver samples by XRD analysis.

Samples	Minerals	Formula
Silver sample	Silver	Ag
	Silver oxide	Ag ₂ O
	Chlorargyrite	AgCl
	Acanthite	Ag ₂ S
Copper sample	Copper	Cu
	Cuprite	Cu ₂ O
	Tenorite	CuO
	Paratacamite	Cu ₂ Cl(OH) ₃
	Malachite	Cu ₂ CO ₃ (OH) ₂

The investigation of the copper object by SEM showed the surface was pitted and etched; whereas the EDS and XRD analysis of the object revealed the alloy consists of 79.30% copper and 0.26% tin. That is meaning; the alloy is pure copper. The mineralogy of the corrosion products were Cuprite, Tenorite, Malachite and Paratacamite. The researches on copper alloy artifacts showed that the corrosion crusts formed during their stay are different, but according to

their morphology, there are three general types (thin, medium and thick) characterized by elements specific to physical deterioration (cracks, pits etc.) and chemical alteration (primary and secondary chemical compounds) [18]. The Primary patina, named noble patina, due to its aesthetic and protection function, is formed on the object in the period of use by pure chemical or electrochemical processes, in the presence of oxygen from the air, of sulfur, or of hydrogen sulfide derived from the cysteine and cysteine in the skin, due to manipulation, friction and thermal treatment [19].

The corrosion pustule originates with formation of cuprite, cuprous chloride also be present in the pustule, the cuprous chloride that forms can react further to produce Paratacamite, while the presence of malachite indicates that the artifact corroded in hydrogen carbonate activity [20, 21].

The treatment processes

Both the vitreous material (enamel) and the metal support (copper and silver) were taken into consideration when carrying out the conservation treatment. Because of these objects uniqueness and high archaeological value, treatment of these objects had to be approached with well-established methods with known long – term results, it had to be taken into consideration, and both the enamel and the metal parts had to be stable and had to stay together during and after treatment.

Mechanical cleaning

The mechanical cleaning process for interior metallic surfaces by spoons, sponges and soft brushes were selected to remove the bulk of the patina, the objects sometimes needed to be wetted very regularly with methylated spirits in order to help through the mechanical cleaning process [22].

Chemical cleaning

Regarding of silver object, The treatment was carried out as follows: a solution of 5-30% formic acid in de- ionized water is effective for dissolving copper compound without affecting weakly corroded silver. A solution of 15% ammonium thiosulfate in distilled water with a 1% non- ionic wetting is effectively for removing both tarnish and silver chloride [23] (Fig. 12).



Fig. 12. Interior surface of silver object no.28: a - before treatment; b - after treatment

For copper object treatment carried out as follows: a solution 10% Rochelle salt followed by a solution 10% Citric acid is effectively for removing copper corrosion products (Fig. 13a and b). Then all objects should be thoroughly rinsed with water and dried and finally insolated by using 4% Paraloid B-72 [24] (Fig. 14a and b).



Fig. 13. Interior surface of copper object no.29: a - before treatment; b - after treatment



Fig. 14. Interior surfaces of copper and silver objects: a - before treatment; b - after treatment and isolation

The treatment process of enamels

At first, the exterior surfaces of two objects were cleaned by soft brushes to remove the dust deposited on the enamel surfaces. Then, chemical cleaning was carried out by using different solvents such as acetone and ethyl alcohol through the cotton swaps. The missing parts in the object no. 28 were replaced by Araldite PY 1092 with hardener HY 1092 which mixed with percentage 2:1. This material has many advantages including; low viscosity, transparency and durability [25]. After curing the filling areas were polished by abrasive paper.



Fig. 15. The object no. 28:
a - after cleaning the exterior surface and replacement of the missing parts,
b - after treatment process.

Finally, Paraloid B-72 (ethyl methacrylate/methyl acrylate copolymer) 3% dissolved in acetone was applied by brush to consolidate the deteriorated enamel and to reattach flakes (Fig. 15a and b). After the treatment process finished, the objects have to exhibit at the museum at relative humidity (RH) with rang between 35- 40% [3].

Conclusions

The first aim of the project was to adopt a conservation process that would render the objects stable and presentable. A second aim was to learn about the conservation, investigation and analysis of composite the corrosion copper, silver objects covered with colored enamels. All aims were met and from that perspective, the conservation project was successful.

The obtained results by EDX analysis showed that colored enamels have been subjected to high environmental moisture through the exhibition at the museum for a long time. This result in leaching of the alkaline elements mainly potassium, sodium and calcium and concentrated them on the surfaces. The chemical and physical changes result in degradation ranging from a network of fine cracks (crizzling) to larger open cracks, a loss of translucency and flaking of the enamels. These deterioration phenomena accompanied by corrosion on the metal substrate in the interior surfaces. Treatment procedures including mechanical and chemical cleaning with different solutions and acids for cleaning the interior metallic surfaces were carried out. A 15% ammonium thiosulfate solution was effectively for removing both tarnish and silver chloride, as well as a solution of 10% Citric acid is effectively for removing copper corrosion products.

Treatment process of colored enamels was carried out by using Araldite PY 1092 with hardener HY 1092 for replacement the missing parts in the exterior enamel surfaces, whereas Paraloid B-72 dissolved in acetone with concentration 3% was applied as a consolidant.

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Received: March, 24, 2014

Accepted: October, 30, 2014