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TESTING COATINGS FOR ENAMELED METAL ARTIFACTS

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Abstract

This research aims to test the efficiency of coating materials to protect Champlevé enameled silver and copper artifacts. Enameled copper and silver coupons were prepared to replicate original artifacts. Paraloid B-72 and microcrystalline wax were applied in different procedures onto test coupons then exposed to elevated relative humidity to perform an accelerated ageing condition. The exposed coupons were investigated to measure the color change and the weight gain occurred to evaluate the coatings performance and to compare the impact of changing application procedures of coatings on the protection effectiveness of enameled metals against corrosion and deterioration. The results indicated that the best coating procedure that met both aesthetic and corrosion protection was afforded by a monolayer of 3% Paraloid B-72.

Keywords: *Metal artifacts; Champlevé enamel; Protective coatings; Paraloid B-72.*

Introduction

The terms “enamel” is directed generally to all vitreous substances, of numerous and varying composition, fused with application of heat upon different bases [1]. The art of enameling metals is defined as the process of applying small granules of enamel to metal and firing at high temperatures [2], for the purpose of decoration [3].

Enamel is produced from a mixture of silica, alkali compound, which lower the melting temperature, lead oxides, salts of soda, potassium, boric oxides and various metallic oxides. Enamel can be transparent, opaque or opalescent [4, 5]. There are several methods used in enameling such as cloisonné, champlevé, painted enamel, grisaille, basse-taille and plaque-a-jour, etc., [6]. The art of enameling has been practiced from very early times [7]; it was practiced by the Egyptian, Phoenicians, Assyrians, Greeks, Romans and Etruscans [6, 8]. By the third century B.C., the enamel process had spread to Europe and the process continued to move slowly to Asia Minor and the Middle East, India and China, and lately to Japan [9]. Deterioration of the enamel layers is much more common than corrosion of the copper substrate, which is usually well protected by the coatings [10], enameled antiquities my also undergo both metal and glass corrosion. Metal corrosion products would probably be the main reason for the occasional lifting of the enamel from the metal surface, while the corrosion of glass would normally be the cause of opaqueness of the enamel [11]. The process of corrosion sets in as soon as the glass or enamel is made when exposed to the ambient atmosphere [12]. Enamel can suffer from physical damage due to handling which force the enamel to fall away or to the breakdown of the vitreous enamel itself [13]. Damage to a glassy enamel surface may easily result from direct mechanical breakage, from being bent, dropped or hit [14].

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Incomplete fusion of enamel during manufacturing can result in an aspect that is possible to be confused with natural deterioration by induced humidity, temperature and atmospheric pollution [15, 16]. Since enamel is essentially glass, it can exhibit many of the same signs of its deterioration such as loss of translucency, cloudy appearance, colour alteration, weeping, efflorescence, drizzling, flaking, crusty or waxy deposits, iridescence and devitrification [17-19]. Enamel shatters easily if it is knocked or dropped, once breaks, it can flake away from the base. Loss of enamel could allow moisture to enter causing copper alloy backing to corrode and push more enamel off [17]. Water is the major chemical agent of deterioration for glass and the susceptibility of glass depend greatly on its original chemical structure [19]. Not only are fluxing ions leached from the glass network by water, but also any colouring metal ions present. Alternatively, the ions may change colour in situ by oxidation; thus from manganese ions, black manganese dioxide (MnO2) may be deposited and the red copper (I) of enamels may become a green copper (II) colour. Moreover, colouring ions from the environment may be taken up [15].

Old restorations on enamels composed of several layers of diverse coatings onto the metal i.e., copper, various materials to fill the losses in the enamel, and pigments and mediums for in painting [20]. Coatings were sometimes applied to unstable enamels, either to the whole surface or to the degraded areas only. The aim of the coatings was to consolidate the enamel surfaces and to provide a barrier layer against environmental fluctuations, thereby stopping or slowing down ongoing degradation of the enamel and the metal substrate [21]. Invasive treatments such as “hot restorations” by remade in enamel and new piece is attached on top of the original copper support and restorations with tin-lead solder have been used for consolidation and reattachment of fragments, it is obtained by scratching the enameled surface around the area to be repaired, to expose the copper substrate, then the solder is melted and flowed over the surface of the copper to be joined and abraded after rapid hardening. These strong restorations are very difficult to remove and are considered irreversible.

In addition to what is known as “cold restorations” and coatings the main characteristic that these restorations have in common is the layering of at least four materials (beeswax, he natural resins such as shellac or Canada balsam, varnish i.e. gum mastic, dammar and sandarac, synthetic resins such as polyester resin and polyurethane varnish, these restorations do not age well. Loss of cohesion between the different layers, weak adhesion to the copper, flaking of the varnish, changes in the in painted colours and copper corrosion products can occur when materials are used for treatments which increase acidity [20].

Objects with champlevé enamels for example, have large areas of exposed metal, which was often coated to prevent corrosion. Unfortunately, the coating was sometimes applied to the enamel surface as well. The specific coatings such as Incralac (which contains benzotriazole, and used on silver and silver-gilt) and cellulose nitrate lacquers, such as Ercalene, Frigilene, and polyvinyl acetate, have been used, these coatings, however, failed to provide the protection that was originally intended because they create microclimates which promote degradation processes underneath [21]. Coating enamels can have positive and negative aspects. Coatings may give some protection from atmospheric moisture and can secure flaking surfaces and restore translucency by filling in cracks. However, a coating can cause problems as well [22]. It is hard to find easy solutions for the complex problems encountered in the treatment of unstable enameled metal composites [21]. The ideal restoration would be made of just one material that is stable and reversible [20], as both the enamel and the metal substrate must be taken into account when carrying out the conservation treatment [23].

This study deals with testing some of the various restoration materials and methods applied to protect archaeological enameled metals in corrosive environments.

The historical background of the case study: the case study is a set of a champlevé enameled metal tray and six cups. They are given the documentation number 72 and locate at Aljazera Museum, in Cairo Egypt. The artifacts originated in the city of Hyderabad in India in the 19th Century (Figure 1).

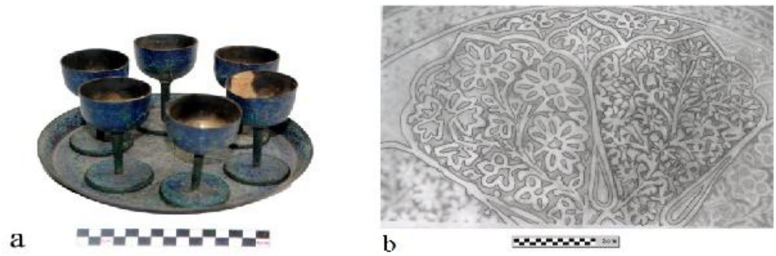

Fig. 1. Objects decorated with champlevé enamel:
a. enamelled artifacts; b. detailes of the enamel decorations

Enamelling on metals is most successfully practiced in many parts on India [24, 25]. In spite of that, there is no mention of enamelling in early indian texts before the 15th Century. The only available reference found on this subject is in the Ain-i-Akbari written in the 16th Century by Abu'l Fazl, during the reign of the Mughal Akbar Emperor. According to *A. Hunter, 1876* [26] Abu'l Fazl used enamel to work on cups, flagons, rings and other articles in gold and silver. Champlevé enamel was mainly used as decoration for jewels, sword-hilts, horse trappings and the handles of daggers [27].The technique was probably brought to India from Europe through Persia in the 15th or 16th century with other enamelling techniques [28].

Materials and methods

The samples for analyzing are: 15 pieces of copper coupons were cut from sheet metal to the size 3x6x0.5cm and 12 pieces of silver coupons were cut from sheet metal to the size 2x1x0.5cm. All the coupons were etched chemically to produce engraved decorations according to the proposed designs (Figure 2).

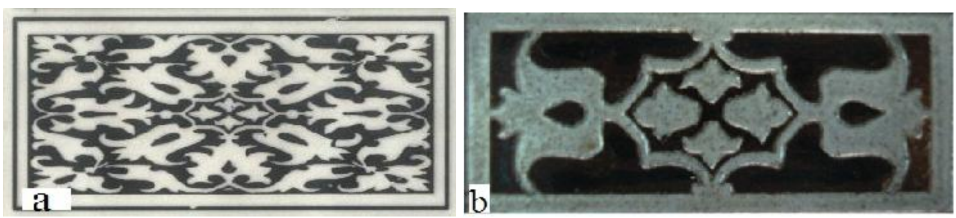

Fig. 2. Engraved decorations made on test coupons: a. on copper; b. on silver

Enamel powder was applied onto the engraved recessions in three different colors to produce green, blue and turquoise champlevé enameled decorations (Figure 3).

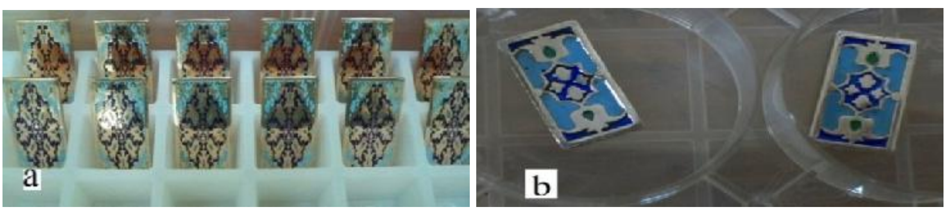

Fig. 3. Test coupons after enameling: a. copper coupons; b. silver coupons

This procedure is meant to replicate the antique case study. The enamel powder was as close as possible in chemical composition and physical properties to 18th century enamel. JEOL

JSEM 5400LV EDX Lin l ISIS - Oxford, SEM-EDX is used for the analysis of antique and new enamel.

Coupons were cleaned, rinsed with distilled water, degreased in aceton, then air dried. Coupons were weighed before the application of protective coatings, which contained Paraloid B-72 and microcrystalline wax in different application methods, as given in Tables 1 and 2.

Microcrystalline wax was prepared by dissolving 13.5g of wax in 20mL of toluene [29], this was applied onto coupons by brush and left for 24 hours to dry. Paraloid B-72 was prepared by dissolving 3% w/v in acetone, then applied by brush onto the coupons and left to dry. Coupons were weighed after the application of the protective coatings and placed in a tightly closed microclimate polyethylene box (36x24x13cm), with 85$\pm$5% relative humidity(HR) for 6 months (Figure 4). This HR value was achieved by using a supersaturated solution of potassium chloride salt (KCl). The coupons were removed every 4 weeks for reporting visual observations. An accurate laboratory balance was used for measuring the weight gain of test coupons and Color-Eye ® Spectrophotometer was used for measuring the color change.

Table 1. Coating materials tested on copper coupons and their methods of application

Coupon no.	Coatings
1A, 2A,3A	Blank
4A, 5A, 6A	One layer of 3% Paraloid B-72
7A, 8A, 9A	One layer of 3% Paraloid B-72 + one layer of microcrystalline wax.
10A, 11A,12A	Double layers of microcrystalline wax.
13A, 14A, 15A	One layer of microcrystalline wax.

Table 2. Coating materials tested on silver coupons and their methods of application

Coupon no.	Coatings
1B, 2B,3B	Blank
4B, 5B, 6B	One layer of 3% Paraloid B-72.
7B, 8B, 9B	One layer of 3% Paraloid B-72 + one layer of microcrystalline wax.
10B, 11B,12B	One layer of microcrystalline wax.

Fig.4. Microclimate used for the test with a hygrometer and temperature measuring device.

Results and Discussion

EDX analysis results show that there is a similarity in chemical composition between the antique and new enamel used for the experiment. In order to prepare enameled test coupons of copper and silver and to replicate the original case study, a known oxide composition enamel powders were used. Enamel coulors in both types contain silica and lead in varying percents. Table 3 shows results of EDX analysis of new and antique enamel.

Table 3. EDX analysis results of new and antique enamel.

Oxides	Blue enamel Wt.%		Green enamel Wt.%		Turquoise enamel Wt.%	
	A	**N**	**A**	**N**	**A**	**N**
SiO_2	55.61	39.7	64.16	49.83	64.39	37.61
Na_2O	5.22	25.61	2.60	6.50	11.52	12.85
P_2O_2	ND	1.07	ND	1.76	ND	3.25
SO_3	11.10	6.02	ND	5.26	ND	6.93
Cl_2O	ND	1.00	ND	0.75	ND	1.02
K_2O	9.72	3.36	7.52	3.49	6.69	14.35
TiO_2	0.24	1.36	1.00	2.81	0.09	ND
Cr_2O_3	ND	ND	0.57	2.52	0.17	ND
Fe_2O_3	0.93	3.38	2.13	4.05	1.94	2.44
CuO	4.14	2.76	8.40	15.64	5.88	7.32
ZnO	2.33	1.83	3.47	1.81	0.27	0.81
PbO	6.14	7.25	1.20	5.59	0.92	6.25
MgO	0.85	6.66	0.86	ND	1.79	7.16
CaO	1.25	ND	7.64	ND	4.32	ND
As_2O_3	1.05	ND	ND	ND	ND	ND
ZrO_2	0. 96	ND	0.15	ND	0.27	ND
CoO	0.45	ND	ND	ND	0.01	ND
ZnO	ND	ND	3.47	ND	1.98	ND

Notes: A - Archaeological enamel; N - New enamel; ND - not detected

Weight gain measurement

Change in weight indicates damage to the enameled tested coupons, lesser increase in weight corresponds to the better performance of the coating material used and the effectiveness its application. Coating materials and their methods of application on copper and silver coupons are given in Tables 1 and 2. Results of weight change of blank and coated copper and silver coupons during 6 month exposure are presented graphically in Figures 5 and 6.

To evaluate the performance of the tested materials with either copper or silver coupons the following equation were used:

$$\textbf{\textit{Performance}}\ \mathbf{(\%)} = 100 \times (WT - WT')/WT$$

where: *WT* - represents the average weight gain of the untreated coupons after 6 month, *WT'* - represents the average weight gain of the treated coupons after 6 month.

Figure 5 shows that one layer of 3% Paraloid B-72 gave the best performance as the least increase in weight occurred. On the other hand the double layers of microcrystalline wax failed to protect the enameled copper coupons.

Coatings efficiencies on copper can be ranked in this order: one layer of 3% Paraloid B-72 > one layer of 3% Paraloid B-72 + one layer of microcrystalline wax > one layer of microcrystalline wax > double layers of microcrystalline wax.

Figure 6 shows that one layer of 3% Paraloid B-72 on silver coupons gave the best performance as minor increase in weight occurred. On the other hand the one layer of microcrystalline wax failed to protect the enameled silver coupons.

Coatings efficiencies on silver can be ranked in this order: one layer of 3% Paraloid B-72 > one layer of 3% Paraloid B-72 + one layer of microcrystalline wax > one layer of microcrystalline wax.

It is noticed that the performance of each coating material is affected by the method of its application i.e., one layer of 3% Paraloid B-72 on either copper and silver coupons gave the greatest protection efficiency 75% for copper and 70.5% for silver respectively. However, the application of one layer of 3% Paraloid B-72 + one layer of microcrystalline wax shown fewer results 68.97% for copper and 52.63% for silver. Nevertheless a one layer of microcrystalline gave weak performance 46.51% on copper coupons and the worst results 22.63% on silver coupons. Double layers of microcrystalline wax gave also poor results 23%. Results are summarized in table 4. The performance and efficiencies of the tested coating materials were compared in Figures 7 and 8.

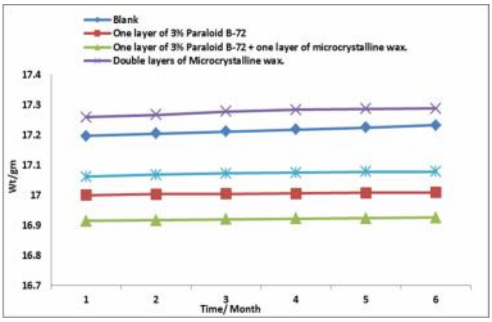

Fig. 5. The weight gain of copper coupons in 6 month.

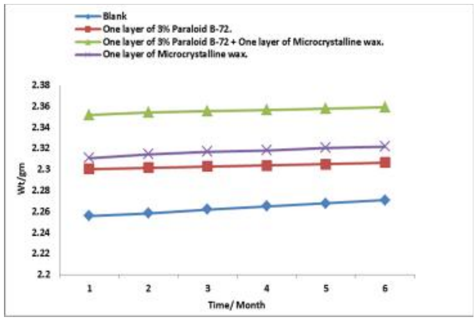

Fig. 6. The weight change of silver coupons in 6 month.

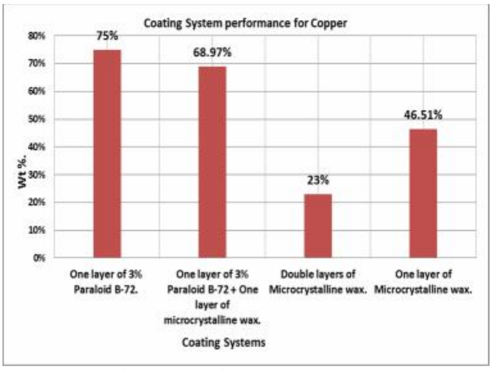

Fig. 7. Performance of coatings on copper coupons.

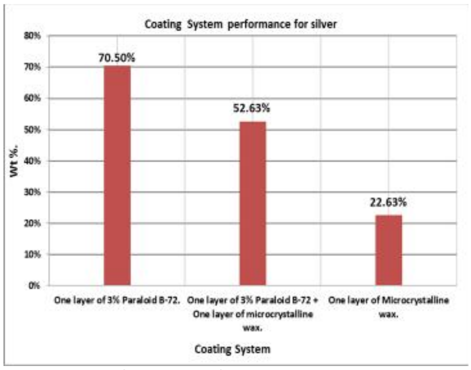

Fig. 8. Performance of coatings on silver coupons.

Table 4. Results of weight change test of copper and silver.

Coatings	Performance %	
	On copper	On silver
One layer of 3% Paraloid B-72.	75%	70.50%
One layer of 3% Paraloid B-72 + One layer of microcrystalline wax.	68.97%	52.63%
Double layers of microcrystalline wax.	23%	untested
One layer of microcrystalline wax.	46.51%	22.63%

Colour Change measurement

To evaluate colour changes induced by coating materials, the colour of the face (enameled side) and back (metal side) of copper and silver test coupons were measured before and after exposure to moderate HR (%) conditions. Results of colour change test are given in Table 5.

After 6 month of exposure to deterioration conditions, all the tested coupons changed their colour but in different rates. The colour change can be observed even with the naked eye in the form of opacity, yellowing of enamel colours and formation of corrosion products on the back of the coupons. The colour change (ΔE_{ab}) was determineted by CIE L*a*b* colorimetry method [30-35].

It was observed that copper coupons no. 6A, 8A, 10A and 13A, and silver coupons no. 5B, 8B and 11B exhibited colour changes on both sides, enameled face and metal back review Table 5. Results shown also that copper coupon no. 6A and silver coupon no. 5B, which were coated with Paraloid B-72 exhibited the slightest colour change if compared with other test coupons which were coated with other materials.

Table 5. Results of color change test (ΔE_{ab}) of copper and silver coupons from the face and back

Coupon no.	Coating	ΔE_{ab}	
		Front	**Back**
1C	Blank.	7.84	24.92
6A	Copper coupon coated with one layer of 3% Paraloid B-72.	2.45	2.71
8A	Copper coupon coated with one layer of 3% Paraloid B-72 + One layer of microcrystalline wax.	4.26	4.97
10A	Copper coupon coated with double layers of microcrystalline wax.	4.08	4.39
13A	Copper coupon coated with one layer of microcrystalline wax.	5.53	5.35
5B	Silver coupon coated with one layer of 3% Paraloid B-72.	2.49	0.31
8B	Silver coupon coated with one layer of 3% Paraloid B-72 + one layer of microcrystalline wax.	6.06	9.44
11B	Silver coupon coated with one layer of microcrystalline wax.	7.11	6.62

The aim of the application of coatings was to consolidate the enamel surfaces and to provide a barrier layer against environmental fluctuations, thereby prohibiting or slowing down ongoing deterioration of the enamel and the metal substrate [21]. Early restoration of enameled objects was performed using natural resins such as shellac or animal glue and its derivatives, but these materials shown some drawbacks. They were susceptible to shrinkage, embrittlement and even falling away, so that the enamel is left prone to further damage [13].

Wax can provide some protection against both the environment and handling. So it is still a common, easy and effective choice for protecting metals and other materials both indoor and outdoor [36, 37]. Hydrocarbon waxes like paraffin wax, beeswax and microcrystalline wax are all used in conservation of metals, but paraffin wax and beeswax when used onto copper alloy objects can cause the formation of organometallic compounds that liberate free fatty acids or dicarboxylic acids. Waxes can never be completely removed from porous objects, they may interfere with subsequent application of conservation materials [38], more over they collect dust, attract molds and fungi, and disfigure the artifact when turned white by time [37]. Micro-wax coating can both dehydrates and protects the artifacts from moisture in the atmosphere. It can also be reapplied at any time or removed in boiling water or an oven, but unfortunately it is impractical to use on larger artifacts [39]. Microcrystalline waxes are commonly used as coatings in conservation of metals. Renaissance™ and Cosmoloid 80H™ waxes are the most commonly cited waxes for the protection of both outdoor monuments and indoor metal artifacts [40]. Among the large number of wax-based coatings tested in different studies, some authors consider this kind of protection as a low-maintenance system. Thus, these coatings systems have only limited long-term stability and require considerable maintenance to provide good protection properties for long duration, and some authors have reported that regular application of waxes must be done two or three times per year [41 - 43].

Paraloid B-72 is widely used in conservation as a coating and a consolidant on glass, enamel and metals [13], it was also used to reattach loose flaked enamel [21]. Incralac, which is an inhibitor enriched Paraloid was used to lacquer copper alloys but it did not provide alone a barrier to the acetic acid emissions from the wooden storage cabinets [32].

C. Maggioni et al., 2012 [44], found that sometimes the successive interventions of integration and protection gave rise to a yellowish mass, because of Paraloid deterioration. The metal surface and the enamels can alternatively be protected by Incralac spray and a thin fog of microcrystalline wax, to reduce the excessively shiny aspect of the coating [40]. This is in agreement by *G. Bailey, 2012* [45], pointed out that the application of a consolidant and a coating, i.e., vapor barrier, such as Paraloid may serve to slow or halt oxidation [41]. Paraloid can be considered as an all purpose conservation material as *M.I.H. Martín, 2012* [46], for example, used it to fix fragile enameled sheets onto the metal surface with a solution of 3% Paraloid B-72 in acetone [42], whereas *J. Day, 2012* [47], suggested using Paraloid B-72 for conservation of all enameled metals objects [43]. The current study proved this suggestion and verified that a monolayer of 3% Paraloid B-72 protected enameled silver and copper metals rather than other tested synergy and did not affect the esthetic appearance of the surface. Moreover, microcrystalline wax did not enhance Paraloid B-72 effectiveness, and failed itself to give good protection either in one layer or double layers.

Conclusions

This research focused on testing coating materials to be applied to protect enameled silver and copper artifacts. Paraloid B-72 and microcrystalline wax were applied in several procedures to find out the best application method which ensures corrosion resistance and doesn't affect esthetic appearance. The experimental study accomplished by the preparation of champlevé enameled copper and silver coupons using decorative motives related to the style of original artifacts. The coupons were exposed to high humidity to accelerate ageing and tested to report any change in weight and colour. It was found that different procedures of coatings applications gave different results.

The results of weight gain and colour change tests indicated that the procedure of applying one layer of 3% Paraloid B-72 gave the best performance if compared with other tested procedures on both enameled silver and copper coupons. The procedure of applying one layer of 3% Paraloid B-72 + one layer of microcrystalline wax gave average protection, while the procedure of applying one layer of microcrystalline wax and the procedure of applying a double layer of it did not give satisfactory protection for both copper and silver coupons and caused greater colour change.

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