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Deliverable

D3.2. A guide for multi-material palette preparation

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Executive Summary

This report describes the preparation of the reference samples. The physical and chemical properties of the latter are investigated in deliverable 3.1. The reference samples are separated into two main groups. The one consists of a panel of colour reference samples reflecting the aesthetic style and stratigraphy of byzantine iconography. The second group consists of metallic reference samples reflecting the composition and manufacturing technique of mediaeval and renaissance metal works of art. Some metal reference samples have been treated with protective coating commonly used in conservation process.

The reference samples play an important role in the evolution of the project as their study feeds with the necessary datasets other activities and studies. Particularly, these datasets will be used in training the spatiotemporal simulation algorithms (WP5), they will be used for calibration of the developing scanning techniques (WP4) and most importantly they will assist in the extraction of the material specific ageing models.

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1. Introduction

A major objective of Scan4Reco project is to study the ageing procedure of art objects. To achieve this target, the development of reference samples which will be subjected to artificial ageing is required and their state will be monitored over time with the under development diagnostic techniques. These reference samples have been created according to pre-defined requirements as presented in deliverable *D3.1 Material related Booklet*.

1.1 Purpose of this report

The purpose of this report is to present the methodology followed to create the two groups of reference samples, which are paintings (Byzantine iconography) on the one hand and metallic objects (sculptures, challises) on the other hand. These samples must simulate real art objects.

In the case of paintings, the samples must reflect the aesthetic style and stratigraphy met in Byzantine iconography. Hence, the way the panels created following the basic principles of preparation and treatment as well as incorporation of the various pigment combinations used in Byzantine iconography tradition.

As concern metal reference samples, they have been made taking into account the manufacturing techniques and the alloy composition used in the past. In particular, the proper techniques of cast and post cast working, finishing and coating have been performed in order to simulate as much as possible actual metal works of art.

1.2 Scope of this report

This document mainly presents the methodology of sample creation in section 2. This section is divided in two main parts. In section 2.1, the preparation of paint samples is presented. In section 2.2, the preparation of metallic ones is presented. Finally, section 0 concludes the report.

1.3 Work package interdependencies

This work is the outcome of task 2 of the work package 3 (T3.2). Once the reference samples are created, they will be subjected to artificial ageing (T3.3) and simultaneous monitoring of their state in order reference data to be collected supporting the extraction of the material specific ageing models (T3.4). Another contribution of the reference data collection is the production of a ground truth dataset for the calibration of the scanning techniques (WP4), for example to examine if the FT-IR spectroscopy results specific spectra of the known materials. Also, the reference dataset will be used for training of the simulation algorithms to be developed in WP5. The interdependencies of the current task (T3.2) with rest tasks in the same work package as well as with the other work packages are illustrated in Figure 1.

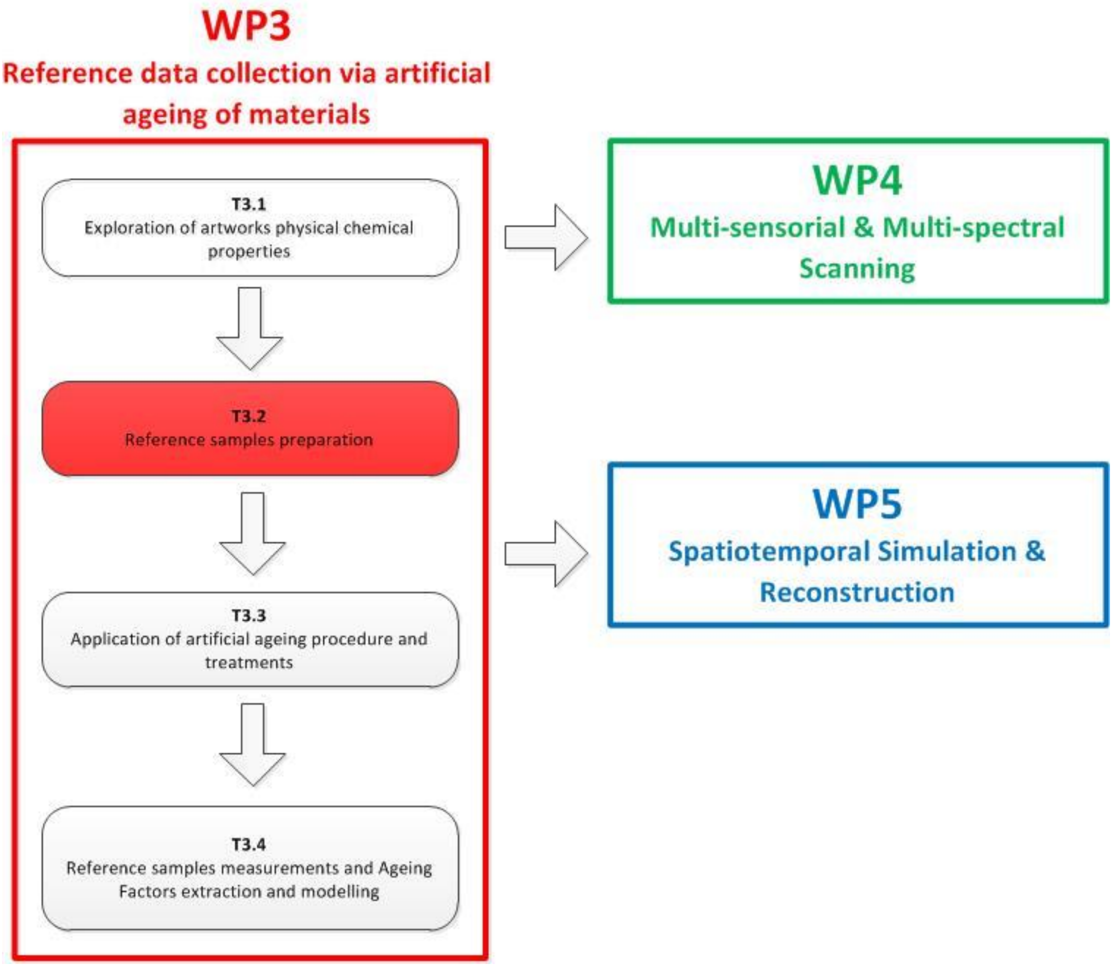

Figure 1 Overview of the interdependencies of T3.2 with the other tasks in the same work package (WP3) as well as with the other work packages.

2. Methodology

2.1 Paint Samples

2.1.1 Sample preparation

The preparation of colour samples, the choices for the preparation conditioning materials (plaster, chalk and rabbit-skin glue), the binder (egg yolk) and colors were made with much care in order to approach the genuine art of Byzantine painters. We also tried to emulate the technique of Byzantine painters using original recipes from literature [1][18][20][21][22][23][24]. Nevertheless, possible presence of additional materials, e.g. inert materials in pigments from industrial companies was not avoided.

2.1.2 Panel preparation

It was decided that the wood does not play a crucial role in the effect of color perception because it is completely covered by white preparation. Depending on the environmental conditions and the type and the cutting of wood, there are many distortions and changes with time as it expands and contracts, is moistened and dried. Therefore, changes of the wood affect the painting surface, creating cracks, even loss of material.

The research is limited on the colour perception, the behavior of colours and colour changes, on the binder and the substrate preparation. However, we chose a type of solid wood, durable and economical, which is not easily deformed. We ordered plank plywood with dimensions 1.25 x 1.50m and with thickness of 1.5cm, which was cut into boards of 45 x 30.5cm on which comfortably fit 60 samples of 4 x 4cm.

2.1.3 Glue

Firstly, the wood is treated with a rabbit-skin glue layer before applying the preparation. The glue-water ratio is 1:12, i.e. 1g glue powder in 12ml of water. The glue soaks into the water for at least 6 hours, and the mixture is then warmed slowly to the bain-marie (with care not to boil). Next, the glue is laid on the wood surface with a brush. The surface will be puttied and left to dry for about 10 minutes.

2.1.4 Preparation Layer

For the putty, more diluted glue mixture, 1:15, and hydrated plaster $CaSO_4 \cdot 2H_2O$ (Bologna gypsum) are used. The glue-plaster and glue-chalk is 1:1 volume ratio. When still warm, slowly add plaster to glue and a knoll in the container will be created. Then it is left half an hour in order the grains to break prior to meddle. Because the two phases tend to be separated, the chalk $CaCO_3$ is stirred frequently during caulking, and it may require re-heating in hot water in the bain-marie.

The chalk $CaCO_3$ is laid on the board with a large brush in thin uniform brushstrokes. Then it is left about half an hour to an hour to dry before applying the next layer. The surface is covered with more layers, vertically and horizontally. Four layers were applied with a brush and the fifth and last layer with a spatula to form a smooth and uniform surface.

We left the boards two weeks to dry thoroughly before burnishing them. Then rubbed with sandpaper of different particle size from coarse to fine, to create a smooth and glossy surface suitable for painting with tempera. On the back of the timber and on the sides were first used coarse sandpaper No. 80 and, then, the No. 360.

The squares, where the samples were placed, were etched with a pencil. As aforementioned, 60 square regions were created whose dimensions are 4x4cm.

2.1.5 Binder preparation

In egg tempera painting tradition, the binder was prepared with egg yolk and water. To separate the egg yolk from the egg white, the egg is fractured in the middle allowing the egg to fall in a bowl. You pass the yolk from the shell to remove the most of the egg white. After the yolk is flipped in the palm and is passed from one hand to another, each time washing palm with water. Then you grab the yolk from its skin with two claws (otherwise you can drill the skin slightly) and jerked into the cup to break the skin and poured the yolk clean. Then, it is shuffled with the desired amount of water to create a suitable fluid emulsion, which is left for at least an hour to settle.

2.1.6 Colour layer preparation

2.1.6.1 Samples of combination of colours

There are no specific requirements regarding the ratio colour-binder. Each pigment by nature requires a certain percentage carrier in order a homogeneous thick paste to be made having the respective absorptive capacity. We tried to create the colour with the appropriate concentration of each pigment in order to exploit its reflective ability.

According to the Byzantine iconography, successive layers of lightings and writings were applied [49]. Where the lightings are white, we add some white lead and a proportional amount of binder in the same mixture of initial colour layer to "open" the colour. The second lighting involves adding extra white so as to provide distinct gradations of colour (grayscale). Cracking was observed in the first few samples where lightings have a low pigment concentration because after the addition of the white lead pigment, these samples have a high concentration relative to the binder. Moreover, some samples contain a writing layer, which comprises mixing the initial colour layer with some carbon black or red ochre.

Both panels consist of the same colour samples placed in the same positions in both panels, but different preparation layer. The first panel has preparation layer of chalk and the second of plaster. The composition of colour layers as well as the relative position of these samples on both panels are the same and described in Table 1. Also, both panels in their final state are shown in Figure 3 and Figure 4. The way of samples fabrication regarding their stratigraphy is also illustrated in Figure 2.

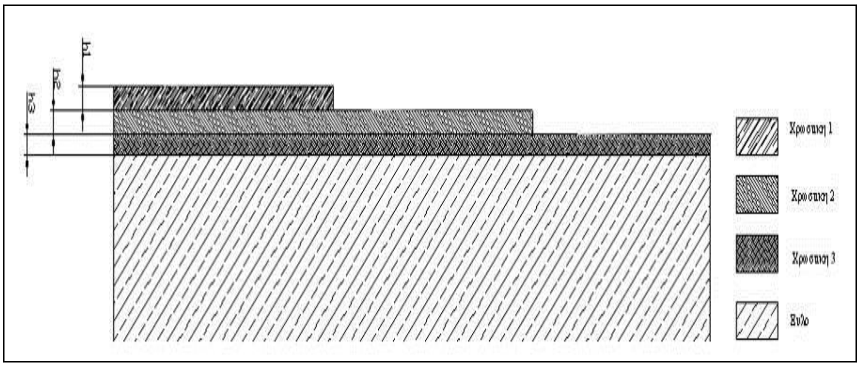

Figure 2 Way of samples fabrication. Illustration of the expected stratigraphy.

Table 1 Description of the composition and relative position oft he samples in both panels.

No	Preparatory Underpainting	Coats	Light	Coats	Glaze	Coats
1	Massicot	4				
2	Naples Yellow	7				
3a	Yellow ochre	6	2 Yellow ochre + White	3		
3b	Yellow ochre	6	1 Yellow ochre + White	3		

3c	Yellow ochre	6			
3d	Yellow ochre	6			Yellow ochre + Red ochre	3
4a	Red ochre	6	2 Minium	7		
4b	Red ochre	6	1 Cinnabar	5		
4c	Red ochre	6				
5a	Warm ochre	10	2 Warm ochre + White	3		
5b	Warm ochre	10	1 Warm ochre + White	4		
5c	Warm ochre	10				
5d	Warm ochre	10			Warm ochre + Red ochre + Black	3
6a	Hematite	8	2 Hematite + White	3		
6b	Hematite	8	1 Hematite + White	6		
6c	Hematite	8				
7a	Burnt sienna	6	2 Burnt sienna + White	4		
7b	Burnt sienna	6	1 Burnt sienna + White	4		
7c	Burnt sienna	6				
8a	Caput mortuum (P) + White	11				
8b	Caput mortuum (P) + White	11	1 Azurite	2		
9	Minium	7				
10a	Cinnabar	9	2 Cinnabar	3		

			+ White			
10b	Cinnabar	9	1 Cinnabar + White	5		
10c	Cinnabar	9				
11a	Massicot	4				
11b	Massicot	4				
12	Naples Yellow	4				
13a	Yellow ochre	4	2 Yellow ochre + White	2		
13b	Yellow ochre	4	1 Yellow ochre + White	3		
13c	Yellow ochre	4				
13d	Yellow ochre	4			Yellow ochre + Red ochre	2
14a	Red ochre	4	2 Minium	3		
14b	Red ochre	4	1 Cinnabar	4		
14c	Red ochre	4				
15a	Warm ochre	4	2 Warm ochre + White	2		
15b	Warm ochre	4	1 Warm ochre + White	3		
15c	Warm ochre	4				
15d	Warm ochre	4			Warm ochre + Red ochre + Black	3
16a	Hematite	4	2 Hematite + White	3		
16b	Hematite	4	1 Hematite + White	3		
16c	Hematite	4				
17a	Burnt sienna	3	2 Burnt sienna	2		

			+ White			
17b	Burnt sienna	3	1 Burnt sienna + White	3		
17c	Burnt sienna	3				
18a	Caput mortuum (R)	3	2 Azurite + White	2		
18b	Caput mortuum (R)	3	1 Azurite	3		
18c	Caput mortuum (R)	3				
19	Minium	3				
20a	Cinnabar	4	2 Cinnabar + White	2		
20b	Cinnabar	4	1 Cinnabar + White	3		
20c	Cinnabar	4				
21a	Green earth + Yellow ochre	4	1 Yellow ochre + White	3		
21b	Green earth + Yellow ochre	4				
21c	Green earth + Yellow ochre	4			Red ochre + Black	3
22a	Caput mortuum (R)	3	2 Caput mortuum (P) + White	2		
22b	Caput mortuum (R)	3	1 Caput mortuum (P) + White	3		
22c	Caput mortuum (R)	3				
23a	Caput mortuum (R)	3	2 Caput mortuum (R) + White	2		

23b	Caput mortuum (R)	3	1 Caput mortuum (R) + White	3		
23c	Caput mortuum (R)	3				
24a	Red ochre	4	2 Caput mortuum (P) + White	2		
24b	Red ochre	4	1 Caput mortuum (P) + White	3		
24c	Red ochre	4				
25	Warm ochre	4				
26	Warm ochre	4				
27	Caput mortuum (R)	2				
28	Caput mortuum (R)	2				
29	Cinnabar	3				
30	Cinnabar	4				
31a	Green earth	12	2 Green earth + White	2		
31b	Green earth	12	1 Green earth + White	5		
31c	Green earth	12				
31d	Green earth	12			Green earth + Black	4
32a	Verdigris	13	2 Verdigris + White	3		
32b	Verdigris	13	1 Verdigris + White	7		
32c	Verdigris	13				
32d	Verdigris	13			Verdigris + Black	8

33a	Malachite	3	2 Malachite + White	2		
33b	Malachite	3	1 Malachite + White	3		
33c	Malachite	3				
33d	Malachite	3			Malachite + Black	2
34a	Azurite	6	2 Azurite + White	3		
34b	Azurite	6	1 Azurite + White	3		
34c	Azurite	6				
35a	Ultramarine	9	2 Ultramarine + White	4		
35b	Ultramarine	9	1 Ultramarine + White	6		
35c	Ultramarine	9				
36a	Cobalt blue	8	2 Cobalt blue + White	3		
36b	Cobalt blue	8	1 Cobalt blue + White	3		
36c	Cobalt blue	8				
37a	Prussian blue	3	2 Prussian blue + White	2		
37b	Prussian blue	3	1 Prussian blue + White	3		
37c	Prussian blue	3				
38a	Indigo	8	2 Azurite + White	4		
38b	Indigo	8	1 Azurite	2		

38c	Indigo	8				
39a	Indigo	4			Azurite glaze	6
39b	Indigo	4				
40a	Burnt sienna	8	3 Warm ochre	6		
40b	Burnt sienna	8	2 Red ochre	6		
40c	Burnt sienna	8	1 Hematite	6		
40d	Burnt sienna	8				
41a	Green earth	3	2 Green earth + White	2		
41b	Green earth	3	1 Green earth + White	4		
41c	Green earth	5				
41d	Green earth	3			Green earth + Black	2
42a	Verdigris	8	2 Verdigris + White	2		
42b	Verdigris	8	1 Verdigris + White	3		
42c	Verdigris	8				
42d	Verdigris	8			Verdigris + Black	4
43	Verdigris	9				
44	Azurite	5				
45a	Ultramarine	3	2 Ultramarine + White	2		
45b	Ultramarine	3	1 Ultramarine + White	3		
45c	Ultramarine	3				
46a	Cobalt blue	4	2 Cobalt blue + White	2		
46b	Cobalt blue	4	1 Cobalt blue +	3		

			White			
46c	Cobalt blue	4				
47	Cobalt blue	4				
48a	Indigo	4	2 Azurite + White	3		
48b	Indigo	4	1 Azurite + White	2		
48c	Indigo	4				
48d	Indigo	4	2 Azurite + White	3	Azurite glaze	2
48e	Indigo	4	1 Azurite + White	2	Azurite glaze	2
48f	Indigo	4			Azurite glaze	2
49	Indigo	3				
50a	Prussian blue	4	2 Prussian blue + White	2		
50b	Prussian blue	4	1 Prussian blue + White	3		
50c	Prussian blue	4				
51	Green earth	4				
52	Green earth	4				
53	Verdigris	7				
54	Azurite	3				
55	Ultramarine	4				
56	Ultramarine	4				
57	Cobalt blue	3				
58	Indigo	3				
59a	Yellow ochre + Black	4	1 Yellow ochre + White + Cinnabar	3		
59b	Yellow ochre + Black	4				

59c	Yellow ochre + Black	4	Red ochre + Black	3
60a	White + Black	3		
60b	White lead	4		

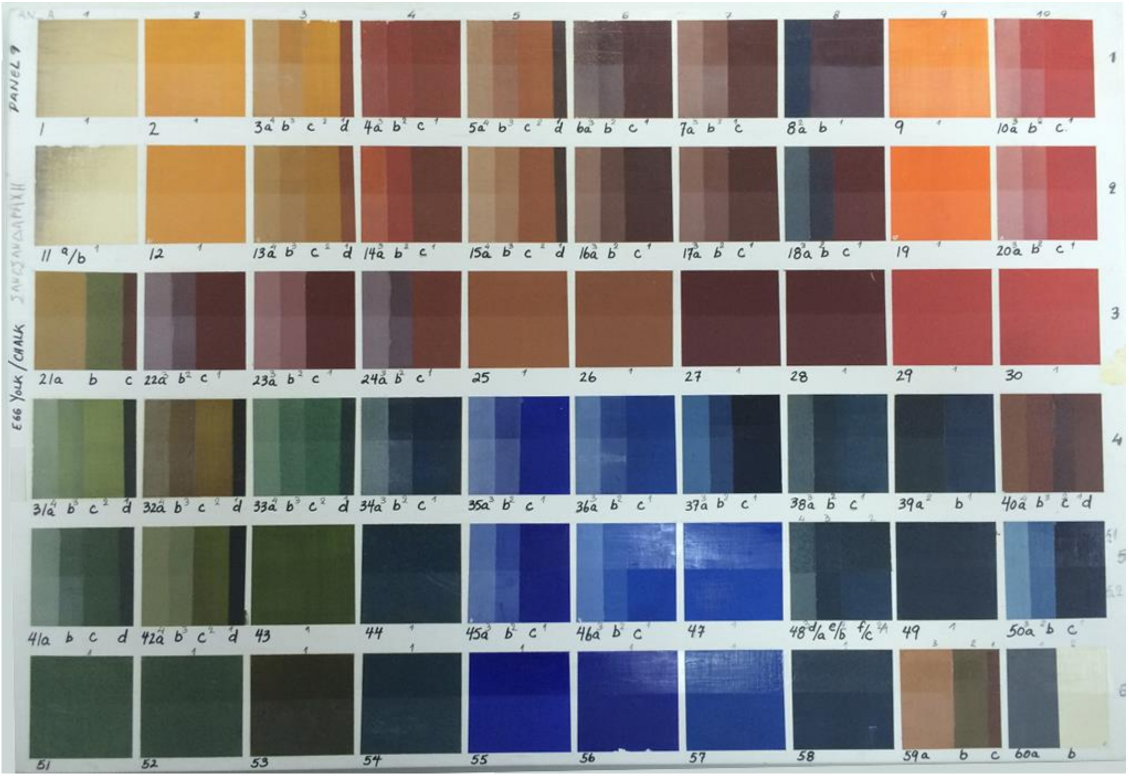

Figure 3 Panel of samples pallette with chalk as preparation layer.

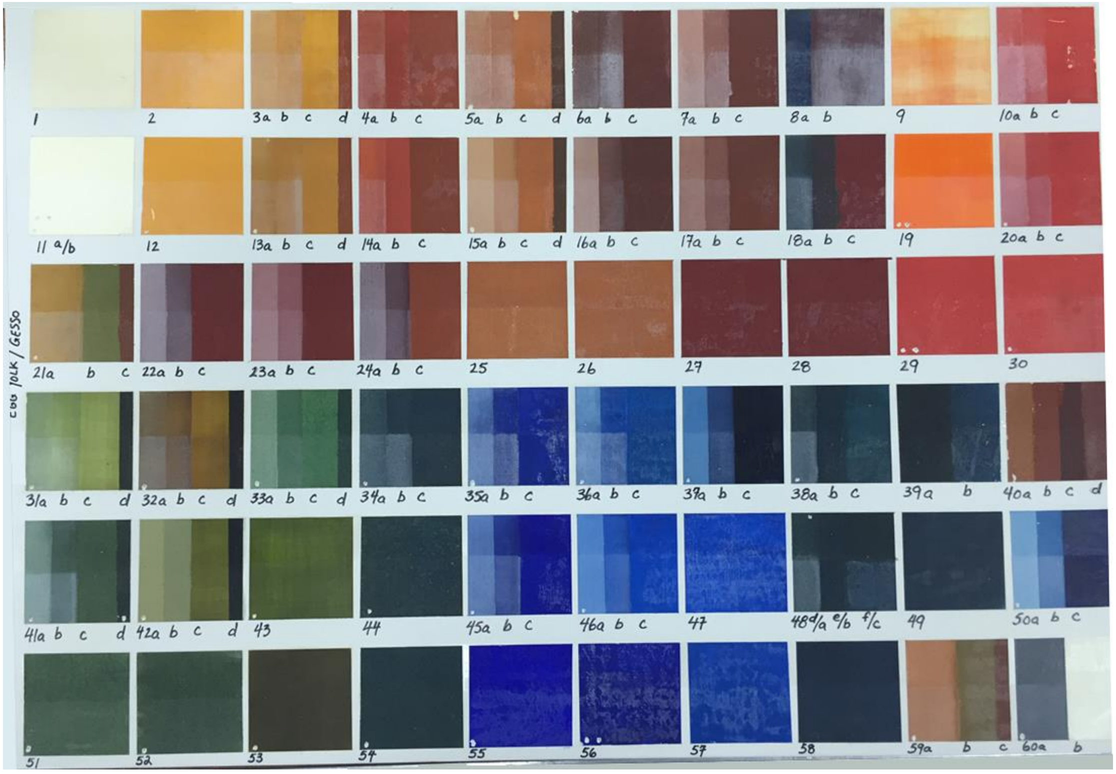

Figure 4 Panel of samples pallette with plaster as preparation layer.

2.1.6.2 Samples of the same colour and different thickness

In order to study the penetration of the various radiations emitted by the different modalities, we also use existing reference samples of one pigment with gradually increasing thickness over white and black background The two different backgrounds are selected since they are the 99% and 2% reflecting materials of the radiations that will be used from the modalities acquiring information using electromagnetic waves in the visible and the infrared area of the spectrum. These modalities are actually the most of the selected ones for scan4reco. In the case of the tomographic technique (ultrasounds of high frequencies the dark background which is the Carbon Black is highly absorbing material and with chalk in the form that is described in deliverable 3.1 and this one) is highly reflecting.

These samples will also serve as the samples in order to measure the uncertainty of the measured values according to ISO ASTM 906-12 and EN-14127 related to the measurement of the reflection coefficient (UV-VIS, IR spectroscopic mapping techniques) and the thickness measurements (Ultrasound of high frequency respectively).

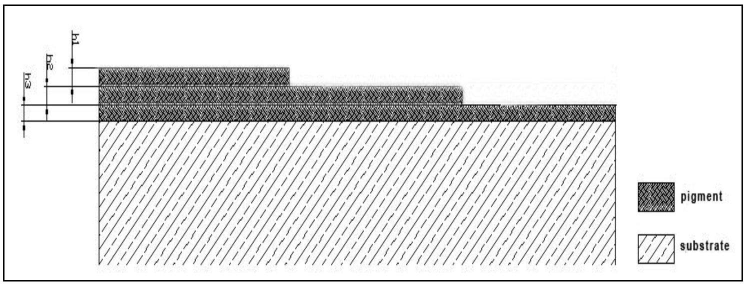

Figure 5 Panel 6 of samples of one pigment Palette with gradually increasing thickness

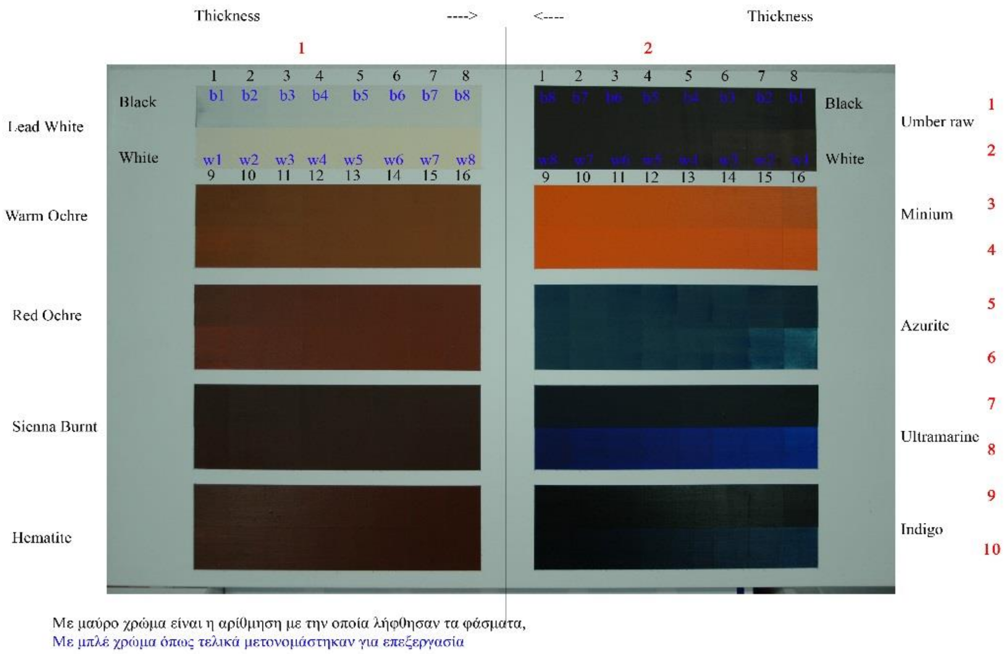

Figure 6 Panel 6, Layers of gradually increasing thickness of the same pigment.

2.1.6.3 Clone - "Phantom" Icon

According to the findings described in deliverable 3.1 especially for the icon of Hodegetria the clone icon is already under creation. The way that this icon is created is following the way that it was created on the 14th century. The preparatory layers as well as the paint layers as well as the lightings of the mantles or the faces are also following the way that the corresponding reference samples are created and vice versa simulating with high accuracy the real objects. The overpainting will be created the next months.

Figure 7 Mantles' preparatory layer

Figure 8 Mantles' preparatory layer more

Figure 9 Faces preparatory layer more

Figure 10 Faces preparatory layer more

Figure 11 1st flesh layer

Figure 12 1st flesh layer more

Figure 13 2nd flesh layer

Figure 14 Final result (initial painting)

The result is very near the initial painting revealed after the conservation treatment of it (see images in deliverable 3.1):

Figure 15 Iinitial painting, real icon

Figure 16 Final result (initial painting) clone

The initial measurements are already performed and will be presented in deliverable 3.4. We are presenting in this deliverable the infrared imaging that was acquired in the area of the face in cross relation with the infrared image that was acquired from the initial painting of the real object revealing the overpainting. The Infrared imaging of the real painting revealing the underpainting and the inafared image of the initial painting of the clone are in very good agreement among them! The initial design, which was revealed in the infrared image, performed by the iconographer is in very good agreement with the revealed design.

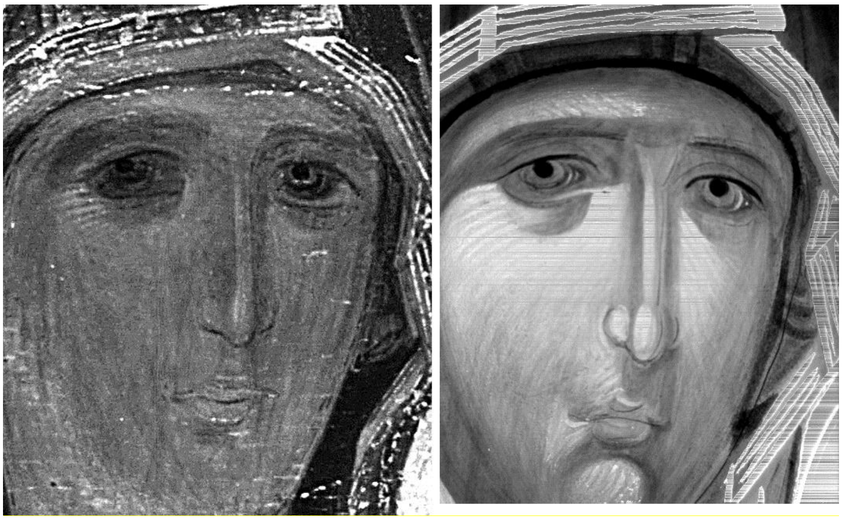

Figure 17 Infrared imaging of the real painting revealing the underpainting and the inafared image of the initial painting of the clone.

2.1.7 General notes during painting

The *azurite*, *malachite*, natural *cinnabar* and *green earth* are very coarse-grained pigments, which create difficulties in their uniform application with brush. The granules of pigments tend to deposit in the carrier and therefore require constant agitation. After the first coat, these pigments in general worked more pleasant, especially cinnabar. The *green earth* generally requires high pigment concentration and prior to being applied it was ground on a tile with a spatula using a small portion of carrier in order to crack the coarsest grains. This procedure was not followed in the cases of *azurite* and *malachite* because, according to the literature, the best colour performance is achieved when composed of coarse particles.

It was observed that *verdigris* has not good compatibility with the binder. The very fine particles tend to float and, generally, *verdigris* requires persistent blending to moisten the granules. It is quite transparent, requires a high concentration of the pigment, requires many coats for the better performance of colour and requires homogeneous coating of the preparation layer. Also, a gradual deterioration of colour from bright green to brownish green was observed as well as different colour performance depending on the dilutions.

On the other hand, *Prussian blue* requires minimum concentration of the pigment to provide colour. Actually, its hue tends to black when there is high concentration of pigment. Due to the high colouring capacity minimum concentration of the pigment is required for the lightings. The intense blue colouring, i.e. *ultramarine*, *indigo*, *Prussian blue*, need much care regarding their concentration in order not to become too dark (not to lose their blue tint).

The *Naples yellow* has a very good coating ability. However, granules tend to aggregate. *Massicot* has also good coating ability. For unknown reasons, however, a rapid change in colour from intense pure yellow to gray-green was observed. There appears to be some reaction with light, in contrary to literature which states that is stable.

Furthermore, the *lead white* has good coating ability, but it tends to dry quickly and continuously requires the addition of binder to maintain good fluidity and surface cracking to be avoided when dry.

Good behavior in application of the colour sample is observed in pigments *caput mortuum* and *red lead*, which are fine-grained hence they have very good compatibility with the binder. Dispersion is easily achieved to create a uniform layer with excellent coating ability. Generally all ochres are worked relatively easily.

In general the colors are laid evenly on the preparation of chalk, which exhibits greater absorbency of the binder. Often seen that satisfactory coating of the surface with the color is obtained with fewer layers on the chalk, whereas, plaster requires two or more layers to reach the same optical effect. Typically the colors appear brighter to the eye when placed on the chalk.

Finally, the board with preparatory layer of chalk shows large cracks during the preparation, which is due to evaporation of the glue during the application.

2.2 Metallic Samples

The preparation of metal samples for the simulation of dynamic processes (such as ageing or restoration treatments) has be done taking into account the artistic techniques and the alloy composition of the past. In order to have meaningful mock-ups of metal artefacts, the proper techniques of cast and post cast working, finishing and coating as resulting from D3.1 have been applied.

In the EURs document (D2.3) indeed, the respondents pointed towards the need that the effects of restoration and maintenance treatments, as well as the application of layers of protective and finishing materials be as faithful as possible in order to provide real, complex systems for studying (EUR/MC/01). The metallic mock-ups will provide a description of the outmost surface structure and appearance in a quantitative and objective way through the measurements of the following properties (EUR/MC/02):

- regularity of micro-3D structures (texture)
- colour of opaque or glossy parts,
- opaque, glossy or mirror-like behaviour
- micro distortion that the object produces when reflecting the surrounding environment, or how it diffuses light
- level of roughness,
- level of outer layers transparency

Also physical and chemical features of the subsurface structure like molecular and elemental composition of the layers, morphology of the layers, adhesion and cohesion of the layers, presence of cracks and detachments, thickness of the layers are of great importance to provide a full description of the ongoing phenomena on the metal surfaces (EUR/MC/03).

2.2.1 Silver samples

2.2.1.1 Preparation of silver alloy coupons

Silver has been known and used since ancient times due to its pleasant white color, its reflectivity, polishability and shine. Since pure silver is too soft for most application, it is almost always used in alloyed forms. Centuries of experimentation have determined that the most suitable alloys contain an addition of 7.5% to 20% copper. Silver-copper can be alloyed together in any desired proportion (Figure 18) and these alloys have been much used in jewellery and silversmithing work. In this binary system, if the content of copper is low, less than 8 %, the visual properties of the alloy, in terms of colour, reflectivity and tarnish resistance, are very close to pure silver. However, the melting point is lower and the workability is higher than for the pure metal. These features make the silver-copper alloy a good choice for sculptural forming, chasing work and deep drawing. This alloy combines good formability during working and the capability to keep its shape when finished. By means of a good control of the copper content in the melt, alloys have been developed over time in which particularly good workability and optimal visual properties have been combined. Over the course of time, certain alloys have been developed to match some visual requirements or to meet the needs of a particular working technique. For example, alloys with a high melting point are preferred for enamelling because coloured enamels must be fired at 750°-800°C. The most common silver-copper alloys in silversmithing are Ag970, Ag925, Ag900, Ag835, Ag800 and Ag720. Metal designation systems legally refer to the precious ingredients of an alloy, so Ag900 means that of 1000 parts of an alloy, 900 parts are silver, the remaining 100 parts consist of the addition metal, in this case copper. Ag 970 shows surface properties very close to fine silver because of the low copper content (colour and tarnishing resistance are the same as pure silver). Because of its high melting point, this alloy is particularly well suited for enamelling and, since it can be easily deformed, it is a good choice for sculptural forming and chasing work. Ag 925 is the English "sterling silver": due to its working and wearing characteristics, it is the preferred alloy for silver jewellery. The alloy shows colour and tarnish resistance similar to pure silver and combines good formability while working with necessary stability in use. From Ag 900 to higher copper content, the alloys no longer have the fine silver colour; the latter can be achieved by repeated pickling after the work is finished. Nevertheless, these alloys are used for mass produced manufactured jewellery and massive work because of their low cost.

32 silver coupons (7 cm x 2.5 cm) were cut from a sterling silver sheet (Ag 92.5%-Cu 7.5%) 0.1 cm thick. The relatively large silver coupon size was chosen to avoid edge effects. Before treating, the coupons were finished by smoothing the edges by means of a grinder. The surface was then polished using progressively finer abrasive paper and grounded with abrasive pastes of decreasing granulometry. After thorough rinsing with acetone, the silver coupons were air dried at ambient conditions.

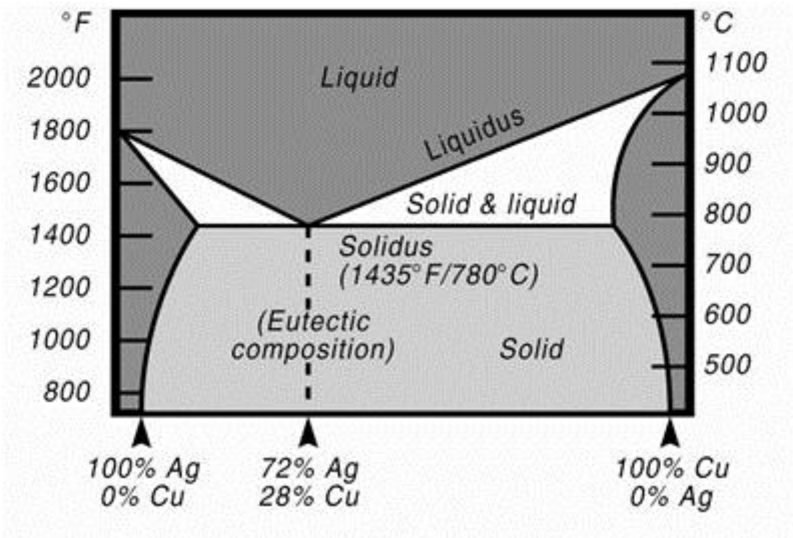

Figure 18 Silver-copper phase diagram
http://www.lucasmilhaupt.com/en-US/about/blog/2014/3/liquidus-vs-solidus.

2.2.1.2 Finishing techniques

Real heritage silverworks often exhibit subtle details worked by many different finishing techniques (engraving, repoussé, chasing, and etching). The visual characteristics as well as the ageing pattern of silver items depend on both the alloy composition and the working technique used to shape the surface.

Among the many possible techniques, we made the decision to reproduce chasing and engraving on the coupons since they are very common on Middle Ages and Renaissance silverworks. This should allow reproducing the visual properties of an actual worked metal surface as well as its behaviour against the resistance to tarnish. Chasing is a metalwork technique used to define or refine the forms of a surface design and to bring them to the height of relief required (Figure 19). The metal is worked from the front by hammering with various tools that raise, depress, or push aside the metal without removing any from the surface.

Engraving can be described as the process in which a hard, shaped and sharp piece of steel, called “graver” is pushed forward through the metal’s surface continuously curling the metal while leaving behind a small furrow (Figure 20). The shape of the graver and the angle at which it is held will decide the furrow shape. Many combinations of graver’ angle and shape are possible, each leading to a particular style of engraving (Figure 21). Small hand held graver is called “bulino”. Its use allows producing exquisite renderings in metal by creating thousands of small dots or lines.

Figure 19 Detail of an historical silver item with chased surface.

Figure 20 Detail of an historical silver item with engraved surface.

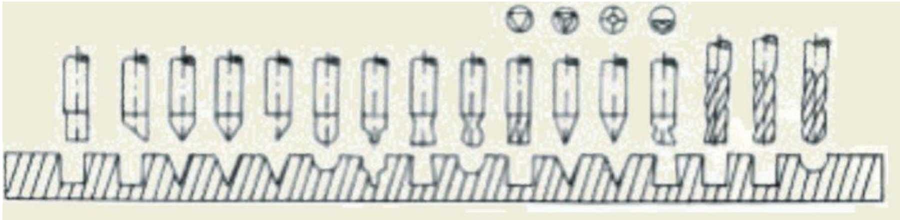

Figure 21 Shape of different gravers and the relative furrow shape

Two series of 8 coupons each underwent chasing of the whole surface. The process was made to simulate the visual features induced on the surface by one of the most common working techniques. Chasing was made by heating the coupons on a mild fire and pickling them. Each coupon was then put on an anvil over a leather cloth and the surface was processed by a punch and a lightweight hammer (Figure 22).

Figure 22 Punching the silver coupons

Engraving was simulated by incising a furrow on each coupon with a graver.

2.2.1.3 Application of protective coatings

The common pollutant hydrogen sulfide (H_2S) is well known to be the primary cause of tarnish on silver objects, occurring at concentrations as low as 0.2 parts per billion, which can be built up also in tightly sealed storerooms. The source of it is supposed to be indoor-generated pollutants. Passive methods of sulfide mitigation for storage and display environments are the goal of most museums. When these non-invasive methods are not feasible, however, silver artifacts are coated to protect against the easily-developed tarnish that detracts from the appearance of objects, obscures important details, and creates time-intensive cleaning and polishing maintenance work. The choice of coating is crucial, since coating failure can result in even more destruction to the object than occurs with no coating at all. A failed coating may require significant time for removal, cleaning, and recoating. The repertoire of coatings currently in use in the conservation field is rather limited. Only limited test reports of those coatings exist in the literature and the use of some is controversial, with conservators reporting conflicting experiences with their use.

Here we focus on three coatings currently used by conservators for indoor silver protection, namely a nitrocellulose lacquer, an acrylic polymer, and a microcrystalline wax.

The three materials are acknowledged by the metal conservators' community for their stability and reversibility as well as for their good aesthetic properties.

On account of excellent appearance, ease of application, and tarnish prevention, cellulose nitrate lacquers have been the most popular coatings for this purpose. Cellulose nitrate coatings are broken down by ultraviolet light, however, and reapplication is necessary after 10–20 years. The acrylic resins Paraloid B-72, B-48N, and B-44, which are so often used by conservators on other types of artefacts because of their stability, are also applied on silver, despite their well-known tendency to yellowing and discoloration. Microcrystalline waxes have also been used for coating silver, particularly when a multi-material item must be protected.

The three coating materials tested in task 3.2 are among those widely used by conservators on silver, although each is known to have drawbacks. They include nitrocellulose lacquer (trade name Zapon supplied by Lechler), acrylic resin (Incral 44 supplied by CTS) and microcrystalline wax R21 (supplied by Bresciani). Zapon lacquer was diluted with a blend of 20v% isopropyl alcohol – 40v% isooctane – 40v% acetone, in a percentage of 70wt% of the lacquer. Incral was diluted with butyl acetate 70wt%. The microcrystalline wax was diluted 2wt% in cyclohexane and applied after gently warming it.

Coatings were applied to the silver coupons by brush, leaving an untreated strip on each coupon for measurement reference (Figure 23). The application of two overlapping coatings was made by parallel brushes. Microcrystalline wax was polished with a cloth. Coated silver coupons were air dried. A progressive number from 1 to 32 was engraved on the back of the sample in order to have an unambiguous identification of the sample. Each coating was applied on four coupons, two smooth and two chased, for a whole of 32 coated samples. One smooth and one chased coupons were left untreated as reference.

Figure 23 Set of silver coated samples (smooth and chased).

In Table 2 the layout of coatings is shown. Coatings were applied on the coupons according to the most common practices, namely one or two coats of nitrocellulose or acrylic resin. The so-called "double layer protection" was also included in the tests, with a coat of microcrystalline wax on top of a coat of either nitrocellulose or acrylic varnish. This type of protection is mainly used on multi material items when the nitrocellulose and the acrylic are applied locally on silver and the wax coating is spread both on silver and the surrounding materials.
The aim of having a range of materials and application procedures on the coupons is to test the Scan4Reco system on a variety of situations pretending real cases and to check the ability of the system to distinguish materials and thicknesses, which look similar by the naked eye, and to enhance the different response toward exposure to pollutants.

Table 2 Layout of coatings on silver coupons.

Smooth surface	**1 coating of nitrocellulose lacquer**	**2 coatings of nitrocellulose lacquer**	**Half surface with 1 coating and half with 2 coatings of nitrocellulose lacquer**
Chased surface	1 coating of nitrocellulose lacquer	2 coatings of nitrocellulose lacquer	Half surface with 1 coating and half with 2 coatings of nitrocellulose lacquer
Smooth surface	1 coating of acrylic emulsion	2 coatings of acrylic emulsion	Half surface with 1 coating and half with 2 coatings of acrylic emulsion
Chased surface	1 coating of acrylic emulsion	2 coatings of acrylic emulsion	Half surface with 1 coating and half with 2 coatings of acrylic emulsion
Smooth surface	Double layer: 1 coating of acrylic emulsion + 1 coating of wax		
Chased surface	Double layer: 1 coating of acrylic emulsion + 1 coating of wax		
Smooth surface	Double layer: 1 coating of nitrocellulose lacquer + 1 coating of wax		
Chased surface	Double layer: 1 coating of nitrocellulose lacquer + 1 coating of wax		

2.2.2 Bronze samples

2.2.2.1 Preparation of bronze alloy coupons

Among the possible copper alloys, the most encountered ones are those with tin, called "bronze". In past times, often lead was added to the mixture of copper and tin, producing a series of ternary alloys of copper-tin-lead with lower melting temperatures, making the bronze easier to cast and economizing on the use of tin, which was relatively expensive in the ancient word.

The tin bronzes can be divided into two categories, the low tin bronzes and the high-tin bronzes. The former contain less than 17% tin, the maximum theoretical limit of the solubility of tin in the copper-rich solid solution (Figure 24). Most ancient alloys have tin contents less than 17%, generally around 13%. The superior properties of such an alloy made it much appreciated by the ancient metallurgists since at this level the bronzes can be easily cold worked and annealed. The bronze shows a segregated structure, usually with a core dendritic growth rich in copper and an infill of the alpha+delta eutectoid surrounding the dendritic arms. The cooling rate and the kind of casting involved greatly affect the amount of interdendritic delta phase.

For this study a 90% copper - 10%tin was chosen, since it is representative of most ancient alloys used for statuary, apart from impurities or trace elements. A binary alloy with an approximate tin content of 10% was also much employed in the Renaissance times, when sculptors rediscovered the antiquity and the materials used for ancient monumental statues.

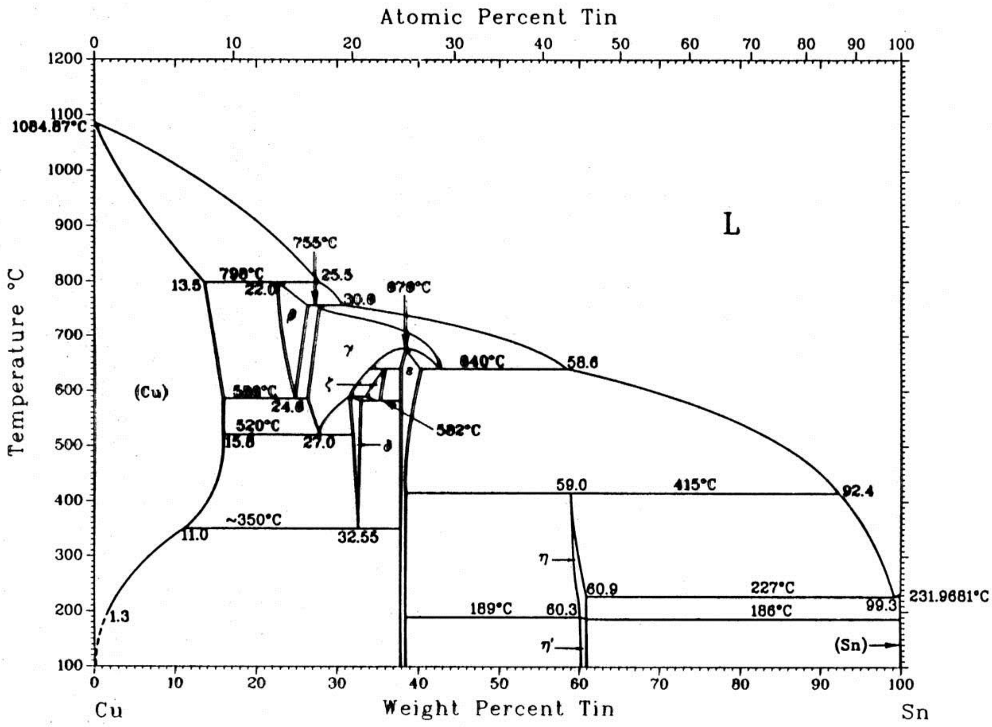

Figure 24 Copper-tin phase diagram [48]

The coupons were prepared by casting in order to have a genuine uneven surface from the visual point of view, including micro cracks and defects (Figure 25). A mould 0.4 mm thick made of refractory bricks was made at first, with sizes which allow obtaining three 8 cmx5 cm coupons. The 90/10 bronze was melt at 1100°C and poured in the warmed mould.

After casting, the ingot was removed from the mould and cooled down slowly, and then it was cut into three coupons. One face was polished carborundum paper sheet. Finally, the coupons surface was refined with pumice powder, a finishing process which was used in past times. On the rear, a progressive number was stamped on each coupon. An overall number of 19 coupons were produced.

Although patina layers are generally encountered on the surface bronze objects, the coupons were not patinated. Patinas on bronze artistic or historical objects can be naturally occurring or artificially created. A number of different patinas exist, with varying composition, color, glossy, stability, thickness and so on. Due to this broad range of variations, which makes it difficult to choice a specific patination recipe, the decision was made to not apply or create any patina on the coupons surface.

Figure 25 Magnified image of the uneven surface of a coupon showing defects and micro holes (left), compared with the uneven surface of an actual contemporary copper-alloy artifact (right).

2.2.2.2 Application of protective coatings

Unprotected outdoor bronze corrodes readily when an electrolyte meets the metal. The metal, acting as the anode, readily oxidizes while a cathodic reduction reaction of O_2 and H_2O occurs. Protection from bronze corrosion is thus very important when trying to conserve bronze sculpture situated outdoors. Protective coatings are thus commonly applied on outdoor bronzes. Significant features commonly indicated by conservators to be of importance for a coating are the weather resistance, the visual appearance the coating gives to the bronze surface and the ability of a coating to be removable. Among the most used materials encountered in bronze protection are wax coatings and synthetic resin belonging to the acrylate polymer class. A debated role in slowing down the corrosion is that of some molecules that act as corrosion inhibitors and are added to the protective blend. The most renewed inhibitor is benzotriazole (BTA). Since the requirements that a coating must have are rarely exhibited by a single material or material class, the application of a layered coating is a common practice, so that to exploit at best the aesthetic, durability and resistance properties of each material.

In Scan4Reco, we chose to lay both wax and non-wax commercial products and some layered combinations of them. The aim of having many coatings is to check the capability of the system to detect differences of the surface and sub-surface properties of the coated bronze samples at various stages of the aging process.

The assessment of the extent of unevenness is among the aims of the application of the Scan4Reco set of measurements. This is indeed a critical point since the distribution of the coating product and how this affect its performance is so far not fully investigated.

To the purpose, a blend of waxes traded under the name of Soter (supplied by Bresciani), much employed in Italy was used. Soter consists of 20-24 wt% crystalline wax, BTA and synthetic organic polymer, dispersed in turpentine and esthers. Two kinds of Soter wax were mixed, 50wt% OC 501(light and matt) and 50 wt % LS 202 (dark and gloss), after melting them with a hot (70°C) water bath. A second wax was also chosen for application, traded under the name of Reswax (supplied by CTS). Reswax consists of a mixture of microcrystalline and polyethylene waxes. It was dissolved in two solvents to check if any difference in the coatings exists and is detectable due to the influence of the solvent properties, mainly the evaporation rate. Reswax was prepared both as 21 wt% blend in ligroin 100-140 (boiling point in the 100 °C-140°C range) and as 21 wt%

blend in isooctane (boiling point 99°C). Two commercial acrylic coatings were also chosen, Paraloid B44 (supplied by CTS) and Incral44 (supplied by CTS). The former is a registered trademark resin composed of methyl methacrylate and ethyl acrylate copolymer. Paraloid B44 is also the primary ingredient in Incral44, together with BTA. Incral44 was used as a 30 wt% solution in acetone, while ParaloidB44 was dissolved 15 wt% in acetone.

As far as the application is concerned, the bronze coupons were warmed up before the application of coating until the surface was warm. A small strip was left on each sample with no coating as reference. The layout of coating application is given in Table 3. Two replicas for each coupon were prepared so that the overall number of treated samples is 18 (two sets of 9 treatments each) with an additional, not treated coupon. When a double or triple layer is applied a criss-crossed brushing modality was used. Microcrystalline wax was polished with a cloth. To the naked eye, the surface of coupons looks very uneven, with areas where the coating material looks to be not present and areas with evident piling up. A progressive number from 1 to 19 was engraved on the back of the sample in order to have an unambiguous identification of the sample (see Figure 26).

Table 3 Layout of coatings on bronze coupons.

One coating	**SOTER WAX**	**INCRAL44**	**RESWAX (LIGROIN)**	**RESWAX (ISOCTANE)**	**PARALOI D B44**
Two coatings	PARALOID B44 + RESWAX	INCRAL44 + SOTER			
Three coatings	SOTER + INCRAL44 + SOTER	RESWAX + PARALOID B44 + RESWAX			

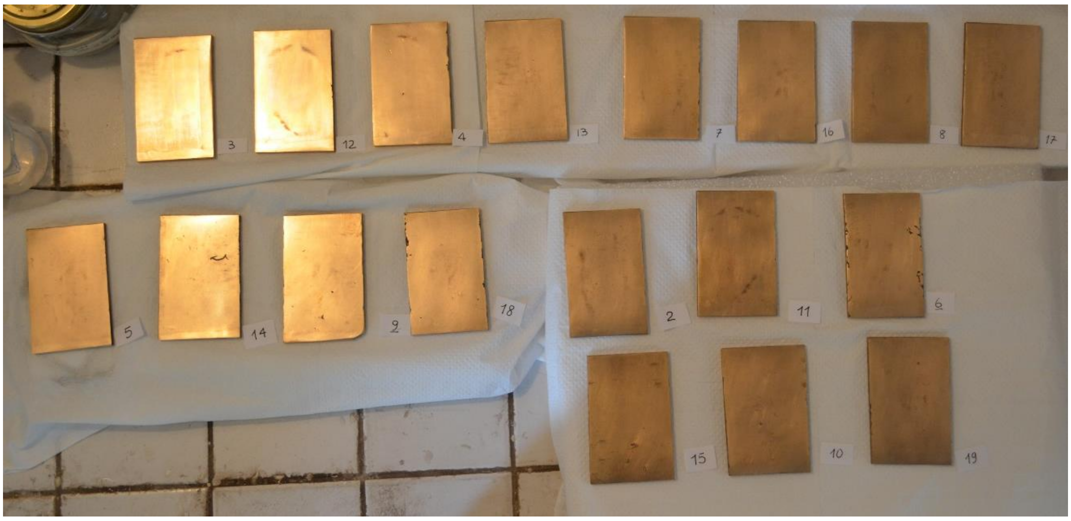

Figure 26 Bronze coupons after coating.

2.2.2.3 Application of transparent patinas

Little copper-alloy sculptures created for collections usually have an artistic patina and/or patches of different finishing materials for aesthetic and protection reasons as well. Many recipes exist on ancient patinas, transparent as well as matt ones. These patinas show a range of colors and glossy, depending on the artist choice, the period of creation, the purpose of patination.

Some of the very many recipes and variations for patinas were chosen to check the capability of the system to detect the presence and the thickness of different layers on the surface. The co-existence of patches of different composition and thickness on the object' surface, which are not visible to the naked eye, is indeed very challenging to the conservators' work, particularly as far as the cleaning of the surface is concerned.

We focused on reddish hue transparent patinas that are often encountered on Renaissance Florentine bronze statuettes. An overall number of 10 samples were made, according to the recipes listed in Table 4. Among the recipes chosen for testing in Scan4Reco, there are the so called "spirit varnishes", consisting of natural resin dissolved in alcohol, the "solvent varnishes", consisting of natural resins dissolved in monoterpenic oils, like lavender oil, and the "oleo-resinous varnishes", containing both natural resins and oils. They were applied on sheets of an alloy with approximately the following composition: Cu 88%, Pb 2%, Sn 6%, Fe 0,1%, Ni 0,2%, Sb 0,04%, P 0,03% and Zn 4%. A number was engraved on the front of the sheet for the unambiguous identification of the patina recipe applied on metal.

The sheets were degreased with diluited sulphuric acid, the surface was then brushed with a steel brush and polished with fine abrasive papers. The patinas applied on the alloy sheets are shown in Figure 27.
The recipes include all natural components: natural resins (mastic, sandarac, shellac, Burgundian pitch, Venetian turpentine, gommagutta), natural oil (linseed oil), terpenic oils (turpentine oil), natural dyes, giving the patinas a reddish or gold-like tone (Rubia, dragon' blood, aloe, gamboge). Some of them include inorganic Fe oxide - based pigments, like sanguigna, iron oxide and hematite.

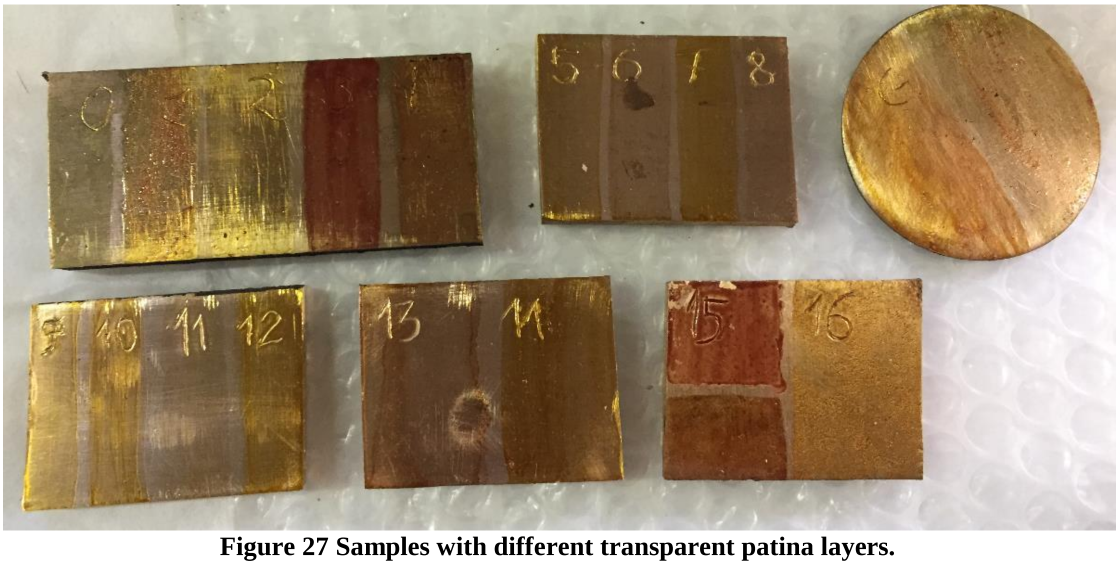

Figure 27 Samples with different transparent patina layers.

Table 4 Layout of samples of patinas on copper alloy.

Sample 0	mastic resin + linseed oil
Sample 1	mastic resin + linseed oil + lacca di robbia
Sample 2	mastic resin + linseed oil + sanguigna
Sample 3	mastic resin + linseed oil + iron oxide
Sample 4	mastic resin + linseed oil + hematite
Sample 13	sandarac + shellac+ dragon' blood + Venetian turpentine; (*solvent ethyl alcohol, 1 coat and 2 coats)*
Sample 14	sandarac + dragon's blood + aloe +gamboge *(in ethyl alcohol, 1 coat and 2 coats)*
Sample 15	Top: Venetian turpentine, hematite in turpentine oil Bottom: hematite in linseed oil + 1 top coat of linseed oil
Sample 16	gommagutta in linseed oil + Rubia
Sample G	Left Side: sandarac+shellac+dragon' blood+Venetian turpentine; *(solvent ethyl alcohol)* Right Side: mastic resin+linseed oil+Rubia+Burgundian pitch

3. Conclusion

The samples and the clone icon are subjected to initial measurements using the various modalities which will be presented to forthcoming deliverables. From the initial measurements the samples appear to simulate with very high fidelity the techniques and thee styles of the art objects. This will result to have a basis for the calibration of the methods and techniques that will be developed within the project Work Packages 4 and 5.

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[49] Scan4Reco Deliverable 3.1 Material Related Booklet