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Executive Summary

This report summarizes and presents the methodology followed in order to analyse the materials under investigation and their corresponding physical and chemical properties. The materials of interest in the Scan4Reco project consist of paintings from Byzantine iconography and metallic objects (silver and copper) from Medieval and Renaissance metalworks. The document presents the historical and bibliographical sources that determine the nature of these materials as well as categorizes them. This document aims to lay the foundations for choosing and preparing suitable mock-ups samples for studying the ageing procedure of these materials. A well-established experiment ensures the successfulness of the scientific effort. This deliverable is the establishment of the creation of the reference samples on which measurements using the various modalities will be performed in order to target optimally to their final development.

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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 is required. The samples will be subject to artificial ageing and their state will be monitored over time with the under development diagnostic techniques. These reference samples must have specific well-defined properties similar to the real art objects in order the study to satisfy the actual needs of conservation science. In this document, the physical and chemical properties of the art objects of interest, i.e. Byzantine paintings and Medieval and Renaissance metalworks are examined.

1.1 Purpose of this report

The purpose of this deliverable is to investigate and present the physical and chemical properties of the material types related to the project. Particularly, we focus on paintings and metallic objects. Particularly, the paintings regard the Byzantine iconography, while, the metals refer to Medieval and Renaissance metalworks.

On the one hand, in the case of the paintings, the investigation regards the chemical and physical properties of the materials met in Byzantine iconography. The investigation is based on some bibliography and on studies of real paintings performed at the Art Diagnosis Center of "ORMYLIA" Foundation. Particularly, the stratigraphy in the tradition of byzantine iconography is initially reported. Thereafter, the properties and the role of each layer are described, and, finally, each material and its properties are separately analysed.

On the other hand, in the case of metallic objects, the focus is on Medieval and Renaissance metalworks, particularly on luxury, liturgical and artistic objects made of silver and copper alloys. The investigation is based on literature and on outstanding case studies encountered in the Opificio delle Pietre Dure regular work. In particular, the properties of such metalworks are described starting from the alloy composition. Thereafter, the finishing and decorative techniques are reported as well as the most common degradation patterns. Finally, the aims and the means of protective coatings are described.

Finally, this report aims to provide adequate information for the preparation of the respective samples/mock-ups in order to satisfy the important user requirement EUR/MC/01. The required EUR/MC/01 has been specified in project's deliverable ***D2.3. Scientific end-user and public requirements*** as following:

EUR/MC/01	**Standardized preparation of material samples/mock-ups**	**Important**
The preparation of samples for the simulation of dynamic processes (such as ageing or restoration treatments) must be done taking into account the artistic techniques and the composition of the past. In order to have meaningful mock-ups of painted and metal artefacts, the right techniques of applying preparation and painting layers and of post cast working and finishing must be known and applied. End-users need that the effects of restoration and maintenance treatments, as well as the application of layers of protective, finishing, over-painting materials be as faithful as possible in order to provide real, complex systems for studying. To obtain that, the samples must have a suitable size.		

1.2 Scope of this report

This document is divided in two main parts. Firstly, in section 2, the basic elements of Byzantine iconography are presented, from the style and stratigraphy of real cases of byzantine paintings to the basic materials used. Next in section 3 the metallic art objects and their basic properties are presented. Finally, section 4 concludes the report.

1.3 Work package interdependencies

This work is the outcome of task 1 of the work package 3 (T3.1). Summarizing the basic materials and their properties under investigation, it leads to the preparation of the respective reference samples (T3.2). Subsequently, the reference samples will be subjected to artificial ageing (T3.3) and simultaneous monitoring of their state in order to collect reference data 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). Also, the reference dataset will be used for training of the simulation algorithms to be developed in WP5. The interdependencies of the current task (T3.1) with rest tasks in the same work package as well as with the other work packages are illustrated in Figure 1.

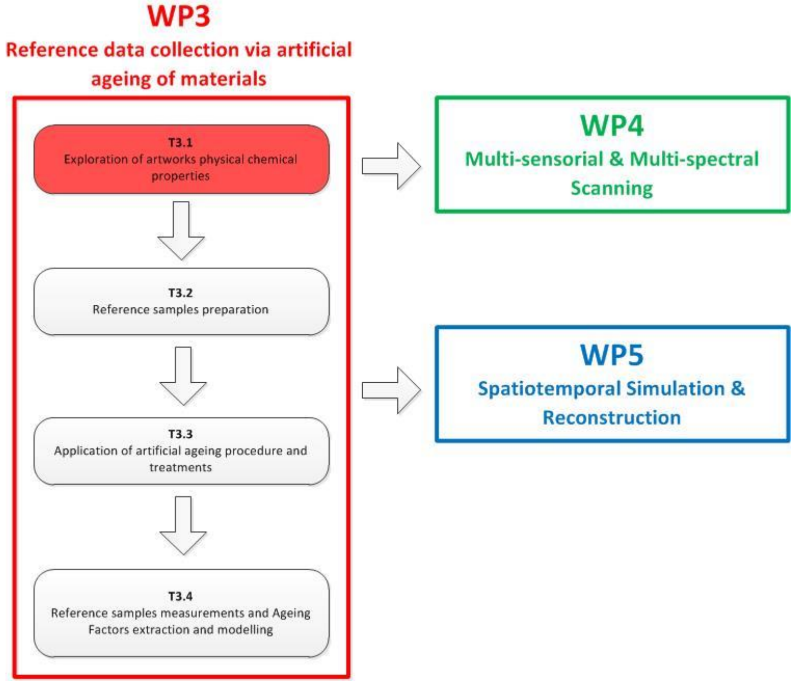


Figure 1: Overview of the interdependencies of T3.1 with the other tasks in the same work package (WP3) as well as with the other work packages.

2. Byzantine Iconography

In this section, the study of the school and the techniques used for painting creation, the style of the creator, the materials used for the creation and consequently of the study of their pathology during the centuries will be described. This is the adventure of the iconography through the ages and along different geographical areas. This is the DNA of the object and corresponds to some of the most important questions of the conservation science. The following documentation is related to the icons and is extracted from our experience (database of “Ormylia” Foundation) providing an integrated paradigm of the use of technological means towards the non-destructive documentation of cultural heritage objects.

We finally focus on a specific object which is briefly described in the following paragraphs because it compromises a very good example of what we deal in every day activity. Documenting an icon, we are called to solve the mystery of what happened to the object during the centuries and thus reveal the hidden beauty of our civilisation. This object is carrying many interesting cases to be investigated and solved since it was painted initially on the 14th century and overpainted later.

2.1 Style and stratigraphy of byzantine paintings

According to the tradition of byzantine art, most icons are similarly made with a specific stratigraphy on wooden body, mainly using the technique of tempera (egg tempera). However, it is possible to come across paintings that have been made on different bodies and materials. We will confine ourselves here to the description of tempera, not only because it is the most widely used technique, but because of its relevance to the study.

Each painting consists of a number of layers, made from a limited range of organic and inorganic materials, which work together to create a united and aesthetic whole. Each layer and each material combination plays an important role, both in mechanical operation and the visual and aesthetic effect of the artwork.

The substrate of the work consists of one or more combined wooden boards. The byzantine icons are made on wood of different trees such as cypress, walnut, pine and others. For small icons, the wood is cut in a board of the desired dimensions, but when icons are relatively large, two or more vertical board are joined with adhesive and two horizontal wooden parts at the rear. There are also icons found in carved frame for further decoration and others joined together to form an altarpiece. The wood supports all the other art materials, providing a solid and stable base. Moreover, it allows the carriage of the art to work and because of its porous character it enables the artwork to “breathe”.

Colours are rarely placed directly onto the wood. Instead, one or more thin-walled ***preparation layers*** are placed on the substrate, which create a bright and smooth surface for painting and help to retain the colour layer on the wood. The preparation layer consists of a number of inert materials such as plaster or chalk, which are held in place by an adhesive material (glue). When several preparation layers exist, the first layers may consist of coarse grained material, whereas, the last ones may consist of thin fine material. According to *Cennini*, these layers are called *“gesso grosso”* and *“gesso sottile”* respectively, where the word gesso relates to the plaster and glue mixture [1]. Also, either a sheet of paper can be welded on the substrate (Russian tradition) or a linen cloth during the preparation stage to enhance the preparation and painted layers.

Moreover, the preparation consists of a mixture of plaster or chalk which is diluted in animal glue and prepared over a low flame. The application of a single layer of diluted glue (size) is usually preceded in order to protect the wooden surface and increase the adhesiveness of the blend. The preparation mixture is spread either with spatula or brush in thin layers by repeated coats - horizontally and vertically – until any possible defects of the wood disappears and a uniform opaque white coating occurs. After dried well, the grinding of the dashboard follows; the surface is rubbed with fine sandpaper to create a smooth surface suitable for painting.

Before applying the paint, the artist usually draws a sketch on the cast. It may contain a simple outline with charcoal or a diluted layer of earth colours with brush. Often the pattern shall be prepared on paper and the outline is tapped with a needle, creating a stencil which is placed on the dashboard and is thrown up with coal dust. When removing the paper, the desired pattern appears. Some suggest the “needle method” as a direct preparation process

[12]. The draft pattern may also be in an engraving form, a process which is often followed in cases of halos and building outlines.

The colour layer, which is laid directly on the preparation surface, consists of a wide variety of pigments in powder form. The pigments are mainly classified in two categories: natural and artificial. The natural pigments comprise certain chemical components derived from mineral and vegetable derivatives while the artificial pigments derived from manufacturing salts, including lacquer paints derived from plants and insects. Often these colours were prepared and pulverized in the laboratory of the artist, while raw materials were commercially available. There will be mentioned below some of the most common traditional colours of the Middle Ages:

White:	mainly the lead white
Black:	kinds of charcoal, vine charcoal, carbon black
Red:	natural cinnabar and vermilion; red lead (minium); red ochre variety: hematite, sienna; caput mortuum red lacquers: kermis, grain, alizarin, dragon’s blood.
Yellow:	variety of yellow , orpiment, massicot, Naples yellow, lead-tin yellow, crocus (saffron).
Green:	malachite, green earth, verdigris and mixtures of blue and yellow
Blue:	azurite, indigo, ultramarine blue (Lapis Lazuli).
Metals:	gold leaves and rarely silver

It is understood that a pigment powder alone cannot be welded to the surface and is difficult to spread on the substrate without the help of a viscous material. For this reason, the colours are distributed in an organic ***binder*** such as egg and oil, which was dried to create a hard colour film.

Each individual layer may contain a single colour or blend of two or more colours (e.g. blue plus yellow for green) to achieve a particular desired colour. The first layer is called *preparatory underlayer*, usually consisting of a pigment, and on part of it are placed other layers of different colours to create certain effects of light or shade called *lighting* and *writing* respectively [1], [11], [12]. During the Byzantine years, a number of principles were developed for the technique of stratigraphy of colour layers, where gradations of colours and ranges of tonalities were used for the creation of light and depth.

Usually an entire area of the artwork is covered with the desired preparatory underlayer. Subsequently, a little lead white is inserted to the same colour to make the colour brighter and to create the first lighting that spreads on the part of preparatory underlayer. The second lighting is created in the same way by adding whiter colour in the pigment. In certain cases, a combination of different colours is used or a series of colours of the same hue, where the lighting is created by the brightest colours. On the other hand, the writing is created with the addition of black or dark pigment in the preparatory underlayer colour and is applied to areas of the pattern where the shadow effect is desired. Dionysius from Fourna [11] explains the technique in the use of white colour:

How to apply lighting (photisma) in the garments:

When you want to create lighting to garments in any colour, first apply some colour mixed with white, and cover the area with this light colour to finish the first layer ... From the same mixture create a deeper tincture and apply by mixing it in the shade. Then, you have to do it lighter than the previous colour and apply the lightings, using white for the most intense...

Theophilus [1] describes how to achieve the illumination by using a number of different red colours. The mixture (colours) for mantles:

Place the mantle with cinnabar and mix a little red (rather ochre) at the same and draw the lines. Then add a little minium with cinnabar and draw the first lighting. After that draw the (second) illuminate with neat minium. Finally add a little black with red and create writings along the outside.

Other common combinations of lightings include a preparatory underlayer of indigo with a first illumination of the azurite and a second illumination of azurite with white, and the same procedure with caput mortuum as preparatory underlayer. The red ochre is also illuminated with a purple shade of caput mortuum and white.

An indicative and very well documented icon is derived from our database. This icon is very effective for the case of Scan4Reco project. The particular icon is also related to the kind of the information and the kind of the pathology that we have to document and diagnose, respectively.

	
Figure 2: Initial painting	**Figure 3: Overpainted painting**

In Scan4Reco project for the first time we will the icon of mother of God Hodegetria (a well-known and documented one) from the small village of Afytos in Chalkidiki. Taking into consideration the results of the analysis, we will have the possibility to evaluate the new techniques on an overpainted and the initial painting. The clone will be described partially in Del. 3.2 (current state of creation – July 2016 after the measurements that were perfomred for Del. 3.4).

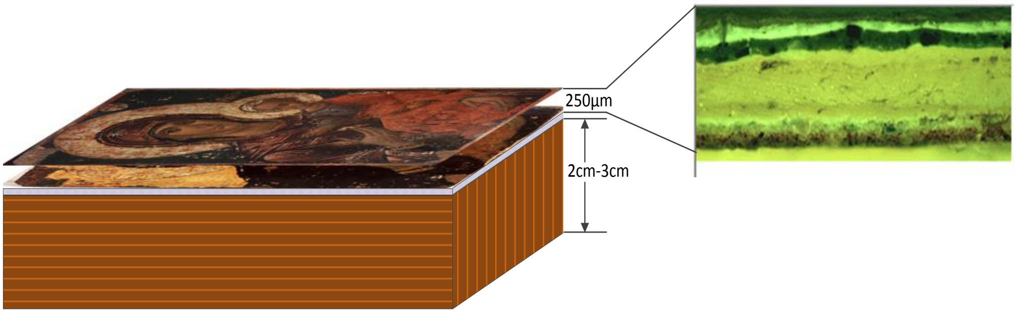


Figure 4: Schematic diagram of the dimensions presented in the previous images. The substrate marked with brown is the wood panel.

The real icon studied in past, the technical details of the icon to be cloned which is the icon of the Mother of God "Hodegetria", Parish church of St Demetrios, Athytos, Chalkidiki, Greece, Palaeologean style of the 14th Century are described next. The icon of the Virgin Hodegetria is painted on a wooden surface consisting of three sections of unequal width. Under the previous documentation using infrared and X-radiography techniques, the second painter didn't want the overpainting to be revealed. Although the joints have been arranged perfectly, the inevitable fissures were not.

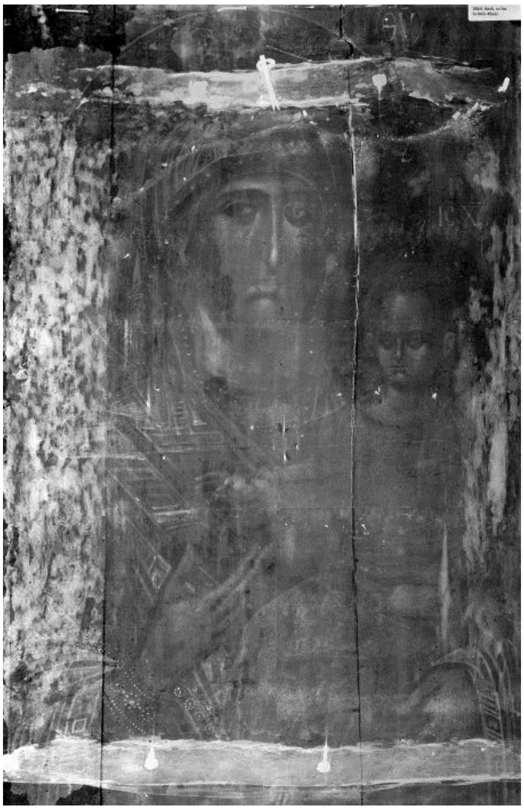
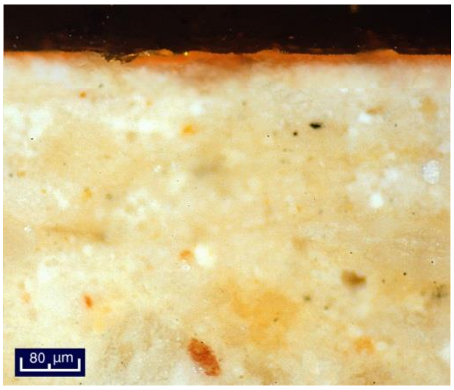
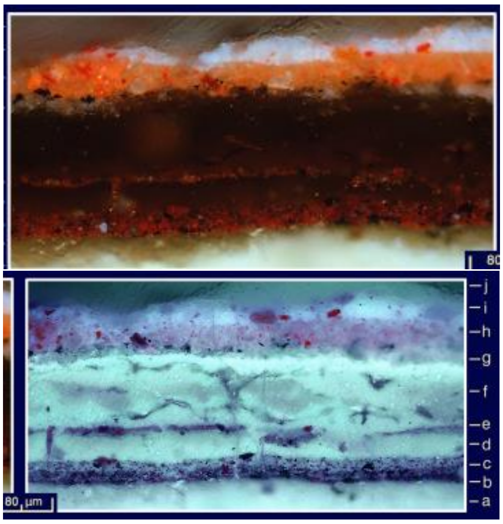


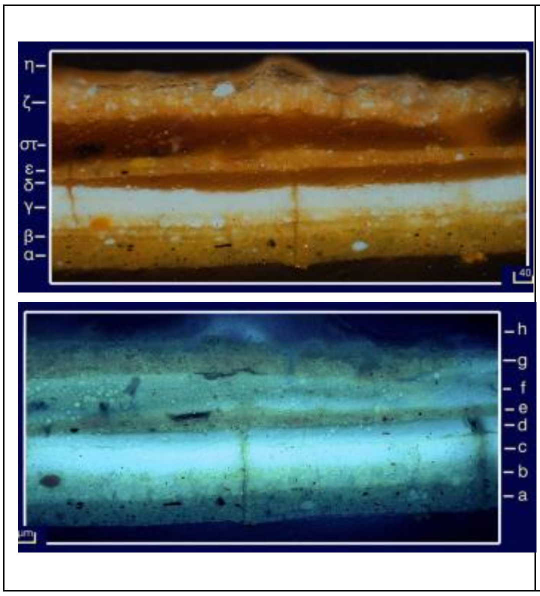
Figure 5: X-Radigraph of the icon	**Figure 6: infrared image at 1800nm, of the icon**

Deep cracks both in the gesso and on the surface's thick layer of varnish were revealed. The fingerprint of the time passed is evident. The latter varnish was unsuccessfully applied, as there is evident that varnish has been spilled in a number of places. At the lower part of the icon scattered beads of wax and burns from candle flame have been detected. These are defects that are usually found on icons that their operational use during services is continued through the centuries. By means of X-radiography and infrared reflectography it was possible to detect that the icon has been overpainted in two subsequent phases and to reveal the original underpainting itself. Aside from superficial damage, the initial icon has been maintained in good condition. Based on the results examination of the paint layers' structure we are in the position to determine the materials and the stratigraphic structure of these icons and thus create a database of reference panels. We can also determine the kind of the information that we should expect to reveal using the tomographic and the spectroscopic mapping techniques using the various modalities of Scan4Reco. Indicative cross sections form various areas are presented. The clone icon is being created according to these findings and specific regions of interest (ROIs) are determined for scanning based on the stratigraphic structure analysis.

	A thin, fine coating of orange bole has been placed on top of the ground (gesso and animal glue with scattered grains of yellow ochre and of carbon black) in order to apply the gold leaf. The gold leaf in the original background, hitherto concealed by a blue-coloured overpainting, had been applied to a thin layer of orange bole mixed with animal glue, by means of the technique of burnished gilding.
	Cross-section in the Virgin's mantle - pink highlight Original painting: a) gesso ground, b) animal glue and gesso, c) red ochre and carbon black, d) varnish: natural resin First overpainting: e) red ochre and carbon black, f) varnishes: natural resin Second overpainting: g) carbon black and grains of lead white, h) light: cinnabar, minium and lead white, i) highlight: lead white, grains of cinnabar and of minium, j) varnish: natural resin.
	Cross-section from Christ's orange cloak Original painting: a) gesso ground, b) animal glue and gesso, c) yellow ochre, cinnabar, red ochre and grains of carbon black, d) mordant, e) gold leaf (gilt line), f) varnishes: natural resin

	Overpainting: g) cinnabar, h) varnish: natural resin.

The faces are painted following traditional Byzantine iconographic techniques. On the olive-green underlay (a mixture of yellow ochre, carbon black, grains of green earth and of lead white) thin, transparent flesh tones of lead white, yellow ochre and grains of cinnabar have been coated. The white highlights, however, are retained as pure lead white. Two subsequent overpaintings, limited to a layer of flesh tone applied directly above the underlying varnishes, have come to light.

	Original painting: a) underlay: yellow ochre, carbon black, grains of green earth and of lead white, b) two shades of flesh tones: yellow ochre, lead white and grains of cinnabar, c) white highlight: lead white, d) varnish: natural resin First overpainting: e) yellow ochre, grains of cinnabar and of lead white, f) varnish: natural resin Second overpainting: g) g) yellow ochre, lead white and grains of cinnabar, h) h) varnish: natural resin.

Conclusions on the characterisation of materials and techniques of the selected icons under study

Extensive worm damage to the supporting materials has affected the state of preservation of the icon’s painted surface; it has suffered from flaking, cracks and decay due to the time passed and the use of it. Furthermore, the successive and widespread overpainted layers have impacted appreciably upon much of its original painting.

What has become apparent from this exhaustive investigation is that, below the overpaintings, the layers of the original icon have been preserved. These are characterised by a limited range of pigments and simplicity in their mixtures.

In the original painting of the icon, the main pigments used were red and yellow ochre, cinnabar, lead white, carbon black, a small quantity of the costly blue pigment, lapis lazuli, and green earth.

Above all, our detailed study of the icon’s painting has revealed the pure, traditional, Byzantine technique – which is understandable when one bears in mind that the Virgin Hodegetria is a representation typical of the Palaeologean era. In the Palaeologean (Byzantine) style a limited number of pigments and simple mixtures constitute the palette. The main pigments used were red (hematite) and yellow ochre, cinnabar, lead white, carbon black, lapis lazuli, and green earth.

In the Cretan (Post Byzantine) style the palette mostly comprises earth pigments: yellow ochre, hematite and green earth. Moreover, natural cinnabar, azurite and blue indigo (the latter used widely in that period) were also employed. Kermes lake is applied in the Virgin’s mantle as a glaze. Finally, carbon black and lead white complete the simple palette of basic pigments. The icons in folkish style, painted by artists of the Galatistan school, contain a great number of pigments: Prussian blue, ultramarine, copper resinate, emerald green, cinnabar, cochineal lake, haematite, minium, yellow ochre, chrome yellow, carbon black, lead white, baryte, and gold powder. Aside from influences received from the West, these artists maintained and respected the traditional method of using egg tempera, avoiding oil painting.

Table 1: Indicative Pigments / Painting techniques from the Byzantine period to the folkish style.

Style	Palaeologean	Cretan	Folkish
Icon	Hodegetria from Athytos (14th c)	Hodegetria from Kalamitsi (16th c.)	Overpainting icon of Hodegetria
Background	Gold (burnished gilding technique)	Gold (burnished gilding technique)	Blue (burnished gilding technique in the halos)
Garments			
Mother of God Tunic	Lapis lazuli *or* azurite	Indigo *or* azurite + lead white in the lights	Prussian blue + lead white
Maphorion (mantle)	Hematite + carbon black in the shadings	Hematite + lead white (in the lights) *and* hematite + carbon black (in the shadings)	Cinnabar as preparation for the underpaint, *and* cochineal lake + lead white (underpaint), *and* cochineal lake (in the shadings) *and* gold paint in the lights
Christ Tunic	Yellow ochre + cinnabar, *or* Gold striations (mordant technique)	azurite + lead white	Emerald green + lead white, *and* Prussian blue (in the shadings)
Cloak (Himation)	Yellow ochre +	Yellow ochre	Cinnabar

	cinnabar, *or* Gold striations (mordant technique)	+ cinnabar, *or* Gold striations (mordant technique)	*and* gold paint (in the lights)
Flesh tones			
Underlay Flesh tones	Yellow ochre + carbon black + green earth + lead white	Yellow ochre + carbon black + cinnabar + green earth + lead white	Yellow ochre + carbon black + lead white
Highlights (Psimithia)	Yellow ochre + lead white + cinnabar	Lead white + cinnabar + yellow ochre	Lead white + yellow ochre + Naples yellow + cinnabar
Inscriptions	Cinnabar	Cinnabar	Medals (sgraffito technique)

The background of traditional, strictly Byzantine-style, portable icons is gold. In the folkish style, a coloured background would replace the burnished gold most likely in imitation of the hues in the backgrounds of wall paintings. The highly luminous blue background was rendered in Prussian blue mixed with lead white. When it was used, gold was strictly confined to haloes and specific decorative surfaces. In painting the mantle of the Mother of God, the chief pigment in the Palaeologan-style icons was hematite, which, in the darkest, chestnut-brown shades was mixed together with carbon black. The highlights were rendered either in soft gradations of hematite mixed with lead white or, more rarely, in pure lapis lazuli or azurite. Cretan artists also pioneered new techniques in their painting of the Virgin's mantle. Hematite continued to be the basic pigment for the underpaint. Highlights were rendered in shades of mixed haematite and lead white while shadows and final outlines ended in heavy, carbon black brushwork. Finally, over the mantle's entire surface, a glaze of red or purple lake was applied, achieving a warmer and more intense harmonised tone. In the Galatistan folkish style icons, it was employed a somewhat unusual technique. The hue of the underpaint was executed with a fine layer of cinnabar onto which a coat of cochineal lake mixed with lead white was applied. Thanks to the transparency of the lake, the underlying cinnabar-based red exuded a warmer tone in the luminous purple hue of cochineal. The highlights of the gentle folds were rendered with gold powder, while the dark outlines were achieved with gradually thickened layers of lake without any addition of carbon black. The blue tunic of the Mother of God, in Palaeologan and Cretan-style icons, was rendered either with costly mineral pigments of lapis lazuli and azurite or with indigo. These pigments were entirely substituted in Galatistan iconography by synthetic Prussian blue or ultramarine mixed with lead white, which are combined with highlights either in gold or in clear blue tones which in turn finished up as pure lead white. In the blue shadings much use was made of deep, dark Prussian blue by the successive superimposition of paint layers, without the addition of carbon black. The green shades are almost absent from Palaeologan and Cretan-style icons of the Mother of God. The Galatistans introduced copper greens (emerald and copper resinate), whether in pure form or combined with a low proportion of lead white, spread in thick covering layers for the painting of the Christ's tunic and of the mantle's lining. The highlights were rendered in gold powder. For the delicate gradations in the shadows of the folds Prussian blue was used instead of green pigments. This unusual combination of blue outlines in a green underpaint is not to be seen in traditional Byzantine art, where dark greens or chestnut brown colour tones prevail. The infant Christ, as depicted in the icons of the Mother of God throughout the Byzantine and post-Byzantine period, was characteristically portrayed in gold-embroidered garments whose underpaint consisted of a mixture of yellow ochre and cinnabar. In the folkish style icons, red cinnabar can be found in Christ's cloak. The highlights of the rich folding were rendered in gentle grades of gold paint and, in rare cases, a mixture of cinnabar and lead white. However, in some cases the painters elected pure yellow ochre for Christ's garments, while the highlights were rendered in pure chrome yellow. While in terms of style the icons of the 19th century differed significantly from all preceding Byzantine and post-Byzantine icons, certain similarities with the Cretan-style have been observed in the painting of flesh tones. The dark olive underpaints resulted from a combination of yellow ochre, carbon black and grains of lead white. In several paint mixtures scattered grains of haematite or cinnabar were also traced; their addition produced a warmer colour tone. Flesh tones were rendered in lead white and a small amount of yellow ochre with grains of cinnabar. The Galatistans, influenced more by the aesthetics of icons from the West, adopted new techniques for rendering expression and for modelling flesh tones, with the result that they leaned significantly away from the traditional severe style of earlier Byzantine iconography. Decorative motifs executed in sgraffito technique, especially popular with the artists of the post-Byzantine era, were employed extensively by painters of the eighteenth and nineteenth centuries. The surfaces on which this technique was applied were prepared with burnished gold or silver and then coated entirely by pigments such as cinnabar, red lake, Prussian blue, emerald green, and, more rarely, lead white. Above these, beautiful and varied motifs were drawn. In other cases the underlying gold was engraved in dense lines or dots thereby giving the false impression of gold-embroidered cloth. These techniques were used in the adornment of the medallions surrounding the inscriptions of Christ (*IC XC*) and the Virgin Mary (*MHP ΘΟΥ*). After comparing the icons of the Mother of God (Palaeologan, Cretan and folkish style) fundamental distinctions were identified in their colour palette. They relate on the one hand to a gradual increase in the number of shades employed, and on the other to their degree of saturation. The exceptionally restricted colour range in icons from the Palaeologan period was enriched during the post-Byzantine period. In icons from Galatista, painted in the folkish style, pure saturated colours of all shades constituted one of the major and characteristic features. The fine, straight brushstrokes of the outlines in Byzantine icons were replaced by wide curvilinear shadows worked gently for the achievement of a naturalistic portrayal of the folds. The flesh is composed of broad luminous surfaces that leave the dark underpaint to operate in the outlines solely as shadow. The manner of the drawing and of the painting of the eyes, nose and mouth suggest Renaissance models. The abstraction of the design, the leanness of the colours, and the spirituality in the expression were the highest achievements of Byzantine art. These particularities gave way to rich decoration, dense drawing, and wide range of colours in the icons of the folkish style. Naturalistic expression, however, preserved in some measure the modesty and the respect for the sacred mood that was required for venerated icons to exude.

The above mentioned results are used in order to support the samples creation and the creation of the clone icon subjected to forthcoming deliverables. The materials chosen and their use for the samples preparation are described in the next paragraphs in a formalistic way:

Properties of Preparation Layer [18]

The preparation aims to create a solid, concise, smooth, flat and uniform surface suitable for the deployment of colour layers. Although it is completely covered by the colour layer, the preparation will play a large role in the operation and in the final perception of the pictorial work:

- strengthens the connection of painted layers with the substrate (carrier)
- rectifies the dissimilarities of the expansion and contraction of the substrate during the change of humidity and temperature
- absorbs excess binder
- determines the texture of the painting surface
- its colour affects the final aesthetic

Finally, the quality of the preparation influences the optical performance of the superimposed colour layers. Assuming that the colour layer is not completely opaque and does not completely cover the primer layer, we conclude that there is some interaction of the preparation with the incident radiation. A part of the radiation is reflected at the interface of the varnish with the air and another part is reflected from the colour area, while the remainder penetrates the outer colour layer where it continues its course, with a concurrent refraction, scattering and absorption of the material until it reaches the layer of preparation.

How the radiation will be absorbed and reflected by the preparation is dependent on its chemical composition and its colour. A typical example of a white preparation absorbs less radiation than a coloured one, resulting in the reflection of the radiation on the outside of the colour layer and the reverse path up to the exit surface. This reaction is even more intense when the colour layer is thin; the colour pigment has poor coating ability and is relatively transparent.

Properties of the Binder [14][18]

The binder operates twofold. On the one hand, it holds the pigment particles in place to create a homogeneous colour film and, on the other hand, it has an influence on the visual properties of the painting. The addition of a binder amends softens and tempers the pigment. This process is called tempering. Today the term tempera refers almost exclusively to egg tempera process, but it essentially means the amendment and mitigation of the colour with any binder.

The binder, from a chemical perspective, should have a high resistance to light and environmental conditions in order to prevent undesired changes over time. Any chosen binder should be further compatible with the pigments. While most colour pigments are useful in a multiple way, there are some that exhibit affinity only to specific binders. In some cases the combination can cause a chemical reaction; hence, a change in colour, whereas other colours simply exhibit better aesthetic compatibility with specific binder.

At the time of applying, the binder should be in liquid state, to form with the pulverized colours a stable and homogeneous paste suitable for coating. The viscosity of the whole system depends on both the concentration of the pigment and the binder liquid. If it is too thick, the paste will be rigid, while in the opposite case it will tend to flow far and the two phases could be separated. Therefore, the behaviour of the colour determines not only the type of binder, but also the adequate liquidity and required quantity of it.

The stability of the system increases during the drying phase restraining the granules and the adhesion to the preparation surface, up to the creation of a thin and durable film. The film drying time depends on both the materials and the environmental conditions. The egg yolk, for example, dries quickly enough in relation to the drying (boiled) oil, even if the drying is accelerated by the addition of certain colours with desiccant forces.

Typically, the organic binder is a sufficiently transparent and colourless material. It is generally considered that it absorbs little electromagnetic radiation, and thus does not prevent the reflective ability of the colour, or in other words the rendering of the painting. This occurs because of the relatively low refractive index compared to many pigments. The refractive index is defined by the ratio of the value of the speed of light in a homogeneous and isotropic material with respect to that in a second homogeneous and isotropic material. That is, the refractive index determines how the light is blocked when it propagates from one material to another and is directly related to the transparency of the colour layer. Generally, the pigment granules are reflecting more light when surrounded by air and less into the binder. As a result, the colour layer reflects the radiation depending on the difference in refractive indices of the pigment and the binding agent. The higher the refractive index of the pigment relative to that of the binder, the bigger the reflected light and therefore the bigger the opacity of the layer.

Properties of Pigments [24][18][25]

The refractive index also determines the colour of a pigment if varied along an absorption region. To be effective, a pigment must have a large refractive index of the colour in which it is attributed. Typically the refractive index is bigger in the region of large wave lengths and lower in the region of short wavelengths. For this reason, the red, orange and yellow pigments commonly have higher refractive index than the green, blue and violet ones. In contrast, the refractive index of the lacquer is determined by its base and is relatively low. When the difference in refractive index of a pigment and a binder is too small, the colour quality of the pigment can be improved by blending it with other pigments of large refractive index such as lead white.

The hiding power is the property of a colour layer to completely cover the surface on which it is laid. That is the ability of the layer to eliminate the reflective capacity difference between two substrates arranged one next to another and is directly related to the thickness of the layer. Generally, the bigger the diffusion and absorption of radiation within the colour layer, the bigger the coating ability (less thickness). The coating ability is generally proportional to the refractive index, and also depends on the particle size and concentration of the colour pigment in the binder.

The size and the shape of the grains of the pigment also play an important role in the performance of the painting. Generally the granules must be sufficiently small and uniform to allow their uniform dispersion within the binder and not prevent the spread of paste by brush. However, there are exceptions of certain colours, such as azurite and malachite which deliver richer colour when the size of the grains is bigger. The granules are sorted by their diameter, but the values can be slightly changed according to the source. The main classification of grains regarding their size is shown in Table 2.

Table 2: Grain Classification

Very small	<0.3μm
Small	0.3 - 1μm
Medium	1 - 3μm
Large	3 - 10μm
Very Large	> 10μm

The grains of the mineral pigments are generally broken with irregular and angular shapes and their size varies depending on the toughness of the mineral and the way of pulverization. They are usually moderate to very coarse as in the case of azurite and cinnabar. The earth pigments derived from natural sediments consist of small granules of various sizes and are usually processed with the pulverization process to be separated. They generally have a heterogeneous composition and most comprehensive form as the green earth, and sienna. Most artificially produced pigments have fine-crystalline form while those formed from metal corrosion (e.g. verdigris and white lead) tend to contain coarse crystals.

Another parameter is the absorption capacity of the pigment, i.e. the amount of binder required to wet the pigment granules and to convert them into a thick paste. This is defined as the required amount of oil per 100 g of pigment. Absorptive capacity depends on the surface area of the grains as a result of their shape and size, the chemical characteristics and the interfacial pigment-binder strains. Typically favored are the pigments that require less binder because the latter can cause discolouration of the colour layer during oxidation.

2.2 Materials

2.2.1 *Preparation Layer*

2.2.1.1 Animal Glue

The glue plays an essential role as a paint preparation material and it is also used as a carrier for the colouring. The adhesive properties of the glue were known in antiquity and were referred to as a binder in Ancient Egypt by Pliny. Cennini described the preparation and glue use in painting, and said his favor for the glue made from parchment and skin [1]. A glue of particular good quality to prepare gesso is the rabbit-skin glue, which had extensive use during the byzantine period and still used today for the same purpose.

The animal glue and gelatin are similar substances belonging to the class of proteins. Their main difference regards purity, wherein the glue is theoretically less pure and is used only as an adhesive, while gelatin is preferred for thinner uses and as colouring agent. Being proteins, the two substances are mainly composed of macromolecular chains made of basic groups of amino acids. The glue is the water soluble sustained heating product of collagen in water. Collagen is the structural protein of connective tissues of animal organs, the main binder component of bones, tendons, ligaments and skin [18], [19].

Although collagen is insoluble in cold water, when heated gradually dissolved. Collagen comprises about sixteen different amino acids and is characterized by a unique composition of amino acids, i.e. glycine, proline and hydroxyproline, which normally form repeating units. The three protein chains are wound together with strong hydrogen bonds. Gelatin is formed by the separation of the chains when the hydrogen bonds are broken and replaced with hydrogen bonds of the water [19].

When soaked in cold water, the glue softens and swells without being dissolved. On the contrary, in hot water it is dissolved completely, forming a thick viscous material with a characteristic odor. However, if the glue gets warm more times, it gradually loses its cohesive force. Moreover, the solution thickens when cooled and forms dense gel which has strong adhesive properties when dries. The coagulation mechanism is based on the cooling of hot hydrosols via complex phenomena of forming hydrogen bonds and creating surface gel [19].

Besides the weldability, the glue efficiency is based on certain properties. First, the liquid must be sufficiently viscous to cover surface irregularities and concluded without creating bubbles. Typically, the viscosity is adjusted by the concentration of the glue in a solvent (usually water). It should be neither low otherwise the adhesiveness will be insufficient, nor high to not impair the normal distribution. The uniform wetting of surfaces is also necessary, which depends on the relative values of cohesion of the glue molecules and the adhesion between this and the substrate.

The coagulation time is considered as an important property of the glue, and it refers to the transition from liquid to solid or pseudo-solid state. It depends on the rate of evaporation of the solvent or its absorbance from a porous object. Glue should also retain partial elasticity and bending quality so as to allow expansion and contraction of the objects after coagulation. Final required condition is the reversibility of the glue to be easily removed even after many years.

2.2.1.2 Plaster

Useful due to its coagulation properties as hydraulic mortar, plaster has been used since ancient times as a building material and wall painting substrate. It is also an important material of the preparation, functioning as inert stucco material and its granules are held in place by means of an adhesive. The white paste obtained by mixing the plaster and the diluted adhesive is called gesso and currently used as a generic term for the prepared repairing material.

Plaster is a natural mineral, calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$. When heats, it is converted into hemihydrate plaster, $CaSO_4 \cdot ½H_2O$ (Plaster of Paris), and anhydrous plaster, $CaSO_4$. It is noted today that hydrate plaster and anhydrous plaster were the main compounds in preparation layers of paintings of Mediterranean countries and Byzantine icons [15], [18].

Plaster deposits are found in abundance around the world. The different species vary in content of impurities, crystallography and size of the granules. Generally, for use in painting, white and fine kind terra alba is preferred. Plaster is a stable material, slightly water soluble. It has a low refractive index and therefore it is not suitable as a pigment.

2.2.1.3 Chalk

Besides its use as mortar in murals, chalk is also used as inert stucco material in painting preparation, mainly in Northern Europe. It is mixed with diluted glue to create a thick paste, which forms a hard and smooth white surface when dries.

The natural chalk is derived from fossils calcifying marine micro-organism structures and it may contain an amount of insoluble mineral. Chalk is a natural calcium carbonate $CaCO_3$ and it mainly consists of the fine crystalline calcite. Calcite is the most common mineral form of chalk that is abundant in nature. Rarely in nature, does it occur in its relatively unstable polymorph of the aragonite which often turns into calcite changing environment [18], [26].

In normal circumstances, all types of chalk are stable to light and they are not affected by hydrogen sulfide or sulfate pigments. Because of the high alkalinity (pH 7.7 - 9.8), it is not compatible with certain dyes and it is rapidly decomposed by acids. In the presence of sulfuric acid, sulfate calcium is formed, which is a more bulky material and it causes peeling of the surface.

Microscopically chalk is fairly homogeneous material and has a low refractive index. Generally, the grains of calcite appear as single transparent crystals, while the chalk is characterized by the presence of minute oval coccolith. Chalk normally ascribes brighter white than the plaster and is more absorbent. It tends to discolour in oils [26].

2.2.2 *Binder*

2.2.2.1 Egg Yolk

Historically the use of the egg, and especially the yolk, as a binding agent in painting was first mentioned by Theophilus [10] and later by Cennini [1]. The author also describes specific recipes, uses and colour differences of the urban and countryside eggs. The yolk, separated from the egg white, is mixed with one part water to create an emulsion. However, according to ancient recipes the addition of other materials such as plasticizers, siccatives or adhesives, is not excluded.

The egg yolk is a very complex and heterogeneous substance. Microscopically it consists of certain particle groups: the granules and globules, which are dispersed in viscous plasma. Partially hydrophobic and partially hydrophilic means that acquires some properties of the emulsion but generally it is not considered real emulsion [20].

The globules are insoluble and mainly contain lipoproteins, phospholipids and water. The granules consist of lipid-protein complexes, and water soluble proteins from plasma and water. Almost half of the yolk consist of water, while the other half of the solid matter of which approximately 66% lipids and other proteins. The majority of lipids are associated with proteins through noncovalent effects [19], [20].

Lipoproteins by their nature are unstable in the absence of water. As a result, the initial drying and curing begins the reorganization of physical state when water evaporates. This implies a change in the organization of proteins and lipids. Effects of sulfo-amino acid form intermolecular bonds (cross-links) between the protein chains [20].

Over time, there is chemical change of the different components, due to oxidation. However, the oxidation does not occur simultaneously in all components, neither made in the same way nor at the same rate, and it is not caused by the same event at a time. Therefore changes caused by oxidation occur randomly, each in different proportions. Cholesterol for example oxidized rapidly and the full loss in egg tempera layers has been reported in less than 20 years [19]. However, there is the maintenance of cholesterol in the presence of verdigris, implied that somehow protect lipids from oxidation [20]. There is also a decrease in the content of certain amino acids, especially when the painted layer is exposed to light. The amino acids which are most sensitive to photo-oxidation under the influence of the violet and visible radiation include: histidine, methionine, tyrosyni, cysteine, cystine, tryptophan and lysine. Moreover, interactions between oxidized lipids and proteins are involved. The lipids are oxidized by the process of auto-oxidation or photo-oxidation, which is accelerated by certain metal ions. As a result, several products are formed as polymerized triglycerides, polymerized phospholipids and other intermolecular bonds between the lipids. During the oxidation of the lipids, free radicals are produced which are the cause of variation of chemical reactions of the proteins. Subsequently, the formation of free radicals of proteins from transfer of the free radicals of lipids causes intermolecular bonds between free protein moieties and proteins, and further polymerization of the protein molecule. It is considered that the properties of old egg tempera layers are attributed to web formation of intermolecular bonds between proteins. Also, the formation of insoluble complexes of proteins-oxidized lipids also occurs.

Furthermore, the catalytic activity of metal ions in lipid oxidation reactions and thereby oxidation of certain amino acids is known. These particularly include the metal ions of copper (Cu), cobalt (Co), manganese (Mn) and iron (Fe). Metal ions can also form complexes with proteins and lipids.

According to experimental investigations [20], the effect of certain metal ions can accelerate decomposition of egg tempera painting film. After artificial aging, samples composed of egg yolk and azurite and vermillion, respectively, showed compounds of high molecular weight. As a result, it appears that the formation of intermolecular bonds between proteins is accelerated. In contrast, the distribution of the same sample proteins with lead white remained unchanged, the same as the original, unstained controls. Samples with verdigris showed completely different behavior, forming only small molecular weight compounds. In some cases, significant protein degradation has reached such an extent as to completely destroy the physical strength of the film. It seems that copper in an acid environment decomposes amino acids and the acid dye may cause hydrolysis. Similar experiments with lighting aging demonstrate that the metal ions of the colouring accelerate oxidation of lipoacids, resulting in a decrease or loss of the principal lipoacid, oleic acid, the greater influence caused by azurite, while it appears that verdigris protects the lipoacid oxidation.

2.2.2.2 Linseed Oil

There is a fundamental difference between the paint films of oil and egg yolk. On the one hand, the oil consists of polyunsaturated triglycerides, relatively small molecular groups, forming larger mesh with the process of polymerization. On the other hand, the tempera consists of lipids and proteins already in the polymeric phase [20].

Historically linseed oil is the most important oil crop drying in painting. It comes from the seeds of linum (usitatissimum), the same plant that produces fiber flax. As a binder in paint, oil was first reported in Theophilus documents and in the Middle Ages replaced tempera in western painting.

Chemically linseed oil mostly consists of five lipoacids forming about 55 different triglycerides [19]. The lipoacids are linear chains of carbon atoms and contain from 18 carbon atoms onwards. Essentially, triglycerides are composed by glycerol esters with lipoacids [22]. The main reactive lipoacids are linoleic acid and linolenic acid. Linseed oil also contains oleic acid, stearic acid and palmitic acid.

There are mainly three stages in the natural aging of the painted film with linoleum: the initial curing and drying, the mature drying and the degradation. The conversion of oil to gel and turns into a semi-solid state occurs because of the chain reaction of free radicals. In the initial stage of the process of autoxidation of the unsaturated lipoacids leads to the formation of intermolecular bonds between them. The presence of certain metal ions from the pigments or siccatives materials accelerates the oxidation process in the order of catalytic power of metals: Cu> Co> Pb> Mn> Fe [20].

The auto-oxidation leads to carbon loss in volatile form of matter and, also, creating alcohols, ketones, aldehydes and short-chain acids which eventually evaporate. These compounds eliminate the characteristic smell of drying oil.

The mesh of glycerol formed after initial drying is by nature unstable and finally hydrolyzed by aging oleic film, whereas, lipoacid groups with intermolecular bonds remain. Metal ions pigments act to balance the load. During this stage, the painting film transformed from flexible to rigid material and the formed polymer is hardly isolated from the surface containing metallic pigments.

The last step is achieved by prolonged exposure of the layer to light, air and metallic pigments. The result is the absolute photodecomposition of the pictorial layer that loses its coherence and gradually turns into powder.

2.2.3 *Pigments*

A pigment is the colouring substance that is usually in the form of insoluble powder, which is mixed with a binder (egg, oil, water, etc.) to produce painting colour. Pigments are categorized into two major categories; those with natural origin and those which are manufactured with artificial methods. They are classified into inorganic substances from natural minerals or artificial salts, which contain metallic elements and are usually in crystalline form and organic compounds with vegetable or animal origin.

A wide range of pigments are originating from natural minerals, either as aluminosilicate substances in granular form or in stone form. In both cases, raw materials require refining processing according to their purity level. Chromatic aluminosilicate substances are comprised of natural reserves of metal salts, such as iron oxides and copper carbonate, along with impurities of sand and black soil. Some can be found in abundance in soil, in a fairly pure state and they only need a little scrubbing and cleaning in order to be suitable for painting. Coloured soil elements belong to this category (ochres and green earth).

It is accepted that chromatic minerals, in the form of stones, require further processing to be converted into powder. Some of them can be found in abundance in soil, while others are considered valuable and are limited to specific resources on earth. Due to their potential hardness and the difficulties arising from their dissolution, as well as their rarity, ancient people often invented artificial ways to prepare some pigments, often from the same mineral.

Artificially produced colours will be further discussed later on. First, we will refer to the scrubbing and cleaning processes of minerals which are of great importance regarding the colour rendering. Primarily, the processing of minerals is essential for the removal of junk impurities and further on the colour sometimes depends on the size of the material particles. After the general scrubbing, impurities are separated by wash, if required. The procedure is called *levigation* and it is often used for the gradation of different properties of the colour. Heavier particles tend to settle relatively rapidly in the water, while light components tend to float. Undesired substances are removed and the process is repeated until only the pure pigment remains. The same process can be applied for the gradation of the granules. Shades of pigments depend on the granules size. Colour is not easily erected when the granules are too thin or too thick [13], [14].

Artificially produced powder colours are basically divided in three categories: salts derived from the direct combination of chemical elements, salts derived from the action of an acid on a metal and salts derived from the decomposition of two or more salts in a dilution. The first category includes *vermillion* (HgS) by the compound of mercury and sulfur. On the other hand, production of *verdigris* (copper acetate) and a number of leaded colours (white lead, massicot, red lead) are examples of the preparation of coloured salts by the action of acids on metals.

The production of a lacquer or colour results from the reaction of alkali on an alum dilution, causing the precipitation of aluminium hydroxide. Alum is a compound of aluminium sulfate and sodium or potassium that is used as a mordant. If potassium carbonate is mixed with an alum dilution, an aluminium hydroxide precipitate is formed, while carbonic acid escapes and potassium sulfate remains. The formed aluminium hydroxide is colourless and transparent enough. On presence of colour materials, it absorbs the colour in order to create coloured compound. The combination of organic colouring material and aluminium hydroxide is called lacquer. Lacquer adopts the transparency of aluminium hydroxide upon which the colour is seated, such a case is *indigo* [13], [14].

2.2.3.1 Yellow

2.2.3.1.1. Massicot and Litharge

Massicot and litharge are the two different types of yellow lead monoxide (PbO). According to ancient sources, such as Pliny, the two oxides have been known since antiquity. Although having the same chemical composition, the two oxides are derived from different sources and have slightly different properties. Massicot is produced by slight firing lead white, which eliminates CO_2 and water, leaving behind a soft yellow powder with a sulfur colour. The colour has fairly good coating ability and resembles the white lead as regards its properties. In terms of microscopy appears almost amorphous. When heated, it can be transformed into litharge and red lead depending on the temperature. Generally, it is not affected by light, but with prolonged exposure to moisture can be reversed in white lead.

Crystalline litharge is formed by the direct oxidation of molten lead metal in the hot air. It is also an intermediate product of the red lead preparation [18], [26]. The litharge colour tends to orange, which is due to the presence of red lead (Pb_3O_4). It is not used as a colour, but it is important siccative for paints and varnishes.

2.2.3.1.2. Naples Yellow

The warm yellow of Naples is the oldest artificially produced pigment and was used as glass pigment for glass in ancient Egypt during the 15th century BC and later as enamel (glaze) for ceramic in Mesopotamia, Babylonia and Assyria although it is hardly recognized for its history in the European painting. As a pigment, it has been lost and reappeared many times in history. According to ancient recipes it reappeared as enamel for ceramics in Italy during the 16th century and it was supposed to be uses for painting almost a century later. The confusion regarding its use is due to the name of the yellow pigments in the ancient references and the existence of another yellow lead based pigment, the lead-tin yellow.

Today yellow of Naples is known as lead antimoniate) with the formula $Pb_3(Sb0_4)_2$, but according to the Sb/Pb ratio the types $Pb(SbO_3)_2$, $Pb(SbO_4)_2$, $Pb_8(Sb0_4)_2$ and $PbSb_2O_4$ exist. The colour ranges from light yellow to orange yellow, depending on the ratio of the two components and the temperature of the preparation. The pigment is produced artificially by the firing of lead oxide with antimony oxide or the salts of the two metals [27].

As a pigment it is very fine-grained, homogeneous, chemically stable, and because of the high refractive index has excellent coating ability. Generally it is compatible with all binders and all other pigments. Microscopically appears amorphous and its fine particles tend to aggregation, creating areas of deeper orange-yellow.

2.2.3.1.3. Yellow Ochre

Generally ochres are among the oldest pigments in the world and their traces have been found in all historical periods. They were considered important colours in the Middle Ages and were in the palette with hues from light yellow to dark brown. The ochre deposits are found in the earth's surface in many parts of the world, making it relatively cheap and accessible.

The ochre is natural earth colour consisting of aluminosilicate materials and its colour is caused due to the iron oxide, either in a hydrated or anhydrous form. The yellow ochre colour owes its colour to the presence of hydrated iron oxide, mainly in the goethite mineral $Fe_2O_3 \cdot H_2O$. Apart from iron oxides, it may also contain impurities of plaster and magnesium carbonate.

Microscopically, the pigment is homogeneous in terms of grain size and composition. It demonstrates stability in all binders.

2.2.3.1.4. Warm Ochre

It is a variant of yellow ochre with a warmer hue.

2.2.3.2 Red

2.2.3.2.1. Red Ochre

Red ochre consists of iron oxide in a substantially anhydrous form with aluminosilicate contaminants. The complexion varies according to the degree of hydration and the origin of minerals. Like all the iron oxides, the red pigment is very stable and insensitive to light. Generally, the pigment tends to dry quickly. Microscopically, the grain size is homogeneous. Often, some dark particles of hematite appear (Fe_2O_3).

2.2.3.2.2. Hematite

The mineral hematite is quite hard, compact and is almost composed by pure anhydrous iron oxide Fe_2O_3. The pigment attributes rich dark colour with purple-red hue. Microscopically, the granules differ from other ochres as they present a form of bright elongated alder.

2.2.3.2.3. Burnt Sienna

The raw sienna is a special form of yellow ochre which got its name from the Tuscan region where the particularly beautiful shade of its colour comes from. As the yellow ochre, the raw sienna is also composed by hydrous iron oxide ($Fe_2O_3 \cdot H_2O$) with aluminosilicate impurities. It generally contains a minimum proportion of the manganese dioxide. Its hue is warmer than the ochre and is relatively transparent.

The rich warm maroon colour of burnt Sienna is a result of heating under oxidizing conditions (calcining) the raw Sienna. By the calcination, the hydrated iron oxide is converted to anhydrous iron oxide. Microscopically, it does not present particular crystalline form and is very homogeneous in colour.

2.2.3.2.4. Caput Mortuum

The thick dark red colour of caput mortuum, with its violet tints is also classified as a type of iron oxide with a 90% content in Fe_2O_3. As the name implies, the pigment is derived from the by-product of the sulfuric acid manufacture by the firing of iron sulfide. The pigment is very stable, homogeneous and has excellent coating ability.

2.2.3.2.5. Minium

Although the mineral minium occurs quite frequently in nature, its use as a pigment in antiquity is questioned. It appears that there was a preference for its artificial version which was known by the 5th century in China and later in the Greek and Roman periods. Vitruvius notes that the red lead was achieved for the first time when the white lead was baked accidentally on fire: "*it acquired a better result in this way rather than the natural material pro-*

duced from the mines". So it seems that the artificial produced product replaced the natural mineral from the early classical period.

It was widely used in China, Japan and Persia and was a popular colour of Byzantine miniatures and manuscripts after the 7th century. It appeared on board painting by the 12th century, but rarely in wall paintings due to its tendency to blacken when exposed to air. It was often found as illumination on cinnabar or as a thin decoration to create a glowing grid that resembles lace.

Chemically, the red lead is a lead tetroxide (Pb_3O_4). According to some ancient recipes, the pigment is produced when metallic lead or its minerals are heated. Other recipes suggest treating the lead with vinegar, and then converting the produced white lead to red by firing. The firing of white lead forms an intermediate product, litharge (PbO). As a result, the pigment usually contains a certain amount of lead monoxide which acts as possible siccative.

Pliny calls it "*the colour of the flame*" and, indeed, the bright intense red colour of minium is mostly characterized as an orange rather than red colour. It is a compact, fine-grained pigment with excellent coating ability. It tends to darken the frescoes with the conversion to brown or black lead dioxide, PbO_2, but is quite stable in oil paintings. When mixed with linoleum, it has been observed in some cases to convert the colour to a lighter complexion.

2.2.3.2.6. Cinnabar

The cinnabar is a compact heavy red mineral (HgS), which is the main mineral of mercury. It was known in ancient Greece during the 6th century BC and probably much earlier in Asia Minor. The most important source of the mineral in the classical era was the mines of Almaden in Spain; other sources also refer to Asia, Russia and China. The preparation of artificially produced cinnabar, known as vermillion, is attributed to Chinese and it was first appeared in Europe during the 8th century. The initial preparation method of vermillion included a mercury compound and sulfur by dry sublimation (dry-process / sublimation). During the 17th in Germany a new method of preparing vermillion was discovered which was more economical and efficient, known as the wet process of production [26].

The pigment is characterized by its rich cherry colour, often located in the folds of clothing and dress of the Virgin, as well as at the pink colour of flesh. It contains tiny grains of different sizes with a crumbly surface. Generally, the mineral and vermillion produced by dry sublimation cannot be distinguished. But the vermillion of the wet method has a characteristic homogeneousness of its grains size. The cinnabar and vermillion are considered sufficiently stable to light, but sometimes tend to blacken especially in egg tempera. The colour change may be due to the presence of impurities (alkali metal halogens) which act as catalysts, converting a stable α-HgS to α'-HgS or meta-cinnabar, which is its black crystalline variant. The browning phenomenon appears to occur more frequently in egg tempera.

2.2.3.3 Green

2.2.3.3.1. Green Earth

The term green earth is applied to the earthy grey-green aluminosilicate minerals found in abundance all over the planet. Green earth is one of the oldest pigments used in painting due to its widespread obtainability in an almost ready to be used form. The colour of the green earth minerals varies from grey-green to oily brown. This pigment is perhaps best known for its usage as a preparatory underpainting for the representation of flesh tones in Medieval iconography. The tradition of using green pigments for the underpainting of flesh has been recorded since the 11th century in a Mount Athos manuscript referencing the green-black underpainting as well as by monk Theophilus (12th century) and Italian painter

Cennini in his Treatise of Painting (14th century). It is considered that green underpainting creates good contrast and helps neutralize the effect of brighter colours like yellow and pink used subsequently complete the flesh.

Green earth pigment is mainly composed of two related minerals, glauconite and celadonite. Glauconite, being the less pure of the two, can be worldwide found in grain form as green sand, while celadonite forms vesicle fillings and linings in altered basaltic lavas. Celadonite deposits of particularly good quality have been found close to Verona, while other known sources are located in Smyrna, Libya and Cyprus. Distinction between pigments composed of the two minerals is difficult. However, it is possible to distinguish them examining their complexion, as celadonite tends to appear cyan. The general formula of green earth is

$$K[(Al, Fe^{III}), (Fe^{II}, Mg)](AlSi_3, Si_4)O_{10}(OH)_2.$$

Due to its low refractive index, green earth is quite transparent and has weak covering power. As a result, it is considered relatively soapy in texture. Furthermore, when used in egg tempera painting, a higher concentration of the pigment is required to produce a satisfying and uniform colour. Green earths are often described as the most permanent of colours, as they are not affected by atmospheric conditions or sunlight and as they do not react with solvent or other pigments. On microscopic scale, green earth appears as a mixture of particles with shades of green, yellow and brown. The size of the grains usually ranges from 0.5 microns to 50 microns.

2.2.3.3.2. Verdigris

With the Shift in oil painting at the end of the 15th century, verdigris was a highly favoured colour and gradually replaced green earth especially in western art, as it produced more intense and vibrant complexions than any other kind of green available at that time period. Although referred to earlier in ancient Greek and Roman sources, its use has been identified with certainty only in the Middle Ages and being more common later in oil paintings of the 15th to 17th centuries. Due to its low refractive index, this pigment tends to be very transparent and as a result it was often used as a lazure or in mixtures containing white lead to produce an opaquer colour. It was a popular landscape colour, but as verdigris is fugitive and very sensitive to environmental factors and degrades to dark brown in time; its beauty was often ephemeral.

Basic verdigris is prepared from copper plates which are fermented. The application of acetic acid to copper produces a bluish-green corroded crust covering the plates, which is gathered and washed. This process produces basic verdigris as well as neutral verdigris, which can be dissolved in strong acetic acid. The general term verdigris refers to all of the copper acetates, each one with a different chemical composition and a unique colour from blue-green to green-blue. The basic copper acetate is formed when acetic acid vapours along with moisture react with copper or copper alloys. The basic verdigris can contain the following types of copper acetates:

- $[Cu(CH_3COO)_2]_2 \cdot Cu(OH)_2 \cdot 5H_2O$ → cyan
- $Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 5H_2O$ → cyan
- $Cu(CH_3COO)_2 \cdot Cu(OH)_2$ → cyan
- $Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 2H_2O$ → green

Neutral verdigris is the neutral copper acetate $Cu (CH_3COO)_2$ - H2O, which occurs when basic acetates are dissolved in acetic acid, or when basic verdigris is ground up with strong acidic acid. On microscopic scale neutral verdigris has a crystallic form and can be completely dissolved in water resulting in a dark green solution.

Verdigris as the unusual tendency to change its colour distinctly forms a bluish tint to green. During the first month the change is quite strong but is there is relatively little change after. The scale of the colour change depends on both the type of verdigris and the binder that is used. It has been observed that the transition to green is usually less noticeable using neutral verdigris with oil as a binder than using basic verdigris with egg tempera as a binder. Furthermore, verdigris reacts with the following binders

- resinates, producing copper resinates
- oil, producing copper oleates
- proteins, producing copper protein compounds

It is well documented, that verdigris is a very good siccative agent, especially for oil based painting and the dye is quite unstable, which may lead to destructive reaction and degradation of other colours that are in contact with it. However, research confirms that verdigris is stable when used with lead based dyes as well as light. It is however sensitive to environmental factors and darkens when mixed with sulphur derivatives.

2.2.3.3.3. Malachite

The malachite mineral results from weathering copper ores and it can be found on the upper levels of copper ore deposits. In nature, malachite is associated with the rarer azurite, containing less chemically bound water. The sources of malachite during the Middle Ages are not known with precision; however, there are rare references of malachite deposits in mines in Hungary and Lyon, France from antiquity.

A particular feature of the malachite is that the performance of the colour depends on the size of the particles. The richest intense green colour is obtained by the coarse pigment (40-160 microns), while the fine species produces a pale green colour. The chemical compositions of both malachite and azurite consist of basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$ and $2CuCO_3 \cdot Cu(OH)_2$. On microscopic scale, fine grade malachite grains are spherical and have a fractured and colourless appearance, while coarse grade malachite particles exhibit pleochroism (an optical phenomenon in which a substance appears to be different colours when observed at different angles, especially with polarized light), which varies from colourless to intense green. The malachite mineral may also contain traces of azurite and cyprite (Cu_2O). Malachite is compatible with painting techniques but works best with tempera painting and it is subject to blackening when mixed with sulfuric dyes.

2.2.3.4 Blue

2.2.3.4.1. Azurite

The blue basic copper carbonate, azurite, is a natural pigment much more popular than the green counterpart. In nature, azurite occurs along with malachite in mineral deposits in Hungary and eastern France, near Lyon, known since antiquity. It is considered as the most important blue pigment in European painting throughout the Middle Ages.

Apart from its use for the painting of folds, the bright blue pigment is mixed with white to create sky colours and form lazure in indigo.

The pigment has a natural bright blue colour that may tend towards green. Like malachite, its colour depends on the grain size, whereas, coarse grade grains yield the most beautiful complexion. Furthermore, the azurite pigment colour depends also on the present concentration of malachite and cuprite mineral, which are often associated with azurite. Coarse grade particles have a dark blue colour, while the fine grade particles have lighter hues of blue.

The chemical composition of azurite consists of basic copper carbonate $2CuCO_3 \cdot Cu(OH)_2$. In general, it is unaffected by light, however, it can be darkened when heated, forming cuprite oxide (CuO). Azurite can also degrade to a green tint, when it is subject to increase in oxidation, as malachite is a more oxidized form of azurite. It has also been observed that heavy coats of azurite darken, especially when the pigment is separate from the carrier. One possible explanation for this change is the discolouration of the binder or the formation of a thin surface layer of cuprite oxide. According to literature, the pigment gradually losses its colour over time, when in admixture with oil as binder.

2.2.3.4.2. Ultramarine Blue

No other dye was held in highest regard in the Middle Ages than the beautiful blue ultramarine. This rare and precious dye came from the natural mineral lapis lazuli, which was mainly, if not exclusively, found in the quarries of Badakhshan Province in Afghanistan. Archaeological remains of the mineral used in building decorations, statues or other artefacts have been discovered dating back to the Neolithic age, but the first application as a pigment ingredient dates around 6th or 7th century. After the 13th century it became a very important commodity handled by the Republic of Venice and valued equivalently with gold. Due to its very high price, it was usually reserved for the decoration of the garments of Virgin Mary and Jesus Christ and was used under special order of the customer. It was also common practice to use blue ultramarine over underpainting of other pigments as azurite in order to use as less of the precious pigment as possible.

In 1828, French industrial chemist Jean Baptiste Guimet was awarded the prize offered by the *Société d'encouragement pour l'industrie nationale* for a process of manufacturing artificial blue ultramarine and from that point synthetic blue ultramarine became available at a much reduced cost compared to the natural mineral pigment. The so-called French ultramarine is essentially a composition of Sodium (Na), aluminium (Al), sulfur (S) and silicon dioxide (SiO_2) from the raw materials of anhydrous carbonate or sodium sulfate, kaolin, silica, and sulfur. The materials are ground to a fine powder and heated for several hours in vacuum. The result is a green mass, which is rubbed and washed to remove soluble salts. Finally, to extract the final blue pigment, it is reheated rubbed and washed once again. The complexion, the colour and the properties of the pigment vary with the proportion and the type of the raw materials used. In part, the tone of the blue colour depends also on the size of the grains, with bigger grains producing a darker blue.

The cause for the excellent semi-transparent blue colour of the pigment remains a secret, as the composition of the dye varies and is never stoichiometric. For example the following formulas have been given:

- $Na_{6,88}\,Al_{5,63}\,Si_{6,35}\,O_{24}\,S_{2,4}$
- $Na_{6\text{-}10}\,Al_{6}\,Si_{6}\,O_{24}\,S_{2\text{-}4}$

The synthetic blue ultramarine contains spherical particles having a relatively uniform size (0.5 to 5.0 microns) and shape, and is usually of finer grade and better homogeneity than the one prepared from the natural mineral. Conversely, the grains of Lapis Lazuli appear to be irregular and angular, and often contain impurities such as calcite crystals.

The chemical properties of the synthetic ultramarine are similar to those of Lapis Lazuli. It is relatively stable and unaffected by light, and may lose its colour when exposed to acidic environment. Ultramarine is hydrophilic and can be sufficiently moistened by egg tempera. Thus the granules are coated sufficiently by the drying egg and protected from reactions with air [20]. However, when used with oil, the pigment is not moistened to the appropriate level and as a result is less protected, which can the cause for the so-called ultramarine sickness. In general, the strong and bright blue colour is preserved when ultramarine is used with egg tempera as a binder, while in the case of oil painting ultramarine appears darker due to the relatively low refractive index.

2.2.3.4.3. Cobalt Blue

The Cobalt Blue in its pure form is a modern synthetic pigment having been discovered in 1802. It stands out in the blue colour palette due to its strong cyan complexion and brightness, compared to other blue pigments that tend to be darker and approach the black colour when used in heavy layers.

The simplest way of preparing the pigment is by calcination of cobalt oxide together with aluminium oxide to partially produce $CoO \cdot Al_2O_3$. The chemical formula of the dye is defined as $Co_3O_4 \cdot Al_2O_3$. However, the proportions can vary depending on the manner of preparation and the impurity content. On microscopic scale, the grains are bright cyan, moderately thin, spherical and irregular in shape. Cobalt blue is stable to light, insoluble in strong acids and alkali, compatible with all binders and has a good coating ability.

2.2.3.4.4. Indigo

Another very important blue pigment used in the Middle Ages is the natural organic pigment indigo prepared from herbs of the *Papilionaceae (Indigofera tinctoria L.)* family, native to India. There is also a synthetic form of Indigo, discovered in 1870, which has replaced the natural Indigo pigment. The organic pigment is known since antiquity and was probably used in Egypt as early as 2000 BC as a dye for textiles. There are later references by Dioscourides and Pliny of a dark viscous dye, extracted from plant reeds in India.

In Europe a similar plant, woad, from the *Isatis Tinctoria* family was cultivated. A derivative of this plant, the isatin, can be used to produce a blue pigment, which is of lower quality than the eastern variant of indigo.

To prepare the pigment, freshly cut reeds are soaked in a large container, where they are fermented. The glucoside is hydrolyzed to indigo and sugar. The dark precipitate obtained from the process is drained and pressed into plaques and finally is pulverized to produce a very fine powder, which will be used to create the dye [25].

The dark blue pigment was often mixed with yellow colours to produce green tints or white for sky-blue tints. In byzantine art, a special combination included an underpainting of indigo with thin coats of azurite as a lazure.

Even though, indigo has relatively low coating ability, it has good tinting strength and painted layers appear black in reflected light and green blue in surrounding light, especially if the layers are thin.

As a pigment, indigo is sufficiently stable to light and air, insoluble in water, alcohol and ether, but tends to discolour when exposed to ozone and atmospheric nitrogen dioxide. It is resistant to egg tempera membranes, while it dissolves completely in oil, giving the binder its colour. On microscopic scale, the pigment is of very fine grade and individual grains are not visible to normal microscope magnifications.

2.2.3.4.5. Prussian Blue

Prussian blue is the first modern pigment, which was introduced early in the 18th century. It is characterized by its strong colouring power using small concentrations of the pigment with any kind of binder. Its use is not limited to painting; Prussian blue has been utilized in ink production, textile dying, and wall paint and blueprint paper.

The basis of its chemical composition consists of $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ and $KFe[Fe(CN)_6] \cdot xH_2O$. There is a wide variety of complexions and properties depending on the method of preparation and the various additives, such as barium sulfate ($BaSO_4$), calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and alumina (Al_2O_3). The term iron blue refers to all these variants.

Since its introduction, the number of applications of Prussian blue increased until the 20th century, due to its versatility and higher stability compared to indigo. Characterized by the dark blue colour with a slightly greenish glint, it tends to resemble black. Due to its relatively low refractive index, it is quite transparent. Furthermore, it has very strong colouring ability, requiring minimum quantities of pigment to give a blue tint to white colours.

The pigment has been described as both stable and unstable due to the variety of additives, methods of preparation and choice of binder. It has been observed, that in the presence of white lead, Prussian blue transforms to green, but this phenomenon is explained by the change of the binder colour to yellow. Furthermore, Prussian blue pigments are sensitive to alkaline environment and cannot be applied to fresco painting. Microscopically, the pigment appears amorphous and has very fine particles, from 0.01 to 0.2 microns, which have the tendency to aggregate. Similar to indigo, fine particles cannot be distinguished in oil, even at high microscopic magnifications.

2.2.3.5 White

2.2.3.5.1. White Lead

Historically, white lead is the most important white pigment in painting and one of the oldest artificially produced pigments. Used since antiquity, it was the only white pigment for painting until the 19th century, when this monopoly was abolished with the introduction of zinc oxide.

In painting, white is the colour of natural light and as such it is used to illuminate the objects of the painting. Combined with blue it produces sky tints and with red flesh tints. It was also applied as preparatory underpainting and for different colour lightings.

Until recently, the pigment was prepared with the commonly known Dutch method or stack method, which is slightly different form the method of the Classical and Medieval eras. Stripes of lead are placed in clay containers, which have separate compartments filled with vinegar. The containers are stacked in a warehouse, drowned in manure or bate, which produce heat and carbon dioxide. Gradually, the simultaneous effects of vinegar, carbon dioxide and heat convert the lead into basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$. The resulting crust is scraped off the surface of the metal stripes, washed, dried and finally pulverized into powder.

The pigment has high coating ability due to high refractive index, thus requiring relatively less binder, about 1:10. On microscopic scale, the pigment has fine spherical and uniform particles of 1 to 2 microns. When heated, the pigment turns to massicot, litharge and finally red lead. It is also quite toxic.

Normally, white lead is stable and remains unaffected by light. However, it has been reported to blacken in the presence of hydrogen sulfide with which reacts producing black coloured lead sulfide. This is more common in egg tempera painting, while in oil painting the pigment is protected by the oil layer [26]. Traces of brown coloured led dioxide can also be formed in the presence of microorganisms. Even though, theoretically white lead is incompatible with sulfureted pigments, it is stable in admixture with cinnabar and Ultramarine.

2.2.3.6 Black

2.2.3.6.1. Carbon Black

The black pigment is derived from the carbonation of wood and other organic materials. A popular type in the Middle Ages is produced by the burning of the young shoots of vine and gives a slight blue tinge of black. To prepare the pigment, the charcoal is washed and any residual ash is removed. To guarantee good quality pigment, ancient recipes insist that the burning should be in the absence of air. The chemical composition of the pigment consists mainly of carbon, but never in a pure form as there exist different impurities.

Carbon black has been used since antiquity and has a limited but significant use in byzantine art in the drawing outline and writing. It was rarely used as a pure colour and it was often mixed with other pigments to create grey tints and shades.

Charcoal is very stable pigment unaffected by light, acids and alkalis, and thus is compatible with all painting techniques. It also has moderate to good coating ability. On microscopic scale, the organic pigment is amorphous and its black particles vary in shape and size, often preserving the structure of the wood from which it originated.

3. Silver and copper in Medieval and Renaissance metalworks

Among the most common metals used in Medieval and Renaissance Europe for artistic, liturgical and luxury objects are silver and copper.

While copper – based alloys, like bronze and brass, were mainly used for monumental and small statuary and for medals and panels (to decorate doors or altars), silver was the material of choice for liturgical items. The Christian church has always been one of the most important patrons for the goldsmith's trade. Throughout its history, precious silver or gold coated silver objects have played an important role in its rites and ceremonies. The richness or simplicity of sacred vessels reflects differing ideologies within the Christian church. At various stages of church history special kinds of silver items have been made in response to concerns and beliefs: reliquaries for the venerated remains of saints, crosses for processions, alms dishes for the collection of gifts for the poor. This diversity reflects the complex history of the church. Reliquaries are the containers that store and display relics. Since the relics themselves were considered more valuable than precious stones and gold, it was considered appropriate that they be enshrined in vessels, or reliquaries, crafted of or covered by gold, silver, ivory, gems, and enamel. These precious objects constituted a major form of artistic production across Europe and Byzantium throughout the Middle Ages. Medieval reliquaries frequently assume the form of caskets (chasses) but complex containers in the form of parts of the body, usually mimicking the relics they enshrined are one of the most remarkable art forms created in the Middle Ages for the precious remains of saints. Reliquaries were also fashioned into full-body statues, or bust-length images of saints. As reliquaries, other liturgical objects were made of silver or gilt silver, both for liturgical use (chalices and paters) and for public worship (processional crosses). They also often exhibit complex working techniques and combination of materials. Few Medieval and Renaissance silverworks have come down to posterity. Because of the inherent value of their materials, many were destroyed, or rather, constantly recycled: they were melted down and reused in newer, more fashionable pieces. However, the significance of medieval and Renaissance silverwork goes far beyond its material or decorative value. Precious objects communicated complex meanings and connotations and thus constituted an indispensable part of the medieval language of signs.

Copper alloys, like brass and bronze, have been extensively used since the antiquity: alloys of copper with tin began to be made in the Old Word from the fourth to the third millennium B.C. for utilitarian and decorative use.

Bronze is an alloy of copper and tin while brass is an alloy of copper and zinc to which other elements may be added in smaller amounts. Both bronze and brass can receive various patinations, such as gilding or organic coatings. Bronze and brass were used for the casting of bells, guns, artillery and utilitarian objects such as mortars, but in the fifteenth century they came increasingly into use for the casting of sculpture. Many European cities had bronze foundries, but Florence saw the first true flowering of bronze sculpture. The main monuments e are the two pairs of bronze doors by Lorenzo Ghiberti on the Baptistery (1404–24 and 1425–52) and several key works of Donatello. To the north, a brassier metal was preferred, but the lustrous reddish bronze of Florence set the standard. While outstanding monumental bronze works had been carried out in Florence, notably Benvenuto Cellini's Perseus (1545–54), it was Giambologna who was most influential in translating monument into statuette, and his art was echoed by court sculptors all over Europe, including the Dutch-born Adriaen de Vries and the Munich-based Hubert Gerhard. Beside the life-size statuary and big reliefs, collectors' taste for bronze statuettes coincided with an onset of interest in classical antiquity, which led to the making of several highly refined reductions of Greco-Roman antiquities. The remains of Greco-Roman antiquity—coins, gems, sculpture, buildings, and the classics of Greek and Latin literature fascinated the Italian Renaissance. Artists put any efforts to emulate the exemplary works of the ancients, even striving to surpass them.

In Renaissance Europe, two very different methods have been used for the casting of bronze sculptures: lost wax casting and sand casting. Lost wax casting predominated during most of this period, as it gives the artist considerable freedom to cast complex forms in one piece with fine surface detail. In basic terms, lost wax casting involves the formation of a mold around a wax model. The model is heated, which removes the wax and creates a space into which molten bronze is poured. There are two distinct variations, direct and indirect lost wax casting, determined by the method used to form the wax model around which the mold is made (referred to as the casting model). Although small solid-cast bronzes were made in the early Renaissance, there are many advantages to casting hollow. Less metal is used, which decreases the cost of the materials and the weight of the sculpture and makes it easier to transport and to hold in the hand to admire. More important, a solid-cast bronze is more likely to be flawed as a result of trapped gases and shrinkage porosity.

For these reasons, great effort was put into creating hollow casts with walls of relatively even thickness.

The more straightforward method of lost wax casting, the direct lost wax technique allows the artist to cast directly off of the original model, and is ideal for wax models with complex surface textures as well as large and complex compositions.

In indirect lost wax casting, the artist is free to use a range of materials, for example, wood, clay, or solid wax, to sculpt the original model. A mold is then made of the original model and duplicate wax models (referred to as intermodels) are made in the mold. These duplicate models are used for the casting, thereby preserving the original model. Numerous intermodels can be made from the molds. They can be virtually identical, or, with reworking, numerous slightly different replicas can be made. In addition, an intermodel lost due to a fault in the casting can be replaced with relative ease. Because the original model is preserved, it can be used as a guide for workshop assistants to carry out the final chasing of the bronze, freeing the artist from this laborious task. Because of the tremendous amount of time and materials needed to create a piece mold and a separate model for casting, the indirect technique may be impractical for large sculptures or those with complex compositions that include deep undercuts. The technique of sand casting allows the relatively straightforward creation of replicas. For centuries, the technique was most often applied to simplified forms such as medals, furniture mounts, or flat metalwork. Complex forms are difficult to sand cast. Once a sand mold is formed around a model, it must be disassembled to take the model out. If there are undercuts in the model, the mold must be made in pieces. For this reason, sand cast sculptures tend to be cast in parts that necessitate assembly and reworking of the metal to hide the joints.

3.1 Metals

3.1.1 *Silver alloys*

Silver has been known and used since ancient times due to its pleasant white colour, its reflectivity, polishability and shine. Silver was produced continuously through the Middle Ages in Europe, and even exported from there. In addition to silver mines that played an important part in silver production in the early and the High Middle Ages -Poitou (Merovingian period), Sardinia (11th-12th c.), the environs of Goslar, Germany (10th-12th c.), Freiberg, Saxony (12th-14thc.),- rich silver mines were discovered in the second half of the thirteenth century in Kuttenberg (Kutná Hora), Bohemia, which supplied silver in great quantities until its decline, due to the Hussite wars, in the fifteenth century.

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 7) and these alloys have been much used in jewellery and silversmithing work. The diagram shown in Figure 7 presents the phases existing as a function of the alloy composition and of the temperature (horizontal and vertical lines respectively). The extreme left ordinate represents pure copper (melting point 1083 °C), and the extreme right, pure silver (melting point 960 °C). Between both extremities, there is one liquid phase (L) and two different solid phases, from which one is copper-rich (alpha) and the other silver-rich (beta). Depending on the composition of the alloy and temperature, it is possible to obtain a great variety of structures in the cold metal. The alloy of lowest melting point, called 'eutectic', contains approximately 70% silver and 30% copper (case a, Figure 7). As this alloy cools from the liquid state, solidification is instantaneous when a temperature of 780 °C is attained. The resulting eutectic structure consists of very fine lamellae of both phases, alpha and beta, disposed alternatively. When the silver content is greater than in the eutectic alloy, not only does the proportion of beta phase increase, but also the distribution of both is different (case b, Fig. A). This is because, in this case, the solidification does not occur instantaneously. The time period necessary to complete the passage from liquid to solid allows the 'excessive' silver content (relative to the eutectic composition) to solidify first, in the form of a primary beta phase. Only later, when cooled to a temperature of 780 °C, does the eutectic solidification take place. A third possibility, most frequently found in 'silver' objects, corresponds to copper contents up to 5 or 10%. In this case, the proportion of the silver-rich (beta) phase is even greater, which reduces the possibility of eutectic formation and limits the existence of the alpha phase to a few locations between grains of the predominant beta phase (case c, Fig. A).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 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.

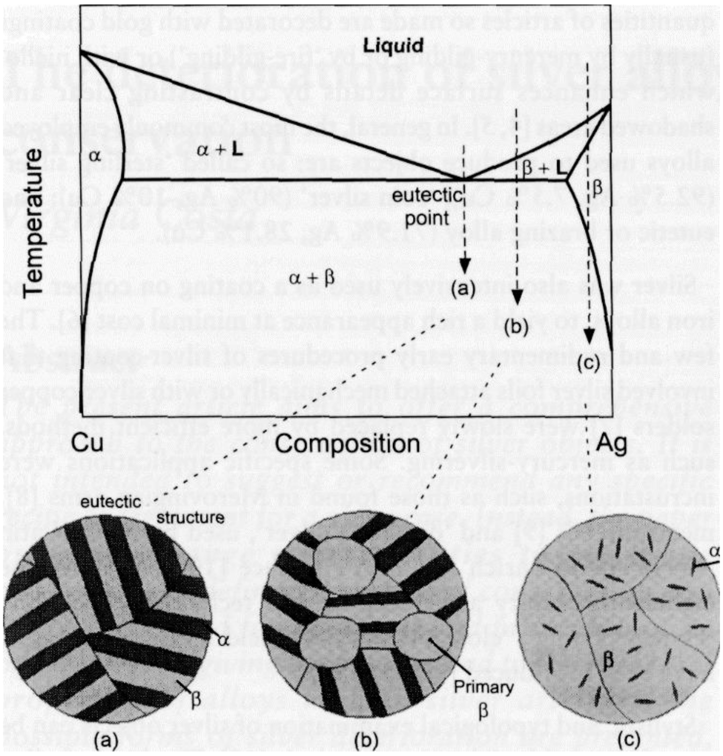


Figure 7: Silver-Copper phase diagram

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 colored 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 (color 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 color 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 color; 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.

3.1.2 *Copper alloys*

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 expansive in the ancient word.

The typical alloy compositions used in Middle Ages are low-zinc brass and bell bronze (20% tin, 80% copper). In Renaissance statuary a composition conceptually similar to that of Classical and Hellenistic bronzes, which often had a tin content around 10% and a low percentage of lead, is often encountered, as well as quaternary alloy (Copper-tin-lead and zinc) used for example for the panels of the Porta del Paradiso by Lorenzo Ghiberti (Baptistery, Florence, Italy) and the Amore Attis by Donatello (Bargello National Museum. Florence, Italy).

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 8). 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.

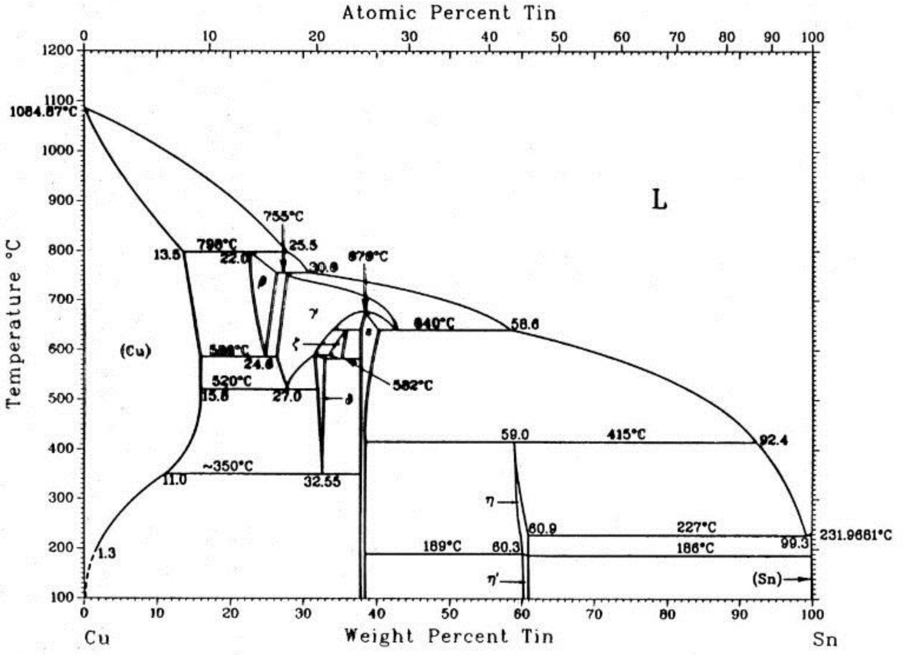


Figure 8: Phase diagram of copper-tin alloy.

Alloys made of copper and zinc have traditionally been described as brasses. They range in colour from a red similar to pure copper through a pleasing yellow to white (above about 45 wt% zinc). The phase diagram for copper and zinc is shown in Figure 9, and the phases relevant to brasses are in the colored region with the lower zinc content. These brasses are single-phase copper-zinc alloys that contain up to about 38 wt% zinc (labelled α in the phase diagram). They have generally good workability, although those with high zinc concentrations are easily work-hardened and must be annealed frequently during working to keep them soft. As the zinc content of brasses increases, the colour of the alloy gradually changes from red to yellow. The yellowest brasses are the single-phase α brasses with the highest amount of zinc. Copper-zinc alloys containing small amounts of zinc (typically less than 9%,) were called gilding brass because they were often-used as a base metal for gilding with gold leaf or by electroplating. Copper-zinc alloys with about 15%, zinc are similar in colour to gold.

Tin brasses are copper-zinc alloys (typically containing greater than 15% wt zinc) to which about 1% wt tin is added. These tin brasses are significantly more resistant to dezincification (i.e. loss of zinc) than the same alloy without tin. Resistance against corrosion of tin brasses is also improved by small amounts (typically in the 0.5-1% wt) of antimony, arsenic or phosphorous.

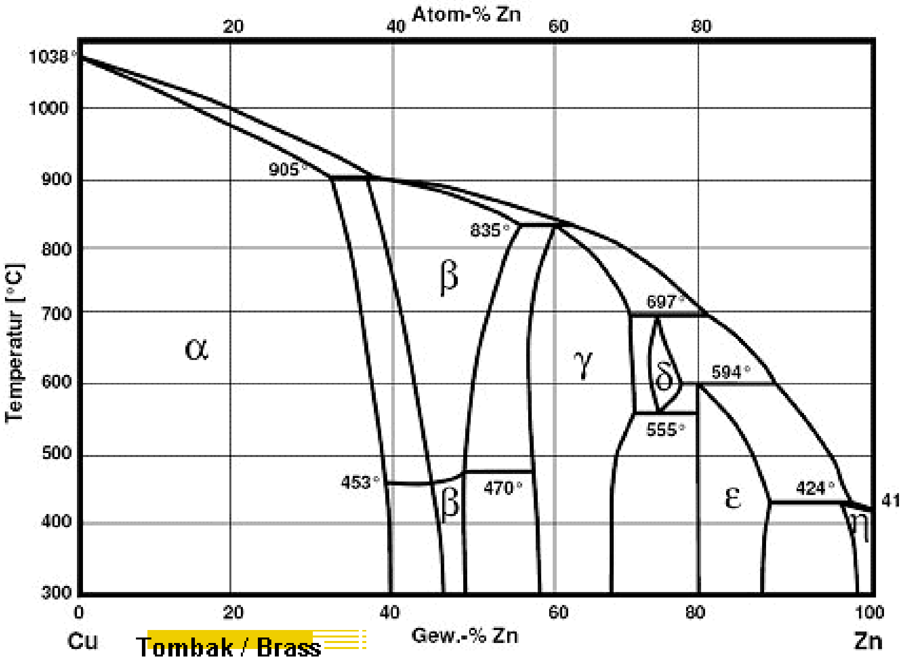


Figure 9: Phase-diagram of Cu-Zn alloy. The colored region shows the range of brass compositions.

3.2 Surface features: finishing, decoration, patination

3.2.1 *Silver alloys objects*

Real heritage silverworks often exhibit subtle details worked by many diverse finishing techniques. 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. The surface was often decorated with techniques such as embossing (raising the metal from the back by beating), chasing (raising the metal from the front), engraving or punched decoration of varying fineness. The different parts were often joined by riveting or soldering (this latter done either at a temperature below 250°C with a tin solder or over 700°C with a hard solder of copper alloyed with gold or silver). The silver core of the object was often further enriched by applications made of the same material. Designs were formed from gold or silver beads, beaded wire (granulation) or twisted wire (filigree) decoration. The real beauty of medieval items lay in the carefully designed contrast between the shining silver or gold and the decoration of the surface with niello, enamel, gems, and coloured glass paste. The addition of various coloured materials greatly enriched the surface of the silverwork. Engraved designs were often filled with niello, a black paste-like mixture consisting of copper sulphide or silver sulphide, and then the surface was smoothed and fired. The result was a stark contrast between the matt black niello and the shining precious metal. Coloured surfaces could be achieved by the application of either transparent or solid enamel (coloured glass fired onto the metal base) as well as of gems and pearls.

3.2.2 *Copper-alloys objects*

When it emerges from the mold, a bronze statue is not yet finished. In most cases, there are faults that must be repaired. Depending on how fine the mold was, the surface of the bronze will appear more or less even. Sometimes a mold is broken during casting, damaging the statue beyond repair. Then the whole object is submitted to another casting, or the faulty segment is removed and replaced by a new element. When the casting is completed, the first work is smoothing the surface to eliminate the imperfections. Several tools are employed: rasps, scrapers, files, polishers, burnishers, and smoothing tools. It is likely that pumice and abrasive powders were also used. The tools were made of stone, steel, iron, or bronze. Their marks can be detected on the surface and that can contribute to understand the fabrication process. Evidences of wax – to-wax joints can also provide valuable clues on the fabrication technique and the casting method. After the surface was finished, the statue was submitted to further elaboration, for the fashioning of hair, eyes, ears, mouth, muscles, bones, hands, feet, and clothing. Special mention must be made of the bronzes made by cold-working. The bronze is annealed - brought to a red heat and then cooled - and hammered. The hammered parts are treated in "repousse" or embossing and completed with dies, swages, and stamps; the surface is finished off with chisels and sharp points, to set off the designs. For cast bronzes in general, the chiseling processes are subordinated to the hardness of the metal. Whatever the composition of the bronze, different operations for obtaining linear details must be distinguished:

- Tracing is done with a chisellike tool with a slightly blunt edge that is pushed with a little hammer; it gives a "linear impression." The metal is displaced, turned again on the sides, and afterward leveled with a hammer;
- Engraving is done with a graver, a sharp, hardcutting tool; the metal is cut and pushed, so that the tool removes a long, thin curl of metal. For wider furrows, a gouge or hollow chisel is employed For circles, rings, or half-circles, as well as for hollow designs, chisels and swages are used (Figure 10);
- For punching, engraving points are used (Figure 11).

Finishing of the wax model as well as polishing and cold working of the metal surface greatly affect the appearance of the surface texture in terms of reflectivity and glossy.

Other marks detectable on a bronze or brass sculpture are casting defects and foundry repairs, which are sometimes hidden by a colored patina layer. Casting defects are revealed by porosity (Figure 12) occurring throughout the sculpture to varying degrees. A wide variety of repairs were used on the sculptures, applied by either at the casting time or later on. These repairs are often made with a different alloy to allow an easy recasting of the infill. Sometimes, the presence of organic past fills on the object (wax and/or resin with or without a pigment) suggests that there may have been one or more past restoration campaigns. Past interventions may be also revealed by fine scratch lines caused by the scraper.

Figure 10: Magnified detail of an engraved bronze surface.

Figure 11: Punched bronze surface.

Figure 12: View of a copper–alloy surface showing defects and pits (South Door of the Florence Baptistery by Andrea Pisano).

When speaking about bronze surfaces, the word “patina” has many meanings, but the most accepted by scholars and conservators is a varnish coating–coloured and frequently translucent–applied over the entire bronze surface either by the sculptor himself or his workshop (Figure 13). In the art-historical literature, these deliberate coatings are not only called “patinas” but also “lacquers” or even simply “varnishes”. These applied patinas were intended to protect the surface, to enhance the beauty of the finished sculpture, but also to hide conspicuously patched defects of casting. Despite the fact that such varnished objects have been kept almost always protected indoors, their surfaces were subject to alterations, either by the effects of time or by deliberate later intervention.

According to the varnish technique it is possible to define three types of varnishes–spirit varnishes, essential oil varnishes, and oil and oleoresinous varnishes, respectively. Spirit varnishes are prepared by dissolving one or more natural resins in alcohol. The varnish dries by solvent evaporation, leaving behind a resinous film, which can be easily re-dissolved because the resins undergo no chemical changes during drying. A second type of varnishes is those in which the resins are dissolved in an essential oil (e.g. oil of turpentine or oil of spike) instead of alcohol. The resulting varnish, however, dries extremely slowly. A third group of varnishes are oleoresinous varnishes containing both siccative oils (walnut or linen oil) and resins. The non-volatile components change from liquid to solid during drying usually by means of oxidation. As a result of this change, the varnish is no longer soluble in the original solvent. These varnishes become tougher, harder and more resistant to solvents when dried by the use of heat, and oil or oil-resin varnishes known since the 8th century were commonly applied for patination and protective coatings on indoor Renaissance and Baroque bronzes.

Many museums in Europe host collections of bronze statuettes made in Renaissance times (Figure 14). In the Renaissance, the passion for collecting bronze statuettes all'antica by contemporary sculptors led to the making of more or less faithful, small-scale reductions in bronze after famous, large-scale antique sculptures. These small-scale reproductions were made to be held and manipulated, since they could be fully appreciated only when taken down and handled, allowing the light to play on their shimmering surfaces. From Italy, where several workshops existed, these statuettes spread all over Europe, often as diplomatic gifts. In these objects, color and character of bronze surfaces are provided by a patina, which may result from natural effects produced by exposure to air or soil, or, more often, deliberate treatments applied by the artist. In such treatments, color, shading, and translucency were created and modified by applying coatings or chemicals. After a careful and laborious cold working—finishing after casting—including scraping, burnishing, and polishing with various grades of abrasives, artificial patinas were standard practice. The colors of those patinas range from black to red and yellow and green. The original patina, despite the manipulation and handling, is still preserved in protected areas of the works. The patina colors were achieved with acids and heat or the abovementioned types of varnishes. These coatings served either to unify the appearance of the sculpture and to emulate ancient bronzes or to enhance the carefully finished bronze surface. Although the original patinas would have been a brilliant color, these coatings have darkened and become more opaque with age. For this reason, these objects underwent re-application of new patinas, either on the whole surface or on deteriorated parts of it, with techniques and material only pretending the original coating. Furthermore, maintenance programs of the collections would have included the periodical application of protective coatings, based on wax, to preserve the patinas from the handling or the airborne deposit. The application of this variety of materials led to the existence of patches of different composition and thickness on the object' surface, which are not visible to the naked eye and this rises challenges to the conservator's work.

	
Figure 13: Example of a translucent reddish patina on a bronze horse	**Figure 14: Large collection of bronze statuettes displayed in a museum.**

While some recipes for metal patination are provided by Theopilus in his *De diversis artibus* of 1110-40, it is during the Renaissance that the interest in everything antique led to an extensive practice of applying a patina on metals. Many Renaissance bronzes were finished with a reddish translucent patina that was partially formed by cuprite and overlaid with resinous finishes. Sometimes, a green varnish was also used in order to imitate the natural patination. It is difficult to determine the original surface appearance of most Renaissance. Some sculptures from this period may have been originally colored red, brown, opaque grey, or black. There is a large variety of possible appearance of these kinds of translucent, principally organic resins or varnishes, which are applied to a surface for reflectivity and to augment the color of the patina. Nevertheless, a full assessment of the patina ingredients is not an easy task, even with the combination of advanced analytical techniques like GC-MS, FTIR and Raman spectroscopy. The implementation of image techniques and of methods to measure thickness and texture would be of help in examining more recent restorations of patina involving wax or other coating resins or varnishes. The surface patina of bronzes often reflects a complex pastiche of events that could have occurred at any stage in the past. The majority of Renaissance bronzes was waxed to seal and finish the patina and is routinely rewaxed as part of their normal maintenance. Due to the abovementioned reasons, the surface of the sculptures varies considerably from area to area, sometimes ranging from pale to dark bluish green to olive green to golden brown.

3.3 Alteration and degradation of copper and silver alloys

The structure and the composition of naturally formed alteration layers on a metal surface depends on the type of metal or alloy, the working technique and the environment (weathering conditions, exposure, burial soil). An alteration layer is generally formed by incrustations of substances coming from the soil or form the atmosphere and by alteration products of the underlying metal. Sometimes, such layers include also organic and carbonaceous substances either from biological organisms or previous treatments (finishing or protective coatings). Thus, layers of different colors, morphology and composition are encountered on the surface of a degraded metal.

The alteration products are due to both the electrochemical corrosion (wet corrosion) and the chemical corrosion (dry corrosion). The former implies a non-local charge transfer by means of a conductor joining the anodic and cathodic areas, while the chemical corrosion is a process where a local charge transfer occurs and is due to a direct oxidation of the metal by agents like O_2, CO_2, H_2S, etc.

3.3.1 *Silver alloys*

Many objects of cultural heritage interest, either of silver alloy or silver plated copper alloys, are displayed in museum window cases or stored in depositories. These artefacts tend to suffer from tarnishing (Figure 15), which is the production on the surface of the alloy of a blackish thin film caused by the interaction of the metal surface with certain atmospheric pollutants, mainly sulphides. In a marine environment, the problem of chlorides is also encountered.

Atmospheric corrosion of silver occurs in the presence of moisture, thus its corrosion depends on relative humidity (RH). In an environmental temperature of 10-20°C, at 90% RH, there are eight monolayers of water on the metal surface and these water layers provide the medium to adsorb atmospheric gases. Gases that can be involved in indoor atmospheric corrosion can be O_2, O_3, H_2O_2, H_2S, COS (carbonyl sulphide), SO_2, HCl, Cl_2, HCHO, HCOOH and CH_3COOH. Sulphides, both in the form of H_2S and COS, are the most harmful pollutants to silver objects, the concentration in the environment that attacks silver being very low, to the extent of 0.2 ppb. The tarnishing reaction mechanisms are:

$$8Ag + 4HS^- \text{<--->} 4Ag_2S + 2H_2 + 4e-$$

$$0_2 + 2H_2O + 4e- \text{<--->} 4OH^-$$

The first reaction is believed to occur in a thin film of water on the silver surface. In dry air, tarnishing does not take place. In the second reaction, oxygen acts as a cathodic species and consumes electrons as indicated in the equation. Typical indoor levels for hydrogen sulphides (50-100 ppt) and carbonyl sulphides (300-500 ppt) are enough to cause tarnishing, the rate of which is increased as the RH and the level of other pollutants (i.e. NO_2, O_3, Cl_2) rise. Their synergistic effects are, however, small in typical concentrations of the gases. Silver chloride is also found as a corrosion product of silver. Chlorine gas and sodium chloride react with silver to produce silver chloride.

Untarnished silver is highly reflective and has a white colour. As the silver begins to tarnish, the initial film is essentially invisible until it is about 100 nm thick. As the tarnish increases in thickness from about 10 nm to 100 nm the film appears coloured (i.e. yellow, red, blue) due to the formation of interference colours (i.e. interference between the light reflected from the outer and inner film surfaces). Slight differences in thickness give rise to iridescent colours. As the tarnish layer becomes more than about 100 nm thick, the film colour becomes black. Under more severe tarnishing conditions (e.g. high RH and high levels of sulphur containing pollutants), silver sulphide may grow as elongated crystals, that have been observed in laboratory conditions as well as in museum objects.

Unlacquered silver objects have been known to tarnish in less than three months. Some studies show that the reaction rate decreases when the sulphide thickness increases. This can be explained by diffusion of H2S through the tarnish film, which becomes more difficult when the layer thickness grows. Prevention of chemical tarnishing is achieved by using barriers such as lacquers to prevent the reactive chemical species contacting the silver.

Figure 15: Detail of a panel of the San Giovanni altar (Opera del Duomo Museum, Florence), tarnished silver-copper alloy.

Some pollutants, like SO_2, that are not harmful to silver, can however affect silver alloys. The less noble components of the alloy can react with sulphur dioxide and produce Cu_2S. Silver alloys can also undergo selective corrosion, i.e. the corrosion develops in some specific areas. In silver-copper alloys, a green surface layer can be observed due to the formation of copper compounds. Removing these compounds leads to a surface richer in the nobler metal, i.e. silver. Native Americans were aware of this phenomenon and exploit it to make a silver-rich layer on silver-copper alloys. The surface of silver-copper alloy can also act like a battery, with the formation of cathodic and anodic regions. The copper-richer phases are anodic regions and undergo preferential dissolution. This process, starting from the surface, can go deep into the bulk, leading to the desegregation of the less noble phases. Also the working technologies can induce corrosion (stress corrosion) on silver objects. Cold working leads to the formation of slip lines and to the precipitation of a less soluble phase, which is commonly dispersed in the matrix as a metastable phase. The slip lines act as a barrier against the impurities and minor phases migration. Thus, an accumulation of phases and impurities occur at the slip lines and regions are formed with mechanical weakness and poor resistance to corrosion.

The blackish film formed with tarnishing makes silver artefacts inappropriate to display. Tarnish can be removed from silver mechanically, chemically, or, sometimes, electrochemically. The removal of tarnish from works of art requires most care and efforts and can raise some ethical questions as each polishing or chemical removal takes away a certain amount of constitutive silver.

Despite guidelines and recommendations point towards the use of sulphur traps in sealed storage containers or display cases, a physical barrier against sulphur bearing gases is the protective solution of choice in most of the cases. Conservators apply a limited number of organic coatings to surfaces of silver artefacts, which meet the requirements of keeping the initial appearance, ease of application, stability in time, reversibility of treatments. Among these are cellulose nitrate lacquers, the acrylic resins Paraloid and microcrystalline waxes. The monitoring of their performance and effectiveness over time is fundamental to ensure a good care of silver items and to make the decision on when to apply a new coating before the onset of tarnishing.

3.3.2 *Copper alloys*

Many factors, such as the composition and the microstructures of bronzes, the corrosive environment features of the context, and others can influence the chemical and structural nature of bronze patinas. Thus bronzes can exhibit complex and heterogeneous corroded structures. Nevertheless, independently of the alloy compositions, patinas of bronze objects have many similar morphological features such as the presence of tin-enriched corrosion layers. The formation process of bronze patinas in natural environments is mainly related to a decuprification phenomenon, the selective dissolution of copper, connected to an internal oxidation of the alloys. The main factors affecting the alteration phenomena of outdoor bronzes are the following:

External factors:

- Chemical composition of the atmosphere and presence of
- Humidity as moisture or rain (promoting factor)
- Sun irradiance (effect of UV and temperature)
- Exposure to other environmental agents, like wind

Internal factors:

- Type of metal or alloy
- Type and structure of corrosion products
- Casting defects
- Exposure of the different portions of the object

Oxygen is one of the most reactive substances of the atmosphere, but the reaction of this gas with the metal surface cannot be considered the key factor of the alteration of a metal surface. The oxide which forms in this reaction is usually thin and compact and tends to form a film well adhering to the metal. It provides a sort of protection to the underlying metal. This interaction is called chemical or dry corrosion and, on a bronze surface, leads to the formation of a cuprite layer. The same happens when the moisture content is low and a thin (10-100 Å) and discontinuous water film occurs on the surface. Cuprite could be transformed into basic carbonates, like malachite, due to the action of humidity. Malachite and other carbonates form green patina with a protective action. This was the regular alteration pattern of ancient bronze artefacts, before the industrial era. Several studies show that the relative humidity plays a fundamental role in determining the corrosion rate. The water film formed on the surface can adsorb gas pollutants, concentrating them and promoting the contact between oxidizing molecules and metal surface. The electrochemical corrosion, however, is the main mechanism through which water acts (***wet corrosion***), with the formation of concentration cells or other types of batteries. The concentration cells can be due to different salt concentrations, differential aeration as well as differential temperature. These mechanisms are responsible for example for the so-called pitting corrosion. The oxide layer on the surface has hygroscopic properties and generally allows the water film formation even when the RH is below 100%, around 60-80%. Also dust and hygroscopic salts like $(NH_4)SO_4$ or NH_4NO_3 promote the water adsorption and moisture formation. When salts are present, the conductibility of the liquid phase on the surface increases and thus also the corrosion rate increases. The content of air pollutants is fundamental in determining the corrosion rate. Gases like SO_2, SO_3, O_3, NO_2 are known to rise the acidity of the liquid film on metals. The solubility of the stable oxide formed on the surface greatly increases when the acidity rises and thus the rate and the extent of the attack also increase.

Numerous alteration layers can be observed on bronzes. They are often classified into two main types, according to the presence or absence of an original surface preserving the original shape of the artifact. In the first type (Type I), the original surface is visible or simply concealed by copper containing deposits or earthy crusts. Often called “noble patina”, this type of layer exhibits remarkable protective properties. It is characterized by a high-tin enriched surface corrosion layer due to copper depletion, also containing chemical compounds of the corrosive context such as carbonates, silicates, sulphates etc. The type II alteration layer exhibit a thicker and much more complex structure than Type I. Nevertheless, an internal tin-enriched layer is systematically evidenced as mainly connected to the presence of oxide or hydroxide compounds, with a relative enrichment in Cl content.

Bronze alteration layers show a broad range of compounds like sulphates, nitrates, chlorides, acetates, formates and oxalates, monocarboxilic acids, alcanes and polyaromatics. The characteristics of the alteration layer on bronze surfaces depend also on the chemical and physical characteristics of both the alloy and the surface.

The decuprification process induces a strong enrichment in tin compounds in the surface layer due to an important selective dissolution of copper ions in the environment. The amount of dissolved copper is quite constant on the whole thickness of the surface of the tin enriched layer, but is depending on the tin content in the alloy. Therefore, as shown in Figure 16, a relationship exists between the tin contents of the alloy and the surface layer of type-1 patinas, for great number natural environments (soil, urban atmosphere, water lake, etc.) and independently of the historic period of the considered bronzes. Thus, the amount of dissolved copper ions released seems to be connected to the corrosivity of the context (soil, atmosphere…) and not to the time of exposure. The more severe the corrosive conditions, the more copper of the bronze is dissolved and, consequently, the more tin content in the surface layer of type 1 alteration layer is high.

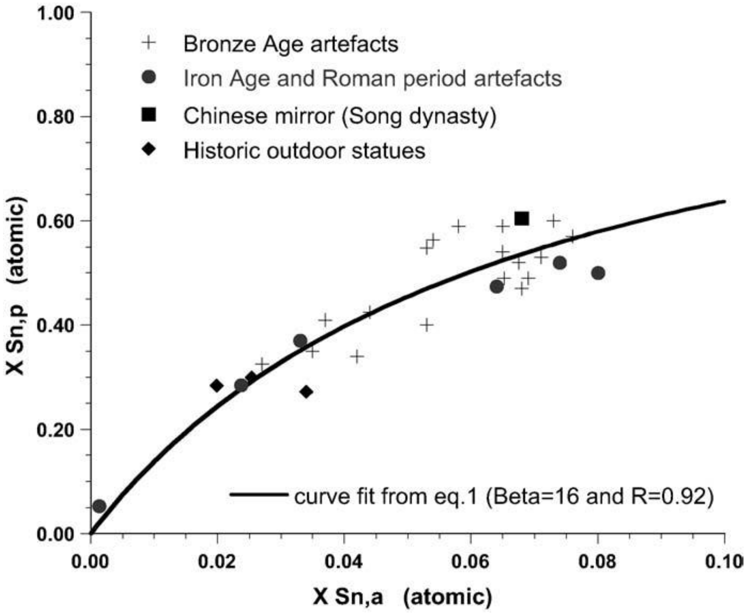


Figure 16: Atomic fraction of tin cations in the passivating outer layer XSn,p as a function of the atomic tin fraction in the alloy XSn,a for bronzes of various origins and different historical periods, from L. Robbiola, J.-M. Blengino, C. Fiaud, Morphology and mechanisms of formation of natural patinas on archaeological CuSn alloys, Corros. Sci. 40 (1998) 2083–2111.

Further effects of the alloy composition on the corrosion behaviour are related to the content of lead. Lead bronzes are more attacked than regular tin bronzes, while the ternary Cu/Sn/Zn alloys are more resistant. High zinc (24-40%) brasses are more prone to dezincification.

Sometimes, also the other elements are involved in patina formation. In alteration layers of brass, zinc sulphates and basic zinc sulphates are observed, in lead- bronzes or brasses, insoluble lead salts are included in the alteration layer.

The objects in their environments reach a steady-state regime, i.e. the thickness of ancient bronze alteration layer is not a function of the time of exposure. This is confirmed by comparing long-term corrosion tests on copper and copper-base alloys exposed in different natural corrosive environments with archaeological samples. The corrosion penetration for the modern alloys and pure copper after less than two decades is typically between 10 and 100 µm, which is equivalent to that usually observed for type-I alteration layer of archaeological bronzes. The average penetration of the corrosion with respect to time of exposure follows globally a parabolic law (Figure 17) in a great number of natural environmental conditions. Consequently, type-1 layers of bronze build up in a relatively short period of time (several decades) in natural environments. The case of thicker layers, also often observed on ancient bronze, is usually the consequence of localized attacks or a non-uniform generalised corrosion (type-II patina). These thicker layers could form during the early stage of exposure, but more generally can form intermittently up to the present (as, for example, in the case of the bronze disease). Consequently, type-II patinas are also not related to the duration of corrosion and to the age of the object.

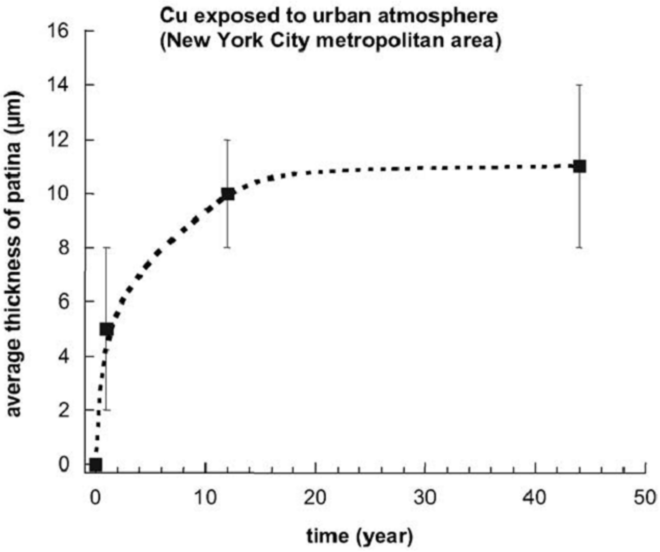


Figure 17: Time corrosion curve (average penetration) (from J.P. Franey, M.E. Davis, Metallographic studies of the copper patina formed in the atmosphere, Corrosion Science 27 (7) (1987) 659–668.)

The aspect of an outdoor weathered bronze sculpture is affected by many factors. The early formation of a cuprite layer can provide a certain protection and slow down the corrosion. On the other hand, a corrosive process which produces green soluble corrosion products leads to the formation of a non-protective layer. These compounds can be solubilized and also produce an electrolyte solution on the surface. An high zinc content in the alloy can slow down corrosion processes, since it is believed to form non-soluble hydrated oxide. An high Zn-low Pb allow, however, exhibits an higher corrosion rate in some corrosive environments.

In the modern era, the rising level of air pollution made people used to green appearance of outdoor bronzes. In the early stages of industrialization, bronze sculpture were covered by black layers containing carbon particles and this kind of "patina" was considered unsuitable if compared to the green layers. Despite the green "patina" are also due to the interaction with pollutants, many artificial patinas were aimed at reproducing the green colour of the surface and this colour was long considered as naturally developed. During the 70s, with a raising awareness to the effects of pollution, more attention was paid to the conservation of outdoor bronze sculptures. In some countries the uneven appearance of outdoor bronzes, with green and black patches and strips, was considered an issue, while somewhere else copper was still believed to naturally become green according to a romantic view.

Actually, the exposure of bronze sculptures to air pollutants produce changes that can be harmful to the life of the object or, sometimes, hinder to acknowledge the proper significance. Generally speaking, a sculpture conserved outdoor for at least two decades show on the surface alternate patches and strips of dark and light green. These areas are related to variable grades of the surface, presence of undercuts, sheltered areas and fully exposed areas (Figure 18).

Areas exposed to rainfall are light green, due to the solubilisation and washing off of copper compounds, the action of the sunshine and the mechanical action of heavy and persistent rain. They are also the most attacked. They are composed of cuprite and brochantite (copper hydroxysulphate), with some posnjackite (hydroxysulphate), atacamite and paratacamite (the latter being hydroxychlorides). On statues recently exposed, antlerite (again a hydroxysulphate) should be the main product in black layers since this compound forms in the early stage of formation of alteration layer. In the horizontal portions, the washing off is the main process of alteration, here a deeply corroded surface occurs and the original surface with the details and working marks, is lost.

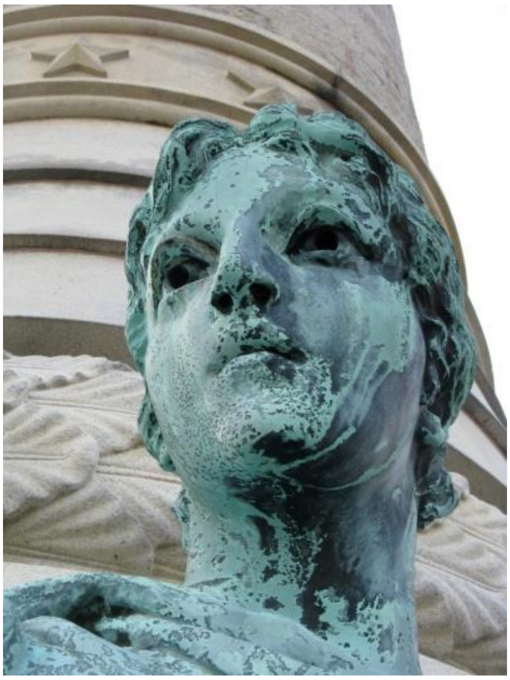


Figure 18: Alternating green and dark areas on a corroded bronze surface.

The higher solubility of copper salts respect to tin and lead compounds leads to the occurrence of cement-grey surfaces in artefacts made of tin, lead and zinc-rich alloys exposed to frequent washing off. This is due to the superficial loss of soluble copper salts, while the alteration products of the other elements are not leached. Vertical green areas, exposed to winds, are better preserved and contain brochantite and other products. Horizontal portions, sheltered from the rainfall, look generally black due to the accumulation of dust. Other sheltered areas, not horizontal, are dark and smooth and represent properly the original surface of the sculpture. They can contain copper hydroxychlorides which can be converted into soluble sulphates and other deliquescent salts through the interaction with humidity and SO_2. This reaction can lead to pitting corrosion. The dark colour is related to crusts containing carbon particles and gypsum. Where the rain water flows, alternating light and dark strips are observed. Orange or brown areas are also encountered, where the action of the acidic rain dissolves the alteration compounds and the reddish cuprite layer is left.

To sum-up, on outdoor bronze sculpture the following situations are observed:

1. Black and smooth surfaces, sometimes with brownish or green aspect, representative of the original bronze surface, with an underlying cuprite layer. They are composed of cuprite and atacamite;
2. Thick black crust overlapping a light green layer and a cuprite layer. The black crust contains soot. It is composed of quartz, atacamite, paratacamite, feldspars and sometime copper hydroxysulphates;
3. Orange or brown cuprite layer (in recent sculptures). Orange strips are also present, due to the leaching of the alteration layer with the solubilisation of the outer layers;
4. Black areas surrounded by light green corroded areas (Figure 19).

5. Corroded rough areas with light green color. These areas are hit by the rainfall or are vertical portions exposed to strong winds. They are composed of cuprite and brochantite (copper hydroxysulphates) (Figure 20).

	
Figure 19: Black and light green areas (type 4).	**Figure 20: Corroded rough areas with light green color.**

Because of all the aforementioned reasons, the bronze and brass outdoor heritage objects are usually protected to slow down the corrosion rate. General requirements for a coating for protection of metallic heritage are:

- Good adhesion of the film formed by the coating to the surface and good penetration into the pores of the metal and of the patina, thus assuring a good protection against corrosion;
- Transparency;
- Barrier performance against water vapour ad air pollutants;
- Ageing resistance;
- Reversibility;
- Non-toxicity;
- Drying at room temperature (for large size sculptures).

As recent surveys among conservators have shown (PROMET EU project 2004-2008, IPERION-CH EU project www.iperionch.eu), despite the proposal of innovative materials for protection, the most applied coatings include waxes (beeswax, microcrystalline wax) and synthetic lacquers (mainly acrylic ones, belonging to the Paraloid group), with and without inhibitors (Benzotriazole (BTAH) is the most popular one). Overlapping layers of different products has shown better long-term performance than a single material layer. Particularly, sandwiches of acrylic and wax have proven to be a good balance between aesthetic and performance requirements.

4. Conclusions

It is evident and clear that within this task and based on the already existing knowledge of OF-ADC and OPD as well as the initial measurements performed within task 3.2 and Task 3.4 a selection of samples was done simulating with high fidelity the under study objects (icons and metallic ones) selected for the scan4reco project. The developed samples with the previously described materials are described in deliverable 3.2.

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