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Oil painting on copper: characterization of the copper support and the feasibility of using pigmented wax-resin infills for paint loss reintegration.

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Resumo

A presente tese está composta em duas partes. A primeira centra-se no estudo de placas de cobre utilizadas como suporte de pinturas a óleo. A pertinência deste estudo prende-se com a escassez de informação actual sobre este tema.

A investigação envolveu a comparação de informação recolhida em tratados históricos de metalurgia, estudos recentes sobre pintura em cobre e arqueometalurgia do cobre, com os resultados analíticos realizados em quinze suportes em cobre de pinturas europeias dos séculos XVII e XVIII. Esta metodologia revelou resultados interessantes relativos ao processo metalúrgico, da redução do minério cuprífero em lingote de cobre, bem como ao subsequente processo de manufactura das placas de cobre.

A purificação do minério cuprífero tratava-se de um processo complexo e dispendioso, envolvendo multiplas fases, que terão sido rigorosamente seguidas, sendo prova disso os altos níveis de pureza identificados nas placas de cobre estudadas.

As análises científicas realizadas nas placas de cobre das quinze pinturas estudadas revelaram também que a manufactura de transformação dos lingotes em placas envolveu ciclos alternados de trabalho de martelagem a frio seguidos de recozimento. A martelagem a frio sofrida pelo cobre permitiu obter uma placa com a dureza adequada, enquanto que o recozimento devolvia a maleabilidade necessária para o trabalho a frio ser realizado sem provocar a quebra do metal.

A segunda parte da presente investigação, centrou-se na procura de uma nova fórmula de cero-resina adequada para utilização como material de preenchimento em pinturas a óleo sobre cobre. Esta nova fórmula baseou-se na prévia caracterização de duas cero-resinas usadas em preenchimentos de lacunas em pinturas a óleo: uma cero-resina utilizada por Leslie Carlyle nos anos 80 (C-PWR) e a cero-resina Gamblin (G-PWR). Ao contrário destas duas cero-resinas de referência, a nova fórmula teria necessariamente que excluir a cera de abelha que reconhecidamente tem um impacto negativo quando usado sobre o cobre. Um nova opção de material de preenchimento é particularmente importante dado que a variedade de materiais actualmente disponíveis não são adequados, por diferentes razões, para o uso neste tipo de suporte.

Apesar da absoluta necessidade de ainda se efectuarem testes de envelhecimento, a caracterização realizada nos materiais puros bem como na mistura da nova fórmula encontrada - KTW5-R1, feita a partir de cera microcristalina Techniwax 9426 e Regalrez 1094 - revelou que esta nova cero-resina apresenta resultados interessantes, nomeadamente: apresenta um valor ácido igual a zero e uma provável estabilidade química, que advém do facto de ser composta apenas por hidrocarbonetos saturados.

O presente trabalho resultou numa apresentação oral e em duas publicações:

Artigo aceite para apresentação e publicação, *Colóquio em Investigações em Conservação do Património*, “Arte e Ciência: Investigação sobre a técnica e materiais aplicados na pintura sobre cobre”, Daniel Vega, Isabel Pombo Cardoso and Leslie Carlyle. Faculdade de Belas Artes da Universidade de Lisboa (FBAUL), Lisboa.

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Palavras-chave: Pintura a óleo sobre cobre, Caracterização analítica da chapa de cobre, preenchimentos volumétricos, Cero-Resina

Abstract

The present work is divided in two parts. Part 1 concentrates on the study of the manufacture of copper plates used as a support for oil paintings since to date, there has not been a great deal of information available. The research involved comparing the information gathered from historical treatises on metallurgy and recent studies of paintings on copper and copper archaeometallurgy, with results from a set of thorough scientific analyses undertaken on the copper supports of fifteen European paintings (dating from the 17th and 18th centuries). This comparison revealed interesting insights into the metallurgic processes used to produce the copper ingot from native copper, and the subsequent manufacturing processes undertaken to obtain the copper plates.

Copper ore purification was a complex and expensive process. Purification included several steps, all of which were rigorously executed as attested by the high level of purity of the copper produced.

Scientific analyses undertaken on the copper supports of the fifteen European paintings revealed that the manufacture of the plates from the ingots involved cycles of cold working alternating with annealing. Hammering took place which would have been aimed to form a plate with adequate hardness, while the intermediate stage of annealing returned malleability so that further intense cold work, necessary to achieve a plate without breaking, could be carried out.

Part 2 focus on the characterization of two wax-resins formulations used as infill materials for oil paintings: a formula used by Carlyle in the early 1980s (C-PWR) and Gamblin pigmented wax-resin (G-PWR). and, based on the negative impact on copper of the acidic beeswax in both formulations, an exploration to find a new formulation with a neutral acid value was carried out. Preliminary trials and testing focussed on the development of a new wax-resin formulation suitable for infills on oil paintings with a copper substrate. New options for infill materials on copper supports are particularly important as the range of infill materials currently available are not suitable, for a variety of reasons, for use on this type of support.

Although ageing tests are still needed, the characterization of the individual materials, and of the new formulation, KTW5-R1, made of Techniwax 9426 microcrystalline wax with Regalrez 1094, showed that this wax resin mixture with an acid number of 0, is likely to be inert in relation to the copper and chemically stable since it is composed of saturated hydrocarbons only.

This work resulted in one oral presentation and two publications:

Paper accepted for presentation and publication, *Colóquio em Investigações em Conservação do Património*, “Arte e Ciência: Investigação sobre a técnica e materiais aplicados na pintura sobre cobre”, Daniel Vega, Isabel Pombo Cardoso and Leslie Carlyle. Faculdade de Belas Artes da Universidade de Lisboa (FBAUL), Lisbon.

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Keywords: oil painting on copper, analytical study of plate, infills, wax-resin

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Symbols and Abbreviations

XR	X-radiography image
RL	Raking Light
XRF	X-ray fluorescence spectroscopy
ASS	Atomic absorption spectrophotometry
ICP-SFMS	Sector Field Inductively coupled plasma mass spectrometry
BF	Bright Field
X-Pol	Cross polarized light
XRD	X-ray diffraction spectroscopy
OM	Optical Microscopy/Optical Microscope
µ-EDXRF	Micro-Energy Dispersive X-ray Fluorescence Spectroscopy
µ-FTIR	Micro-Fourier Transform Infrared Spectroscopy
µ-FTIR-ATR	µ-FTIR - Attenuated Total Reflectance
µ-PIXE	Particle Induced X-ray Emission
SEM/EDS	Scanning Electron Microscopy with Energy Dispersive Spectroscopy
UNL-DCR	Universidade Nova de Lisboa – Departamento de Conservação e Restauro
C-PWR	Carlyle's formula used in the earlier 1980s
G-PWR	Gamblin Pigmented Wax-resin
CCI	Canadian Conservation Institute
ASTM	American Society of the International Association for Testing and Materials
PB72	Paraloid B72
PB48	Paraloid B48
BTA	Benzotriazole
BASF	Badische Anilin – und Soda-Fabrik AG
MW	Molecular weight
Tg	Glass Transition Temperature

PART 1 – THE SUPPORT OF PAINTINGS ON COPPER – COPPER PLATES

1.1 INTRODUCTION

The first part of this thesis focuses on the study of the copper plates used as the support for paintings, exploring the materials and techniques used to produce them. The research involved the comparison of the information gathered from historical treatises on metallurgy and recent studies of paintings on copper and copper archaeometallurgy, with results gained from this thesis work, from a set of thorough scientific analyses undertaken on the copper supports of fifteen European paintings (dating from the 17th and 18th centuries). This research aims to enhance knowledge regarding these supports since, to date, there has not been a great deal of information available.

1.1.1 PAINTINGS ON COPPER – A SUMMARY OF THE STATE OF THE ART

Several authors [1-6] refer to the widespread use of copper plates in Europe in the 16th century for different purposes: covering domes and roofs of churches and palaces; protection of ships' hulls; engravings and etchings; enamelling; and paintings.

According to Speel (1998) there is a reference to the early use of these plates by artists to produce enamel paintings. Speel records that enamelling on brass supports was in use in Europe from the 12th century but in the 15th century copper plates become much more common [7]. Stijman (2012) states that this is possibly related to the fact that after 1430 copper plate production increased greatly as a response to the flourishing printmaking market to supply the demand for the production of all kinds of books. Stijman suggests that Germany was probably the country where the engraving technique on copper plate originated [3].

According to Van der Graaf (1976), painting on copper can be dated from the middle of the 16th century[1], while its decline started at about the second half of the 17th century [8]. Nevertheless, Bowron (1998) [9] states that the technique continued, throughout the 18th century, in countries such as France and Spain; while Horovitz (2012) reports the sporadic interest of painters in this pictorial technique during the 19th and 20th century [5]. In addition, it is important to mention that the majority of European written sources about how to paint on copper date from the second half of the 17th century and from the 18th century [10-12].

Bazzi (1939) states that geographically, the earlier evidence of the use of copper as an oil painting support is associated with Italy[2] [13]. Bowron suggests that, the technique could then have been adopted by Flemish artists, active in Rome, and exported to Northern Europe [9].

The adoption of this kind of painting in Europe is attributed to several factors which can be divided into three main topics: technical advantages identified by artists; social-cultural taste; and economic

[1] Van der Graff (1976) associates this date to some known artists who used this metal support and who are mentioned by Vasari and Van Mander: Sebastiano del Piombo (1485-1547), Bartholomeus Spranger (1546-1625), Pieter Vlerik (1539-81) and Hans Rottenhammers (1564-1623).

[2] Bazzi (1939) reviews the origin of the technique of painting on metal, based on literature sources from Plinio to Pacheco, and concludes that the first paintings on copper were produced in Italy, and that this pictorial technique was already referred to by Leonardo da Vinci in his treatise dated from the end of the 15th century.

reasons. These topics, which are outside the scope of this thesis, have been discussed in depth by several authors; for further information, consult [2; 3; 5-7].

The decline of the production of painting on copper is not well understood [8-10]. The Italian authors, Terenzi (2006) and Rizzo (2008), mention that it was probably due to artists noticing corrosion problems on the support, as well as the limitation of size, since these supports are associated primarily with relatively small format paintings [14,15].

Over the last 40 years several studies of paintings on copper have been published. They cover their history [2, 8, 9, 11, 16, 17], while some include materials and technical characterisation of the pictorial layers [11, 12, 18, 19]. The conservation and restoration of these pieces have received less attention [14, 15, 20-23].

Amongst these publications, some stand out for their contribution to topics which are under study in this thesis, such as the empirical exploration of consolidants [24], a scientific approach to consolidants [20]; the interaction between the support and materials used in the pictorial layers [25]; decay mechanisms [26, 27]; and the technology of silver coloured metal coatings [28].

ANALYTICAL STUDIES RELATED TO THE SUPPORT

To date there are few studies on the copper supports themselves which are used for paintings particularly at an analytical level.

The most frequent techniques applied to the characterisation of the copper support are raking light and X-radiography. The selection of these two complementary techniques is mainly related to their potential to identify concentric rings or regular indents which are connected to the manufacture of copper plates: hammering or rolling [11, 29-31]. These techniques are also used to assess the condition of these objects (fragile areas, cracks) [31]. Analytical studies on copper plates using other techniques are rare (see Table 1).

Though very valuable, the information supplied by these studies cover few actual objects, and it is fragmented and not contextualized within the panorama of European copper plate manufacture during the period under study in this thesis.

The few qualitative and even fewer quantitative studies carried out, only refer to the high purity of the copper plates with no further discussion of the results. In addition, the analytical methodology of these studies lack optimal conditions which could compromise the results (see further discussion in the methodology section 3.1).

TABLE 1 – Survey of analytical studies of copper supports for paintings

YEAR	AUTHOR	ANALYSED OBJECTS	DATE	ANALYTICAL TECHNIQUES					
				RL	XR	OM	XRF	SEM-EDS	PIXE
1970	BUCK [29]	1	17TH C.		√				
1991	SPRING [33]	1	17TH C.	√	√				
1999	MAULE [34]	1	17TH C.	√	√				
2001	IZAT [35]	1	17TH C.	√	√				
2004	KOLTZ [36]	1	17TH C.			√		√	
2012	PITARCH [37]	1	16TH C.				√		
2013	GOMEZ [38]	2	18TH C.	√	√				
2013	SCHMID [28]	7	17TH C.	√	√				
2015	CORREGIDOR [39]	3	17TH C.						√
2015	VEGA [32]	2	17/18TH C.	√	√	√	√		
2015	OLIVEIRA [20]	1	17TH C.	√					
2015	VEIGA [40]	16	17TH/18TH C.				√	√*	

XR: X-radiography image; **RL:** raking light; **XRF:** X-ray fluorescence spectroscopy, **SEM-EDS:** Scanning electron microscopy with Energy Dispersive X-ray Spectroscopy; **PIXE:** proton induced X-ray spectroscopy; **OM:** optical microscopy. √ quantitative results; √ qualitative results; * 3 paintings were analysed

1.1.2 THE STUDY COLLECTION

For this thesis, the reverse of 86 European paintings on copper (20 from the collection of the Museum Nacional de Arte Antiga and 66 paintings from private collections and auction houses), dating from the 17th to the 18th centuries, were studied visually, searching for features that are commonly mentioned in the existing studies: hammering or rolling marks, the shapes of the corners and makers' marks (attesting the quality of the material).

From this group, fifteen paintings (including three fragments of paintings) were selected to be part of a thorough study of their supports following analytical methods commonly used in metallurgical and archaeometallurgical studies (see methodology section 3). These works based on their stylistic and technical features, they date from the 17th and the 18th centuries, while the production centres are attributed to Portugal, Spain, Italy and Flanders (Figure 1). (See Appendix I)

PINT-B

PINT-C

PINT-E

PINT-G

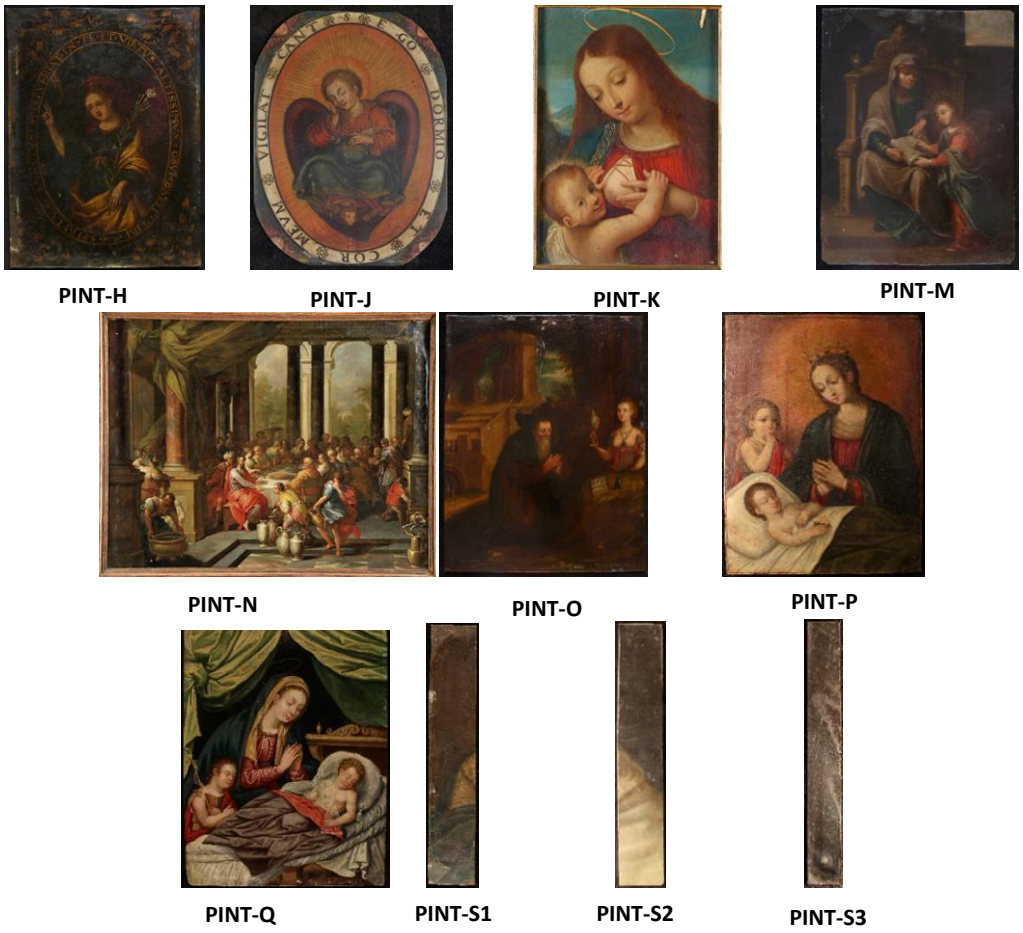

FIGURE 1 – Paintings studied for this thesis

1.1.3 THE MATERIAL: COPPER AND ITS USES

Copper was one of the first metals used by humans, ca. 7000 B.C [3, 42] and has been widely used throughout the centuries [42], for a variety of purposes: the production of coins; the synthesis of green (e.g. malachite) and blue pigments (e.g. azurite); and as noted above, as copper plates for various purposes (e.g. roofing sheets, polished mirrors, protection of ship hulls). As well as for alloys such as with zinc to create brass, which was used for example for military hardware (e.g. guns), civil objects (e.g. frames, candlesticks), church objects (e.g. crosses, liturgical vessels), and jewellery, etc.; and alloyed with tin to form bronze for use in sculptures, bells, etc.

By the end of the 15th century, the copper industry was situated in east, central and north Europe, especially in Germany, Austria, Hungary, Norway, Sweden and Russia, as the main copper mines were situated in these areas [3, 41, 42].

Copper is a transition metal, with the atomic number of 29. It has a melting point of 1083/5ºC [3, 42] and a linear thermal expansion ($^{o}C^{-1}$) of $16.5x10^{-6}$ [42]. Its crystal lattice has a face-centred cubic arrangement [41]. Aside from gold and silver, copper is the only metallic element with colour. It has a salmon pink to reddish colour. Copper can be found in a pure state (or 'native') in nature, as well as in mixtures with other minerals [3, 42].

Impurities usually associated with copper ores are iron, lead, zinc, antimony, and arsenic; less common are selenium, tellurium, bismuth, silver and gold [40].

Pure copper is too soft for practical uses. Due to its ductility, it can be worked cold (e.g. hammering) to increase its hardness. Also, the intentional addition of other metals helps copper to harden. The most important copper alloys are brass (Cu and Zn) and bronze (Cu and Sn). Both increase the hardness of the material [42].

1.2 TECHNICAL LITERATURE

Copper ore, the raw material used to produce copper plates, needs to undergo several procedures before reaching the artist's atelier. These steps can be summarised as: extraction and purification, resulting in copper ingots; copper plate manufacture; and selection for artists[3].

According to Tylecote (2002) the technology for copper extraction and purification did not change substantially during the 17th & 18th centuries, the period under study here. Tylecote states that metallurgical techniques were almost the same since the mediaeval age until the second half of the 19th century, when electrolytic methods were introduced [4].

For this research it was important to study the historical technical literature on mining and metallurgy as there is little published research on copper metallurgy specifically from the 17th & 18th centuries that could be of help in the interpretation of the analytical results obtained in this thesis [43]. The books written by Theophilus (12th century)[4] [44], Vanoccio Biringuccio (1540) [45], and George Agricola (1556) [46] were selected since they are regarded as the most significant for this subject since they contain a large number of observations concerning mining and metallurgical processes [47-48].

Concerning the manufacture of copper plate; this topic is mentioned by several authors who studied paintings on copper in the last 12 years, however these authors primarily rely on the same three secondary sources: Horovitz (1986 & 1999), Wadum (1999) and Komanencky (1998) (see Table 2). For this research, the doctoral work of Ad Stijman[5] (2012) on copper plate manufacture for engraving and etching, is particularly valuable since it includes the study of a wide number of historical and contemporary sources which describe how a plate was obtained from the copper ingot [3].

To understand how copper plates arrived in the artist's atelier, the works of two art historians, interested in paintings on copper, were consulted, Komanecky (1998) and Wadum (1999) [2,17].

[3] The copper trade is outside the scope of this thesis, for information on this topic, consult [18].
[4] For editions consulted see Appendix II.
[5] Ad Stijman is an authority in European plates for etching and engraving. As mentioned in section 1.1, one of the reasons for the beginning of painting on copper was the production and availability of copper plates for printmaking.

TABLE 2 – The 3 sources most commonly cited for plate manufacture by authors studying painting on copper

Year	Authors	Sources			
		Horovitz		Wadum 1999 [18]	Komanencky 1998 [2]
		1986 [31]	1999 [11]		
2004	Pavlopolouv [26]		√	√	
2006	Terenzi [14]		√	√	
2012	Broers [25]	√	√	√	√
2013	Goméz Lanzas [38]	√	√		
2013	Schmidt [28]		√		√
2015	Oliveira [20]	√	√		
2015	Veiga [12]		√		

1.2.1 COPPER EXTRACTION AND PURIFICATION ACCORDING TO SELECTED HISTORICAL SOURCES

This section details the chemical transformation involved from the extraction of the mine until it is cast as an ingot, according to selected historical sources.

According to Theophilus, Biringuccio and Agricola in order to extract and purify the copper, several steps were necessary: the ore extraction (including preparation and roasting); followed by purification (including smelting and refining) (Appendix II) [44, 45, 46].

Preparation – This involves all procedures between mining and roasting; from visual separation of the primary material to its calcination, in order to progressively increase the purity of the material [51]. **Roasting** is one of the most significant steps of the ore extraction because, through calcination, it drives off as much sulphur as possible by oxidation to sulphur dioxide gas (SO_2) [4]. An open furnace is used during this procedure which reaches about 400 ºC, allowing oxygen to react with the ore [49]. Ure (1853) reports that the temperature is gradually increased and becomes high enough to roast the ore without melting or agglutinating it [50]. It has also been suggested that arsenic and antimony compounds might be partially lost by volatilization during the roasting [4, 51].

Forbes (1950) and Tylecote (2002) state that much of the copper ore after 1500 was sulphidic[6], therefore roasting was an important and common procedure [4, 51]. In addition, Garbacz-Klempka (2014) states that the presence of sulphur in the copper matrix of an object is an important indicator of the fact that the metal came from sulphidic ores [52].

According to the literature research (summarised in the table in Appendix II), roasting should be repeated several times. Agricola adds that roasting was successfully accomplished when the colour of the ore was reddish [46]. Rostoker states the red color is caused by Fe_2O_3 formed during the calcination [49], a component to be removed in the next stage.

[6] Copper is widely distributed in the nature. Neolithic man used native copper (pure copper) which was deposited directly in earth's crust. However, copper is usually bonded with other chemical elements to form copper ores. The earliest mining of copper ores started with the surface deposits of oxide and carbonate ores [51]. During Antiquity, the copper demand was so great that superficial ores practically gave out, and miners start digging deeper into the earth to explore sulphidic ores [51].

Smelting – This involves the separation of the metal present in the roasted material from, as Agricola termed it: the "earths, solidified juices, and stones" [46, p.353] or slag, by heating the ore in a furnace while large amounts of oxygen are provided by the bellows.

The importance of this phase is mentioned by Biringuccio who states that "Smelting is a thing essential to the end for which ores are sought, for without it every ore is a useless stone" [45, p. 145].

Tylecote (2002) explained that after this operation was concluded, a "matte (a mixture of copper and iron sulphides) and slag" was obtained [4, p. 108] rich in iron oxide. Forbes (1950) adds that at this stage, matte copper contains only a little arsenic, antimony and silica [51]. He also mentioned that during smelting, fluxes are important not only to facilitate the formation of slagging compounds but to protect copper from oxidation [51]. Fluxes have several functions, primarily: to act as purifying agents (to remove impurities) and as flowing agents (to help the ore melt). For copper ores; lead, litharge, quartz, marble, silica, iron or copper slag (amongst others) could be added [4, 45, 46, 50, 51]. Agricola notes that fluxes were selected according to "the colour of the fumes which the ore emits after being placed on a hot shovel or an iron plate" since they might indicate the types of impurities present in the ore [46, p. 235].

Smelting, is undertaken in a furnace where the temperature reaches at least 1100ºC, a temperature necessary to obtain an oxidizing environment (this temperature is above the melting point for copper). Two immiscible liquids are produced (slag and matte) which are then easily separated [49]. Tylecote (2002) indicates that this procedure took 12 hours and could produce up to 300 kg of matte, and that it was repeated 3 times, or more, in order to enrich the copper content of the matte and to fluxe away the iron as slag [4].

Smelting could also include 'liquation' which basically consisted of adding lead into the forehearth to recover silver from copper. Lead and silver were also separated by the method of cupellation [46].

It is important to note that lead was not always added in this stage, as silver was not always present in the ore. Agricola wrote, "if there is small amount of silver in the ore, no lead is put into the forehearth to absorb silver (…); if there is no silver, copper is made direct" [46, p. 402-3].

Refining – The copper obtained by smelting needed to be further refined before it was malleable enough to be cold worked. This consisted of blowing air into the molten metal, so that remaining impurities were oxidized and deposited in the slag. At this point the copper sulphides formed during smelting begin turning into cupreous oxides. Finally, a technique called 'poling' was used. It consisted of introducing green wood into the molten copper; reducing the cupreous oxide to copper metal while CO_2 is released [46, 51].

The main concern after the whole process had taken place was the quality of the final material. Theophilus advises to "test it thus to see if it is well purified. Hold it with the tongs before it is cooled, while it is still red-hot, and strike it hard on an anvil with a large hammer and, if it breaks or splits it will have to be melted again as before." [44, pp. 144-145]. Biringuccio noted "copper must be pure and without any trace (of impurity), otherwise it cannot be hammered thin" [45, p. 210]; and for Agricola, after refining the material, "if the copper is good it adheres easily to the bar" [46, p. 535].

After refining, the final product was cast into ingots.

1.2.2 MANUFACTURE OF COPPER PLATES

According to an illustration in Agricola's book, copper ingots could be cast into a round shape [46]. Nevertheless, Craddock (2012) states that copper could also be cast into a 'battery plate', a kind of flat rectangle, as this form was the most suitable for the production of copper sheets by hammering [53]. Horovitz (1999) notes that molten metal was poured into an inclined bed of sand for making plates [11]. David Scott (2014) states that this process is possible but it "is very difficult to control" [54, p. 111]. With regard to ingot production in the 19th century, Ure (1853) mentioned that they were usually produced around 30 cm broad, 45 cm long and from 5,5 cm thick [50]. This may indicate that during the 19th century, rectangular ingots were common. Even, if we cannot determine precisely the most adequate or the most commonly used shape of an ingot to be transformed into a plate during the 17th and 18th centuries, either by the historical literature or via analysis, we do have evidence of the physical existence of both shapes (round and rectangular) [42, 52, 53, 55, 56], and both or either could have been used to produce plates.

Horovitz states that the ingots were initially beaten manually with hammers[7] until a plate was formed [3], but hammering could also have been powered by watermills [11]; this method was reported to be common in German towns from the fifteenth century, and from the eighteenth century in France [3, 57].

To form the size required, Horovitz (1999) notes that plates could be cut with shears [11] or "by running a needle or knife along a steel ruler a few times. In the latter case the cut line is aligned with the edge of a table and the extending part is moved up and down until it breaks off" [3, pp. 142-3].

Plates could even be hammered further [3]. While Horovitz (1999) suggests that the final step for producing a plate was to flatten the surface using a manual planishing hammer[11], in more recent research by Stijnman (2012) he states that because copper plates for engravers or etchers needed to be perfectly flat, a series of different materials and procedures was performed, likely by coppersmiths or specialized workmen [3]. Stijnman (2012) provides a description of plate preparation: first, "the plate was fixed between nails on a table or workbench and the surface made level with a tool not unlike a plane" [3, p. 141]. Then, the surface was sanded in stages by using sand stone and pumice stone[8]. Finally the plate was polished, a tightly rolled piece of felt and some oil was rubbed on the surface. The final result was a front surface, shiny as a mirror, and the reverse of the plates, in the view of Stijnman, would be marred by cracks and dents. Stijnman's concludes that the above method was the principal one in use until the 19th century[9] [3].

In the view of Ad Stijman, hammering at room temperature, "gave to engravers' plates a more compact and homogeneous structure, which enable better handling of the burin" [3, p. 141].

Scott (1991) explains that hammering produces dislocations in the planes of atoms in the crystalline structure of copper (face-centered cubic) [58]. This increases density, turning the metal harder while losing ductility and malleability. After a certain amount of hammering the material becomes brittle. Scott states that at this point, the metal would have been annealed in order to induce recrystallization of the

[7] Horovitz mention that these hammers weight up to 500 pounds [11].
[8] Rinsing between stages was necessary in order to remove particles that might damage the surface.
[9] Horovitz states this manufacturing method was "well into the eighteen century" [11, p. 66], Broers agrees saying that "le laminage était neanmoins peu utilise avant le 18th siècle" [6, p. 72]

grains, restoring some ductility and malleability. Cycles of cold-working and annealing are carried out until the desire shape is obtained [58], in this case: a plate.

According to Horovitz and Scott an alternative method to obtain a plate was the use of rolling mills [11, 54]. Stijnman reports that other metals, such as lead, silver and gold, were flattened by roller presses from the end of the 15th century. He also points that copper plates could have been produced using this technology since the 17th century, or even before, if the plates were rolled while still hot, or lead was intentionally added to the alloy [3]. But he states that for copper plates intended for engraving, this procedure would have been quite uncommon and would only have been possible since the second half of the 18th century.[10]

During this research, the reverse of 86 paintings on copper was studied visually and most appear to show almost imperceptible hammering marks. Support for the idea that they were flattened by hammering is reinforced by the scarce literature regarding examples of rolled copper plates used in paintings [11, 29, 33]. Nevertheless, it should be noted that Buck's (1970) analysis of a painting on copper, by Domenicho c. 1604, indicated that the support was produced by rolling [29].

1.2.3 THE SELECTION OF COPPER PLATES FOR ARTISTS

According to Wadum (1999), the choice of the copper plate was not necessarily made by the artists but dealers or patrons [18]. Wadum notes that they likely considered at least four factors: appearance, cost, purity, and the reuse of old plates.

Regarding to the appearance of the copper plates, they could sometimes choose plates with visible hammer-marks, and in other circumstances, perfectly smooth surfaces [2]. According to Horovitz (2012), the physical difference between both sorts of plates was probably related to the producer: the copper-beaters or the coppersmith [5]. This would likely influence the cost of the final product.

Wadum (1999) states that weight rather than size was a decisive factor in the cost; and also that cleaned copper plates were more expensive than those not cleaned [18].

Concerning the purity of the plate, Pernety, the author of a French artist's manual published in 1756, notes that there were two qualities of copper plates; those which were reddish and more 'pure' (a better quality) and those which were yellowish which were less 'pure' (a lesser quality) [59]. According to several authors, pure copper is reddish [4, 52, 58]; It is known that a high amount of any kind of impurity in copper will alter its visual appearance [42]; for example a considerable amount of zinc or tin would result in a yellowish tone, since these two elements (when intentionally added) produce brass and bronze, respectively [58].

Finally, artists could reuse old printing plates for new works. Both Broers and Horovitz refer to engravings or etching being found on the reverse of the support [6, 11].

Komanecky (1998) showed from the examination of 325 paintings on copper dating from the 16th to 18th centuries, that only 15% presented printmaking quality (smooth-surfaces, no marks of hammers, parallel sides and often with rounded corners) [2]. Wadum (1999) concluded, after studying the reverse

[10] The main limitation of using rolling mills was that the bar of copper had to run between rollers when still hot, and so the plate produced would be too soft for engraving. Using rolling technology over cold copper bars was out of question since the hardness of the material would not allow the rollers to flatten the plate [3].

of all known works by Jan Brueghel I on copper, that less than 10% show coppersmiths' punched quality-marks [18].

The examination of the 86 paintings in this study showed that all had square, not rounded corners, and only 2 of the paintings showed punched quality-marks, while only one has an engraving on the back. By comparing these observations with descriptions in the literature [1, 2, 5, 6, 8, 9, 11, 14, 15-20, 22, 24, 26-28, 30-39] these findings appear to indicate that the majority of the 86 paintings were intentionally painted on new rather than reused plates. There is one indication that these plates may have been produced for engraving and possibly in coppersmiths' workshops: Ad Stijnman, based on a 17th century treatise by Bosse concluded that the average thickness for engraving plates is around 0,8-1,5 mm [3]; this is the same average thickness found in the collection of 86 paintings studied.

The presence or absence of punched quality-marks on the copper support may not be significant, since paintings could be made on plates which were cut down from a larger original plate with only one quality mark. Other possibilities are that marked plates could have been more expensive than those which were unmarked, or sold by coppersmiths who did not use quality marks.

1.3 Analytical Methodology

The analytical methodology adopted for this study involved the application of non-invasive and micro-invasive techniques. A selection of analytical techniques that are commonly used in metallurgical and archaeometallurgical studies was made. These, together with the information from the historical literature, allowed the characterisation of the composition and the manufacturing process involved in the production of the copper plates.

Thorough analyses were carried out on a subset of 15 samples (12 paintings and 3 fragments) from the total collection of 86 paintings (see fig. 1). In addition, two modern copper plates, which are known to be very pure and to have been produced one by industrial rolling (PLT-T1), and the other by casting and rolling (PLT-T2), were also analysed for comparison (for analytical instrumentation description see Appendice III).

1.3.1 The analyses performed

The back of each of the 15 paintings were photographed with raking light using a digital camera to investigate the topography of the surface and digital X-radiographic images were taken to investigate whether the compositional homogeneity of the copper plates could be related to a manufacturing process.

This was followed by a preliminary elemental characterisation performed on the back of each copper plate in the subset of 15 paintings using micro-energy dispersive X-ray fluorescence spectrometry (µ-EDXRF). Analyses were performed with the same conditions to those given in the literature from table 1: directly on the plate with no mechanical removal of superficial corrosion [35-38]. As a result the µ-EDXRF analytical results do not correspond completely to the original composition of the copper plates since the corroded surface or patina was not removed. As Craddock (2009) states, "Metals can have

compositions at the surface different from those in their interior (…) Even if cleaning and some minimal polishing is permitted, the composition just beneath the surface may still be significantly different from that of the original body metal" [60, p. 137]. Others authors agree with this statement [e.g. 61; 62].

Although µ-EDXRF can be used for quantification, since there was an opportunity to carry out quantification by another technique with higher sensitivity (see below), µ-EDXRF was not used for this purpose.

1.3.2 ANALYTICAL TECHNIQUES

Small samples, approximately 1,5 mm long, were cut using a jewellers saw blade, from the damaged edges of the plates, always considering the minimum impact on objects and respecting their aesthetic value as a painting[11]. This procedure was justified because:

- The 15 copper plates sampled presented areas in the corners with no paint and showing pronounced physical degradation, therefore samples were easily removed and did not affect the overall appearance of the painting. Furthermore, the sampled areas are hidden by the frames of the paintings (see figure 2);
- Paintings would not be under constant mechanical stress or chemical danger during analysis due to: 1. frequent movement between labs during the project, and 2. the performance of some analytical procedures such as localized pressure over the metallic area studied during micro hardness testing, or chemical attack during etching for microscopy observation;
- The samples allow a detailed analytical study therefore providing crucial additional data, otherwise impossible;
- The existence of organic depositions and chemical alteration on the plate surface were considered negative elements that can mask accurate analytical results, whereas samples reveal the core of the copper plate.

Elemental composition of the copper plates and distribution maps of the chemical elements were determined from the core of the samples, by micro proton-induced X-ray emission (µ-PIXE). These analyses allowed quantitative results, an important complement to the qualitative results obtained by µ-EDXRF. Quantification with µ-PIXE is advantageous because it has lower detection limits; important for understanding the level of purity achieved by the refining processes; and to identify possible additions responsible for physical/chemical modification of the final product.

Optical microscopy (OM), with bright field illumination (BF) and cross-polarised light (X-Pol), was used on samples for the microstructural characterisation of the copper, through the study of grains size and format; as well as for the identification of some inclusions (e.g. copper oxides formed from copper sulphides) and other characteristic features related to the manufacturing process. All samples were observed initially without etching, then were etched afterwards with an aqueous ferric chloride solution, prepared according to David Scott's protocol (120 ml of distilled water; 30 ml of hydrochloric acid; and 10 g of ferric chloride) to enhance microstructural details [54].

[11] The size of the samples was the minimum for representative and meaningful analytical results. Sampling was considered after verifying that the paintings had suitable areas for removal and that their paint layers were stable. Full authorisation from the owners was obtained prior to sampling.

As OM only allows the identification of copper oxide inclusions, SEM-EDS was used to identify other possible types of inclusions present within the alloy.

Vickers micro hardness was performed in order to measure the hardness of the plates which is indicative of the manufacturing process.

Micro X-ray diffraction (μ-XRD) to study the pole figures was used on additional samples obtained from the painting fragments (PINT-S1, PINT-S2 and PINT-S3 and PLT-T2). This technique is capable of establishing if the metal grains at the surface the plates show a preferential direction, which can be directly related to the technique of manufacture (see below).

1.4 RESULTS AND DISCUSSION

A comparison of the information gathered from the literature and the analytical results from the 15 copper plates revealed interesting insights into the metallurgic processes used on the raw material to produce the copper ingot, and of the subsequent manufacturing processes undertaken to obtain the copper plates.

The images with raking light reveal that some of the copper plates have a slightly uneven surface, with some showing smoothed concentric rings (these rings were not always evident in raking light) (Appendix IV.1) The radiographic images[12] reveal the existence of a pattern of oval/irregular thicknesses over some of the plates, confirming the existence of concentric rings previously detected by raking light. It was also possible to observe fragile areas in the paintings' support, which are concentrated in the corners. It was not possible to obtain a radiographic image from the modern plate; due to its thickness no radiation was transmitted, resulting in an even, opaque image.[13] (Appendix IV.1)

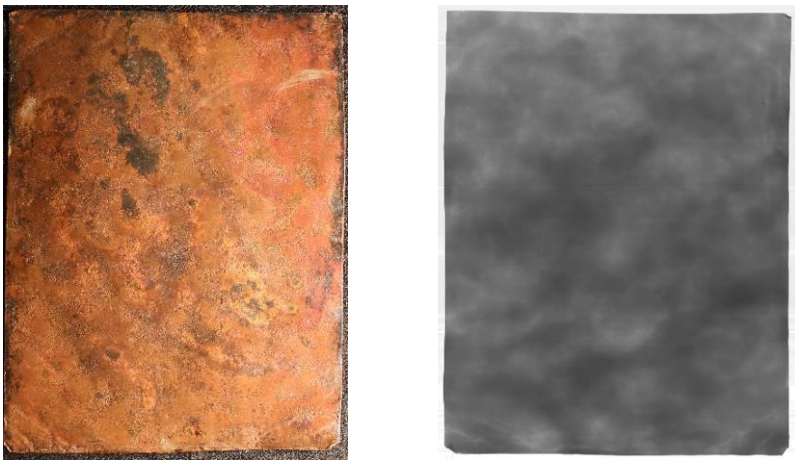

FIGURE 2 – Raking light of painting E and corresponding X-ray digital radiography.

[12] Before acquiring all radiographic images, radiography was first performed on a painting with some paint losses to compare the losses and the surrounding painted areas in order to understand if the paint layers had any kind of influence on the results.
[13] The radiographic images obtained were worked digitally so that the darkest areas correspond to higher thicknesses and/or areas of higher atomic number elements.

Raking light and x-radiography proved to be complementary and were important for an initial characterisation of the copper plates. These initial examination seem to point to hammering as the manufacturing technique used to form the plates (see Fig.2), but often results are inconclusive.

μ-EDXRF analyses allowed a quick identification of the main elements present in the plates (Appendix IV.2). These results indicated that the copper plates are very pure, with only minor peaks that show the presence of other elements. However, as noted above, with this technique it was not possible to obtain quantitative results nor to distinguish which elements belong to the original copper plates and which were associated with alterations at the surface

The purity of the copper plates was confirmed by μ-PIXE analysis (see table 3 & Appendix IV.3). Quantification of the different elements present show that the purity of the copper plates studied varies between 97.16% and 99.28%. These results, attesting the very high purity of the copper[14], indicate that they were made from ingots of excellent quality. Such highly refined ingots would only be possible with a very efficient copper extraction and purification method, which implies a great number of roasting as well as smelting cycles and an efficient refining, as these are necessary to obtain very pure copper (Appendix II).

TABLE 3 - Elemental composition of the copper plates by μ-PIXE; n.d. – not detected.

Painting	Cu (wt%)	As (wt%)	Fe (wt%)	Ni (wt%)	Pb (wt%)	S (wt%)	Sn (wt%)	Sb (wt%)
B	97.16	0.15	0.04	0.33	1.80	0.48	n.d.	n.d.
C	98.78	0.12	0.05	0.38	0.25	0.28	n.d.	0.16
E	98.70	0.06	0.05	0.28	0.57	0.22	n.d.	0.12
G	98.90	0.25	0.04	0.02	0.30	0.35	n.d.	0.13
H	98.63	0.21	0.04	0.16	0.43	0.29	n.d.	0.20
J	98.53	0.14	0.04	0.07	0.76	0.08	n.d.	0.37
K	99.09	0.06	0.05	0.10	0.28	n.d.	0.29	0.12
M	98.92	0.15	0.04	0.13	0.51	n.d.	n.d.	0.24
N	98.23	0.08	0.05	0.17	0.58	0.27	0.53	0.09
O	98.72	0.05	0.04	0.15	0.53	0.14	0.25	0.11
P	99.28	n.d.	0.04	0.18	0.34	0.09	n.d.	0.08
Q	98.70	0.13	0.05	0.05	0.53	0.19	n.d.	0.28
S1	97.88	0.30	0.04	0.32	1.29	0.09	n.d.	0.07
S2	99.25	0.26	0.04	n.d.	0.34	0.10	n.d.	n.d.
S3	98.66	0.35	0.04	0.13	0.47	0.12	n.d.	0.16
T1	99.91	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.

[14] Copper is considered pure above 97-98%.

In order to further interpret these results a study was made of the few publications which provide quantitative results for copper materials within the period under study. These studies included the analysis of copper plates for painting as well as for other purposes, but also, which turned out to be very important, quantification studies of copper ingots (see table 4).

Analytical studies published on copper plates also indicated that the copper used was of high purity. An exception is the results given by Veiga (2015) where one copper plate showed significantly lower purity of only 82%.

Related to the plates, Alfredina Veiga, in her PhD research (2015) gives no explanation for the lower level of copper purity found in one plate of the 17th century [40]. Although the fact that the quantification results provided by µ-EXRF on the surface of the plates tend to decrease the percentage of copper (as the results are masked by the alteration products created on the surface), it cannot be ignored that Veiga's results show clear differences of between 82 and 99%. This could also be explained by the use of lower quality ingots to produce the copper plate. Craddock and Werson [53, 55] cite evidence of ingots in the trade market which were not completely purified, however they note that this material would hardly be workable without further refining.[15] In any case these findings suggest that not all copper plates are extremely pure, and indicate that it is possible that there were coexisting different quality ingots and finished objects, including copper plates.

This variation in purity is supported by the two treatises from the mid 16th century where significant differences are found regarding the number of cycles recommended for roasting and smelting which would have consequences on the purity of the final product. Cost may also be a factor since the purification of copper was an expensive task due to the high amount of fuel and labour needed to complete the process, which may have resulted in a variation in quality related to economics [53].

Table 6 also shows a tendency towards an increase in purity throughout the centuries, with the latest ingots, around the date of production of the copper plates studied here, being those with higher purity (compare Schulz's [56] and Werson's [55] results with the 18th century values reported by Craddock [12]). This is likely related to an evolution in the efficiency of copper refining methods from the 12th to the 18th century. Further study is needed in order to clarify this issue.

[15] Werson's analysis over some ingot dated from the 14th century confirm the existence of such lower quality ingots [55].

TABLE 4 – Published works with elemental composition of ingots and copper plates

( ) element that is not always detected in all analysed objects.

	Year	Author	Object analyzed	Date	Analytical technique		Results	
					Equipment	Conditions	Copper (wt.%)	Impurities
INGOTS	1981	Schulz [56]	57	1140-1340	AAS	elements in dispersion	73.90-96.50	Pb, As, (Ag), Zn, Sb, Ni, Bi, Fe, Cr, Cd, Co, Mn
	2015	Werson [55]	66	14th c.	ICP-SFMS	elements in dispersion	84.6-97.8	Pb, As, Ag, Zn, Sb, Sn, Ni, Bi, Co, Au, Hg, P, S, Se, Te
	2014	Garbacz [52]	27	15th c.	XRF	not mentioned	90.58-98.60	Pb, As, (Ag), (Zn), Ni, Fe, (Sn), Sb
	2015	Garbacz [63]	9	15th c.	XRF	not mentioned	91.40-98.3	Pb, As, (Ag), (Zn), (Sb), (Sn), Fe, (Ni)
	1995	Rehen [113]	15	Late 16th c.	AAS	elements in dispersion	97.68-99.53	Pb, As, Ag, Zn, Sn, Sb, Ni, Fe, Co
	2012	Craddock [53]	20	16th c.	AAS	elements in dispersion	95.20-99.90	Pb, As, Ag, Zn, Sn, Sb, Ni, Bi, (Fe)
			9	18th. C			94.90-99.30	Pb, As, Ag, Zn, Sn, Sb, Ni, Bi, Fe
PLATES	2015	Borges [64]	24	15th/16th c.	PIXE	bulk of samples	97.4-98.66	Pb, As, Ag, Au, Sb
	1922	Coppier [65]	1	17th c.	n.s.	not mentioned	95.00	Pb, As, Ag, Zn, Sn
PAINTINGS' PLATE	2012	Pitarch [36]	1	16th c.	XRF	directly on the surface	copper	Pb, Fe, Tu
	2004	Koltz [35]	1	17th c.	SEM-EDS	directly on the surface	copper	Ni, Fe, Sn
	2015	Corregidor [39]	3	17th c.	PIXE	directly on the surface	Very pure copper	Pb, As, Ag, Au, Sb
	2015	Veiga [40]	12	17th c.	XRF	directly on the surface	82.11-99.60	Pb, As, Ag, Fe, (Ni), Zn, Sn,Sb
			4	18th c.			97.09-99.21	

ASS – atomic absorption spectrophotometry; ICP-SFMS- sector Field Inductively coupled plasma mass spectrometry

μ-EDXRF analyses of the composition of the plates studied for this research reveal the presence of Ca, K, Hg, and Cl which were not detected by μ-PIXE in the core of the samples. These elements could be associated with depositions on the surface (Ca, K), while the presence of mercury (Hg) may be contamination related to the gilding practises at the ateliers [32], and finally, Cl could be related to superficial corrosion products ($CuCl_2$).

Other elements (Pb, S, Fe, As, Ni, Sn and Sb) detected by μ-PIXE were also detected in the core of the samples. The low concentration of these elements (<1.80 wt. %) indicate that they are impurities, as metal contents under 2% are frequently assumed to be ore contaminations, since they are present in lower values normally associated with intentional additions [66].

Among these impurities, lead is the most frequent. In the plates studied the lead content ranges from 0.29 up to 1.8 wt.%. The presence of this amount of lead could be related to several hypotheses:

1. As mentioned in section 2.1, lead could have been added to the smelting ore in order to extract the silver from copper (this is known as the cupellation method) [46];
2. Lead could be part of the original ore, and so this low concentration could reflect an inefficient removal of this element during the smelting cycles, or a

3. Small amount of lead could be added to enhancing the fluidity of the molten copper (as noted in section 2.1, lead was also used as a flux in copper ores).

As mentioned in section 2.1, sulphur was a common element found in sulphidic ores, and during roasting, smelting and refining its concentration was lowered due to oxidation followed by volatilisation. Elemental sulphur concentration in the plates varied between 0.09 and 0.48% wt. These results may indicate that most of the plates were produced from sulphidic ores, and reveal efficient extraction regarding the elimination of sulphur from copper.

Iron is in very low concentration (0.04-0.05 wt.%), this could be related to the efficient removal of this element during the oxidation that occurs during smelting, in that step iron is transferred into iron oxide (FeO_3) and is then incorporated into the slag [4, 51].

Arsenic and antimony, as noted in Appendix II, are consumed during the roasting of the ore.

The elements detected, As, Fe, Sn and Sb as well as Ni are present in only trace amounts up to a maximum of 0.38 wt. % in the copper plate and are all therefore considered impurities.

In summary, the quantification analyses from the 15 paintings in this project as well as the published results suggests that by the 17th/18th centuries metallurgical technology was well developed regarding copper purification, and the trace elements detected are likely in quantities too low to be intentional additions; therefore they are considered impurities and are not thought to significantly alter the properties of the plates (pers. comm. Dr. Rui Silva, December 2015).

In contrast to the paintings on copper studied here, trace impurities were not found in the industrial produced modern copper plate, which points to the use of contemporary electrolytic technology. This results in an extremely high level of purity which would have been impossible to achieve with the use of pre-industrial techniques.

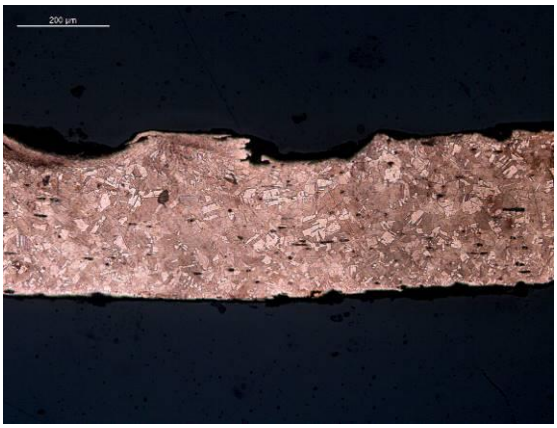

FIGURE 3 - PINT-E. General view of the sample. Twinned and recrystallized grain structure with reasonable grain contrast, can be identified. Sample etched.

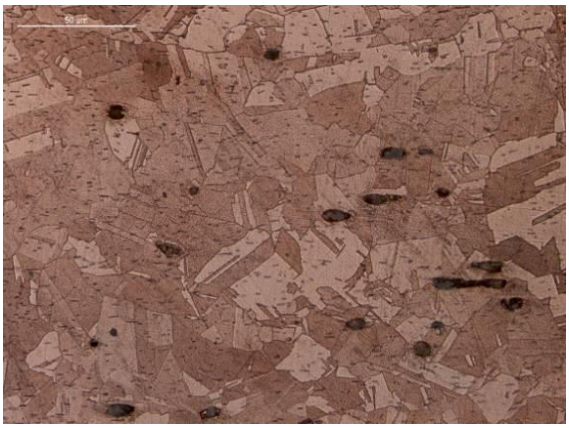

FIGURE 4 - PINT-E. The section shows twinned and recrystallized grain structure, with reasonable grain contrast. Sample etched.

The metallographic results confirm the previous results, that the plates have a very pure copper matrix (see fig. 3, 4 and Appendix IV.4). In OM a monophasic metallic structure composed of alpha phase grains with few inclusions can be identified. Additionally it is possible to clearly distinguish twin

lines in all of the plates, which traverse part or all the individual grains, with polygonal grain boundaries. The identification of this kind of structure shows that the material was annealed after plastic deformation. Some of these twins are slightly bent; this indicates that the grains were subsequently slightly deformed [58]. The overall metallic structure indicates that the plate was shaped by cycles of cold-working (probably hammering) and annealing probably followed by minor final cold-work.

The mechanical operation of cold-working, was probably applied with different intensities. This supposition is due to the observation that there is some degree of variation in the deformed twins across the samples. This is also confirmed by the significant thickness (measured with a Thickness gauge) variations present in some plates (B,M,N,S1 e S3)

TABLE 5 - Microstructural features of the plates based on OM analysis

Code	Grain size (μm)	Phase	Inclusions	Features	Manufacture
B	50-100	α	Cu-O↓	t	(W+A)+FW
C	50-100	α	Cu-O↓	t	(W+A)+FW
E	50-100	α	Cu-O↓↓	t	(W+A)+FW
G	50-100	α	Cu-O↓	t	(W+A)+FW
H	50-100	α	Cu-O↓	t	(W+A)+FW
J	50-100	α	Cu-O↓	t	(W+A)+FW
K	50-100	α	Cu-O↓	t	(W+A)+FW
M	50-100	α	Cu-O↓↓	t	(W+A)+FW
N	50-100	α	Cu-O↓↓	t	(W+A)+FW
O	50-100	α	Cu-O↓	t	(W+A)+FW
P	50-100	α	Cu-O↓	t	(W+A)+FW
Q	50-100	α	Cu-O↓	t	(W+A)+FW
S1	50-100	α	Cu-O↓	t	(W+A)+FW
S2	50-100	α	Cu-O↓	t	(W+A)+FW
S3	50-100	α	Cu-O↓	t	(W+A)+FW
T1	20-50	α	-	t	(W+A)+FW

(t: annealing twins; A: Annealing; W: cold working; FW: Final cold working; ↓: low amount; ↓↓: very low amount.)

When the metal is excessively hammered, or cold-worked, it becomes brittle. It has been shown that Neolithic civilization already understood this principle [4, 40, 42]. The OM revealed that an intermediate annealing, to relieve the internal stress accumulated in the crystalline structure during the hammering, was undertaken. Annealing softens the metal and then permits additional deformation by hammering.

The combination of these two operations in a repeated sequence was used to shape the material and to achieve a smooth surface. According to Scott (1991), the plastic deformation of metals through hammering and annealing, produces changes to the internal structure of the metals, however since hammering and annealing will produce roughly the same microstructure, it is not always possible to distinguish between the processes used in a particular case [58].

Slip bands[16] which result from excessive hammering which was not followed by annealing, were not detected in the plates studied which could indicate that a final intense cold work was not undertaken. Rather they received a last annealing step which could had been followed, or not, by minor hammering.

Table 5 shows that the old plates present relatively large grains and a low content of cuprous oxide inclusions (see figures 4-6 and Appendix IV.4). This table also confirms the information from the analytical techniques discussed above: the plates all show high levels of purity, a single metal phase of this metal can be identified and the boundaries indicate that the plate was probably produced with one or more forging and annealing cycles that could have been followed by final minor hammering operation [(W+A)+FW] .

Another common feature in copper objects that can be identified by OM (Figures 5 and 6), is the presence of copper oxides (CuO_2), which appear as reddish inclusions under cross-polarized light observation. These inclusions can occur during solidification, when dissolved gases, such as oxygen, react with the liquid metal to form oxides (e.g., cuprous oxide [Cu_2O]) however only relatively small quantities were found. This attests for the efficiency of the refining process when the reduction of cupreous oxide to copper metal takes place. In addition it could also be related to the presence of another elements not detected by OM. For this reason, three representative samples of the sub-set of the collection were chosen for SEM-EDS analysis in order to identify any other features.

FIGURE 5 - PINT – K . Identification of cuprous oxide inclusions. Bright field illumination. Sample non etched.

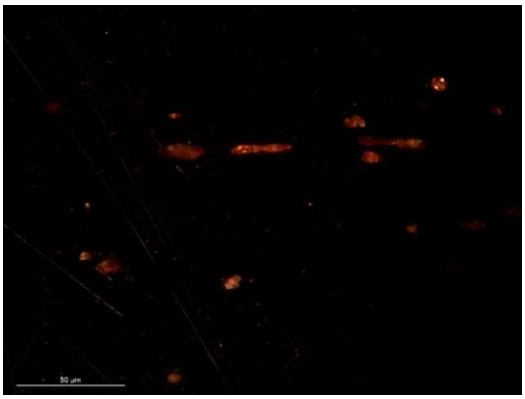

FIGURE 6 - PINT – K . Identification of cuprous oxide inclusions. X-Polarised light. Sample non etched.

SEM-EDS analysis confirmed that the reddish inclusions mentioned above were Cu-O associated, assigned as cuprous oxide (Cu_2O). Other immiscible inclusions of Pb-Sb and Pb-Sb-As oxides were identified which were not recognized by OM (Appendix IV.5). It is important to note that the presence in the copper matrix composition of elements with high oxygen affinity, such as As or Sb, will reduce cuprous oxide formation. According to Silva (pers. comm. Dr. Rui Silva, July 2016), arsenic will act as a deoxidizer by detaining oxygen (lost as As_2O_3 fumes); this will also reduce the formation of copper oxides.

[16]Slip bands can be detected inside the grain as a group of parallel lines [57].

Examination by raking light and by radiography of some plates suggested that some plates were likely made by hammering. This is not evident for all plates. In order to confirm this, XRD to study pole figures[17] was undertaken on four samples removed from the three fragments and from the modern plate produced by casting and rolling (PLT-T2). Results indicate that the old plates have no clear preferential orientation, confirming the idea that they were hammered (Appendix IV.6).

On the other hand, the PLT-T2 shows a pole figure characteristic of cold rolling since the grains show a preferential orientation.

In summary, the results of the analyses carried out suggest that the copper plates in this study were produced using similar metallurgic and manufacturing processes.

The study of the hardness[18] of metallic artefacts can reveal the efficiency of cold-working and annealing cycles.

The Vickers micro-hardness values (see Appendix IV.7) are in the range of 72 HV up to 131 HV. These results add further confirmation that the copper plate manufacturing technology was based on cold-working and annealing procedures, these steps strengthen the material due to the number of dislocations in the microcrystalline structure [67] The Vickers results agree with values in the literature where cast pure copper ranges between 40-50HV.

1.5 CONCLUSIONS

A comparison of the information gathered from different sources: the historical literature on metallurgy, scientific analysis on 15 copper plates, and the recently published studies on paintings on copper, as well as copper archaeometallurgy - revealed interesting insights into the metallurgic processes used to produce the copper plates.

Copper extraction and purification was a complex and expensive process, especially when the copper was sourced from sulphidic ores. Extraction and purification included several steps, all of which were rigorously executed as attested by the high level of purity of the copper.

This high purity could only be achieved through: a great number of cycles of roasting, resulting in trace amounts of sulphur, arsenic and antimony; a great number and long cycles of smelting, resulting in trace amounts of iron; and efficient refining which reduced cupreous oxides inclusions and oxidised remaining impurities such as sulphur.

However, a few examples from other studies revealed the coexistence of copper plates made from ingots of slightly lower quality. This agrees with the historical literature; whereas the objective was to obtain a final material that was pure, the different indications given would necessarily lead to differences in the final product.

Scientific analyses reveal that the manufacture of the plates from the ingots involved cycles of cold working alternating with annealing. Hammering aimed to form a plate with adequate hardness, while the

[17] [Pole figures XRD determines the distribution of the crystallographic orientation of the grains.
[18] The hardness of copper-based objects is influenced by numerous factors, such as the composition of the phase (solid solution hardening), precipitation of different phases (precipitation hardening), grain size and degree of deformation (strain hardening). Personal communication Dr. Rui Silva.

intermediate stage of annealing returned malleability so that further intense cold work, necessary to achieve a plate without breaking, could be carried out.

The results of the analyses undertaken for this study indicate that the copper plates which were examined were all produced using similar metallurgic and manufacturing processes. This research also highlighted the importance of a consistent analytical approach for the study of these plates as the methodology commonly used could mislead the analytical results.

PART 2- INVESTIGATION AND TESTING TO DEVELOP A NEW INFILL FORMULATION FOR PAINTINGS ON COPPER

2.1 INTRODUCTION

The second part of this thesis concentrates on the characterization of two wax-resins formulations used as infill materials for paintings (Gamblin and a formula used by Carlyle in the early 1980s, see below); and, based on the findings, explores preliminary trials and testing results towards the development of a new wax-resin formulation suitable for infills on paintings with a copper substrate. The need for an inert material for infilling paint losses on a copper support is particularly important as copper can be corroded by components in the wax-resin infill materials currently available.

2.2 OVERVIEW OF THE SUITABILITY OF INFILL MATERIALS FOR PAINTING ON COPPER

It has been suggested that paint losses on paintings on copper result from a chemical reaction between the copper support and the paint composite [20, 26, 27, 31]. As a consequence, losses of the paint composite tend to be complete, leaving the metal underneath exposed [11, 24, 25] (see image Appendix V.1).

Aside from aesthetic reasons for re-integrating the paint/ground losses by filling in the lost paint and inpainting the losses, the susceptibility of the copper support to corrosion, even under normal environmental conditions[19] [68-70], offers a strong argument for treating these areas in order to protect against further corrosion of the exposed metal.

Conservation and restoration treatments therefore include the infilling and inpainting of losses on copper paintings, but surprisingly the literature referring to the materials used for infilling is scarce and in some cases commercial products were used where the ingredients were not identified (Appendix VII). The extant literature essentially covers treatments (Table 6) and empirical trials with different infill materials (Table 7).

[19] The ubiquitous presence of moisture, oxygen and airborne pollutants leads to copper corrosion.

TABLE 6 – Published research on treatments of losses in painting on copper.

Authors	Isolation layer	Infill	Type	
			n.aq	aq
Leegenhoek - Wade, 1983 [57]	varnish	hide glue + $CaCO_3$ beeswax + $CaCO_3$	**X**	**X**
Garrel, 1992 [71]	~	beeswax	**X**	
Scott Monvrieff, 1993 [72]	~	Fine Surface Polyfilla		**X**
Berger, 1995 [73]	microcrystaline wax + UVS Retouch Varnish	Mowilith 20 + solvents + pigments		**X**
Maule, 1999 [34]	(PB72:PB48)+ acetone	gelatine putty		**X**
Broers 2002 [23]	PB72+ xylene + BTA	Lascaux Hydrogrund 750 + pigments		**X**

n.aq : non aqueous , aq : aqueous. The identity where known of all materials listed is given in Appendix VI

The literature study reveals that the majority of the treatments include the use of aqueous based infills. Some authors (see Tables 6 & 7), concerned that the presence of water could promote corrosion, suggest the use of an isolating layer that will act as a water barrier prior to the application of the infill. The material most often used for isolation is the acrylic co-polymer Paraloid-B72. Other options (listed in Tables 6 & 7), were non-aqueous, however authors reported adhesion concerns and handling problems during application of the non-aqueous materials. Based on the trials reported in Table 7, while some commercial products were reported to perform well for infilling on copper, the lack of identity of their ingredients and the impossibility of assuring that the same formulations will be used by the manufacture beyond the product tested at the time of publication, means that these commercial materials cannot be relied on, either in terms of their longevity, or in terms of repeatability (how can a conservator know that the manufacturer's formulation will not change).

TABLE 7 - Summary of Horovitz's, Broers' and Rizzo's empirical trials with infill materials.

Authors	Isolation layer	Infill	Type		Observations
			n.aq	aq	
Horovitz, 1996, 2012 [5,24]	PB72	PB72 + chalk	**X**		unsatisfactory to apply, and may be disrupted by PB72 isolating layer.
		Plextol B500 + chalk	**X**		adhesion is difficult.
		Beva 371 + chalk	**X**		spontaneously peeled off on drying
		Fine Surface Polyfilla		**X**	useful when coarse texture is required.
		Rowney Acrylic		**X**	suitable for shallow losses but rubbery and difficult to carve.
		Liquitex Acrylic Gesso		**X**	very spreadable, suitable for large flat areas of shallow loss.
Broers, 2002 [23]	PB72 + BTA	Lascaux Hydrogrund 750		**X**	easy to apply and carve.
Rizo, 2008 [15]	PB72	Modostuc		**X**	good performance.
		Gel Relief (L&F)		**X**	easy to apply, suitable when texture surfaces are required. Become transparent after drying.
		tempera paint		**X**	fills up the loss withseveral applications.

n.aq: nonaqueous; aq.: aqueous, the identity of all materials where known is given in Appendix VI**.**

In terms of the material under study in this thesis, wax-resin fills, as Table 1 shows, there were references in 1983 and 1992 to infills based on beeswax (Table 6). However, Horovitz (1996) reported that beeswax promoted corrosion on copper. In fact, literature covering furniture and archaeological conservation [e.g. 30, 74] reports the development of a green layer and of severe corrosion on copper and copper alloy objects in contact with beeswax. It is suggested by Scott (2002) that this phenomenon is related to the interaction of carboxylic groups of the fatty acids present in beeswax (see below) with metallic ions from the metal support, resulting in the formation of copper soaps. As stated in the literature covering archaeology [75, 76], these organometallics compounds are chemically unstable, attack metallic copper and promote further corrosion. In addition, since four of the five fatty acids in beeswax are the same as the major fatty acids characteristic of drying oils (palmitic, stearic, oleic and linoleic) [77]. It follows that, as proposed by Pavlopolov and Watkinson (2006), beeswax will have a similar effect to that seen between oil paint and copper: the formation of a green layer at the interface between the oil layers and the copper.

Considering the state of the art and the characteristics of paintings on copper, for this thesis it was decided to investigate the properties of wax-resin infills and to explore the potential for finding a formulation without beeswax or other corrosive materials; an alternative which would provide a viable option for infilling losses on copper paintings (detailed further below).

2.3 PROPERTIES OF AN IDEAL INFILL MATERIAL

In her PhD thesis on infill materials for the conservation of paintings completed in 2006, Laura Fuster López identified the ideal properties of a successful infill [78]:

- compatibility with the original materials (chemically, physically and mechanically);
- capability of receiving an impression of texture[20] (if necessary);
- stability to relative humidity and temperature fluctuations;
- mechanically removable (or at least removability is restricted to mild aliphatic solvents);
- long term physical and chemical stability.

In the specific case of paintings on copper, in addition to the properties listed by Fuster-López, infills should also have the ability to be applied in very thin layers to match the thickness of the paint composite[21].

2.4 WAX-RESIN INFILLS – OVERVIEW

Mixtures of beeswax and resins (natural or synthetic) in different proportions with the addition of pigments and fillers, can result in an infill material that is highly versatile. Wax-resins (WRs) were and still are used by conservators and, until recently, they were produced by conservators themselves with

[20] No correct colour-match can be achieved unless the surface structure is reconstructed [73]

[21] On the paintings on copper studied (Vega Project Report, UNL) and as stated in the literature [11, 15, 23,], the oil paint composite on copper supports can be very thin (c. 30 µm). Furthermore paint applications on this non-absorbent substrate can result in significant paint flow which makes the overall surface appearance very even.

no fixed recipe. In recent years they have been commercially manufactured for conservation use by Robert Gamblin [https://www.gamblincolors.com/conservation-colors/]. Gamblin's formulation is based on research by Christine McIntyre for her Master's thesis (2011) in the Conservation of Easel Paintings, in the Conservation Training Programme at Buffalo State College (Buffalo New York, USA) [79].

As a material for infills on copper pigmented wax-resin has several advantages: it is non-aqueous and after application the fill is likely to be relatively impermeable to moisture. Its response to heat means that this material can be easily introduced to the loss in the form of a fluid or a paste. It is capable of forming a very thin layer that does not shrink or crack (in the context of the inflexible copper support, mechanical cracking is not anticipated). For texturing, the fill can be shaped while warm, carved when cold, or the surface can be shaped or modified with a solvent with a low aromatic content (such as white spirit or one of the Shellsols). It is easily removed mechanically or by using solvent as above. Empirical trials indicated very effective adhesion to the copper metal (with the metal at room temperature). However, because the current formulations for wax-resin infills commonly contain beeswax, this infill material presents two problems: as noted above, beeswax has been shown to promote the corrosion of copper; and, it has been reported by word of mouth (Carlyle pers. Comm., 2015), that WR infills can develop bloom. Bloom refers to a thin whitish crystalline layer that develops on the surface of beeswax under specific conditions, which alters the appearance of the surface [80]. This phenomenon has been observed on objects made of beeswax, for example, encaustic paintings, sculptures, and wax seals [84]. Several studies have been carried out to establish the mechanism of blooming [81-84]. Although not completely understood, the most recent results indicate that blooming is related to the migration and recrystallization on the surface, of alkenes naturally occurring in beeswax [84].

Because of the significant advantages presented by pigmented wax-resin infills, particularly in terms of their ease of application and their ability to form very thin layers without subsequent shrinkage and cracking, the thesis work in Part II concentrated on finding a formulation which would eliminate the need for natural beeswax while still providing the positive characteristics and properties of pigmented wax-resin infills. Two successful formulations (detailed below) were used as references for the characteristics sought in the new formula: a wax-resin formula used by Carlyle in the earliest 1980s (C-PWR) and pigmented wax resin sticks which are currently sold by Gamblin Conservation Colors (G-PWR) which also include beeswax.

2.4.1 BACKGROUND, EARLY USE OF WAX-RESIN

Various authors [85-87] report that formulations based on natural waxes including beeswax with natural resin (with pigments and fillers) have been used extensively as an infill material for easel painting and other objects (such as those made of wood, marble and alabaster) at least throughout the 20th century (if not earlier).[22] In 1959, Althöfer suggested the use of synthetic polyethylene glycols (a polymer with similar properties found in natural waxes) to substitute for the wax [88]. Silve Rhbein and Karin Temme (1985) tested a WR made of beeswax, dammar and an inert filler on mock-ups, to study

[22] it was beyond the scope of this thesis to study the historical use of this material

its properties in relation to the restoration/conservation of contemporary art [89]. Fuster López reported on the substitution of natural resin with a synthetic resin. She notes that the substitution probably only happened after the 1950s, when cyclohexanone resin (originally Ketone Resin N, later Laropal K 80) was introduced in the market [86]. Wax-resin infills using beeswax with cyclohexanone resin (Ketone resin N) were in use at the Canadian Conservation Institute (CCI) in the early 1980s[23]. McIntyre in her Master's thesis refers to the use of WR infills based on cyclohexanone resin, Larapol K 80, being used at Buffalo State College (Buffalo New York, USA). For her master thesis, McIntyre explored a new WR formulation which was aimed at finding a substitute for Laropal K 80 after its manufacture by BASF[24] was discontinued in 2000. Her research was later used by Robert Gamblin [https://www.gamblincolors.com/conservation-colors/], in trials which resulted in his product, Gamblin Pigmented Wax -Resin (G-PWR) sticks, introduced after 2011.

2.5 INGREDIENTS USED IN WAX-RESIN FORMULATIONS

2.5.1 WAXES

The term 'wax' derived from the Anglo-Saxon word *weax,* was originally referred to the natural material obtained from beehives; this designation changed to *wachs*, and finally to *wax* [90]. Currently 'wax' has a broader meaning, and includes a vaguely defined group of substances with wax-like properties which are obtained from natural sources such as plants, animals and minerals as well as synthetic substances [90, 91]. They share some common characteristics: translucent solid appearance, low melting ranges, hydrophobicity and a 'waxy' feel [92].

In this thesis, only the waxes used by McIntyre (2011) for her infill formulations will be discussed: beeswax and microcrystalline wax.

Beeswax as a natural product shows differences in composition depending on bee species and their food supply [93, 94]. Tullock (1980) reports that in general the breakdown of individual ingredients in beeswax is: 14% hydrocarbons (alkanes and alkenes), 35% monoesters, 14% Diesters, 3,3% Triesters, 3,6 % Hydroxy monoesters, 7,7% Hydroxy polyesters, 12% free fatty acids, 0,8% acid monoesters and 8,6% of unidentified compounds [93]. Mills (1999) states that its melting point (m.p.) is around 63-64ºC; the softening point (s.p.) is 49-53,3 ºC; and, according to Tulloch (1980), the acid value is between 16 and 24. It is notable that there are studies which report much higher acid values, from 16 to 125 [e.g. 90]. Beeswax can be purchased in a refined or unrefined state. Several treatments can be applied to modify its colour and to remove impurities [90]. However, acid treatments used during this refining are reported to have little effect on the original acid value [90].

Nowadays, mineral waxes are widely used as substitutes for beeswax and for new applications. They are composed of hydrocarbons, and they are a by-product of the production of lubricants from petroleum [95]. Mineral waxes consist of an amorphous and a crystalline phase. Mineral waxes are defined in two groups: macro-crystalline (e.g. paraffin) and microcrystalline waxes. As their name implies, microcrystalline waxes are characterized by having extremely small crystals.

[23] pers. comm. Dr. Carlyle, 2015: paintings conservator Barbara Klempan introduced the formula to paintings conservators at CCI after her training in Copenhagen.
[24] BASF: Badische Anilin- und Soda-Fabrik AG

According to Pillon (2008) the composition of microcrystalline wax includes 0-15 wt% of n-paraffins, 15-30 wt% of iso-paraffins (branched), and 65-75 wt% of naphthenes, with 30-60 carbon atoms and an average molecular weight of 500-800. Microcrystalline waxes have melting points ranging from 60 to 90ºC depending on the ratio of the compounds present in their composition [96].

The uses for microcrystalline waxes in industry ranges widely, from the manufacture of candles, to coatings, printing inks, pharmaceuticals and the cosmetic industry [96, 97].

2.5.2 RESINS

The term 'resin' comes from a Greek word meaning tree sap [98]. The word has no precise definition, rather it refers to polymeric materials that are not yet in their final form or shape [98]. Horie (2010) defines a resin as "an amorphous polymer or oligomer" [99, p. 434]. Resins usually have a medium molecular weight; an amorphous and often complex structure; and like waxes, they do not exhibit a precise melting point [100]. Synthetic resins cover a wide range of materials obtained by the polymerization of hydrocarbons. In recent years, synthetic resins in conservation have been studied by specialists such as Teresa Domeneche-Carbó (2001) and René de la Rie (2005) [101,102]. de la Rie explains that they can be divided in three groups according to the method of synthesis: addition polymers, polycondensates and polyadducts [102].

This thesis concentrates on four synthetic resins which were chosen for testing in the new wax-resin formulation: Laropal A 81 and Laropol A 110, as well as Regalrez 1094 and Regalrez 1126. The reason these resins were selected is explained below (section 2.6.2).

Laropal A, developed by Badische Anilin- und Soda-Fabrik AG (BASF), is a polycondensate resin obtained by the condensation reaction between urea and aliphatic aldheydes (see Appendix VI.2). Laropal A 81 molecular weight (MW) is reported to range from of 3640 to 4300 [102,103]; a glass transition temperature (Tg) of 57ºC; and a melting range (m.r.) between 80-95 ºC. Laropal A 101 has a MW of 2979, a Tg of 73 ºC and a m.r. between 95-110 ºC[25].

Regalrez, developed by Hercules Inc. (and currently produced and commercialized by Eastman Chemical Co), is a low molecular weight polymer, resulting from the polymerization of hydrogenated styrene monomers (see Appendix VI.3). Regalrez was brought to the attention of the conservation field in 1990s when de la Rie first published on its application as picture varnish [104]. The chief difference between Regalrez 1094 and Regalrez 1126 is their molecular weight which modifies their properties: Regalrez 1094 has an average MW of 900, a Tg of 41 ºC and melting point of 95 ºC; whereas Regalrez 1126 has an average MW of 1250, a Tg of 67 ºC and a melting point of 124 ºC[26]. Regalrez 1094 has a lower viscosity than Regalrez 1126.

[25] Information on the Safety Data sheet from BASF.(consulted on January 2016)

[26] Information on the Safety Data sheet from BASF (consulted on January 2016)

2.6 METHODOLOGY

2.6.1 CHARACTERISATION OF CURRENT WAX-RESIN INFILL FORMULATIONS

As noted above, two WR formulations, successful in their working properties and that have been used as infill materials in the restoration of paintings, were selected for study: a pigmented wax-resin fill used by Carlyle in the early 1980s Institute (C-PWR) and Pigmented Wax Resin Sticks which are currently sold by Gamblin Conservation Colors (G-PWR).

The recipe used by Dr. Carlyle in the samples she provided of C-PWR (via Klempan from Copenhagen) were made by melting 4 parts of beeswax to 1 part of Ketone Resin N (a cyclohexanone resin) then adding pigment and chalk (calcium carbonate) to the melt. Dr. Carlyle provided three wax-resin infills which had been prepared in the early 1980s at the CCI: titanium white, burnt umber and an unpigmented sample referred to as neutral.

Gamblin Pigmented Wax Resin Sticks G-PWR) samples were purchased in 2009 and 2015. For the present study, sticks labelled Titanium white, Burnt Umber and Neutral Base (an unpigmented stick) were chosen to compare with the C-PWR samples.

First the properties of the neutral samples were studied, so the results would not be masked by the presence of pigments or filler. The same tests were then used to study the pigmented versions.

There are no specific technical standards for studying properties of WRs. Since wax is the main component within both the C-PWR and Gamblin mixtures, the technical standards for waxes, from the American Society of the International Association for Testing and Materials (ASTM), were followed. The intention was to not only characterize the samples but to identify key properties which could be matched in the new formulation. Therefore the raw materials used for the new formulation (both the microcrystalline waxes and the resins) were also tested. Despite the availability of data-sheets supplied with the new materials, the tests were very useful since results obtained from testing could be compared to the information given in the datasheets. This comparison allowed an assessment of the accuracy of the methodology used in the testing carried out as part of the thesis work.

Reference samples as well as new formulations (both wax and resin) were characterized by Fourier transform infrared spectroscopy analyses (FTIR) (Appendix III).

Melting range and Tg

A Reichert Thermovar HT-1 B11 polarising microscope equipped with a heating stage was used to determine the melting range[27] of the materials. As explained above and in note 27, microcrystalline waxes and resins do not present a sharp melting point but a melting range.

The study of this property is important in order to establish the temperature at which the WR is workable. This temperature cannot be close to room temperature, since that would incur the risk of future deformation/distortion in ambient conditions, also it cannot be too high since the WR must be safely applied to a painting without the potential to cause heat damage to the paint.

[27] The use of this equipment was suggested by Dr. Ana Ramos. Optical observation of wax or wax-resins samples are made on a controlled heating plate; the temperature is registered when the material flows for the first time (softening point) till the moment it becomes completely liquid (melting point)

The study of the glass transition temperature (Tg) is important to determine the behaviour of the material at room temperature: Tg close to room temperature points to a material which is softer and flexible but susceptible to dirt adsorption, while high Tg are associated to brittle materials. WRs should have a Tg higher than the maximum temperature a painting would be exposed to (e.g. direct sunlight in a very warm room).

The glass transition temperature (Tg) and melting point are currently being studied by Differential Scanning Calorimetry (DSC) according to ASTM 4419. This will provide additional data related to the degradation temperature of the materials being tested. Unfortunately, results were not available in time for the present study.

Acid number

ASTM D1386 provides the testing procedure to determine the acid number[28] of pure waxes and was used for testing all the waxes and WRs studied in this thesis. The acid number correlates to the presence of carboxylic groups of fatty acids. As noted above, beeswax is acidic due to the presence of fatty acids which can corrode the copper substrate of oil paintings on copper. Consequently the acid number of the WR ingredients has particular relevance.

Workability, removability, hardness and blooming of the C-PWR and G-PWR samples as well as the new formulations (see section 2.6.2) were assessed as these are important parameters for determining the suitability of using these materials in conservation treatments.

Workability

The first test undertaken was the addition of pigments (titanium white and burnt umber) into the new formulations. The amount of pigment added was 1 part to 2 parts of binder (by weight).

Two of the fragments from old copper paintings studied in Part 1 of this thesis, S1 and S2, were used for testing the workability of the WRs.

Some areas of loss were isolated using Paraloid B-72 diluted in Toluene (15%v/w)[29]. Since paint around losses often require consolidation, and B72 was found to be a viable choice (see note 29), it was considered important to evaluate the adhesion of the WRs to a surface coated with this co-polymer. WRs were heated and applied using a 'wax carving pencil' (Appendix VII) on isolated losses but also on non-isolated losses, to assess their suitability in both situations (Appendix VI.5)

Two weeks after application, the WRs infills were varnished with a solution 20% of the same resin used for producing the wax-resin (Regalrez 1094 or Regalrez 1126) in order to assess possible undesirable reactions between those materials.

Removability

Removal of the different WRs infills were tested mechanically and with solvents after two weeks. A wooden stick was used for the mechanical removability. Mild aliphatic solvents were tested for chemical removal, namely Shellsol D and white spirit, as due to their low aromatic content, they present lower

[28] Acid number is the number of miligrams of KOH necessary to neutralise one gram of the sample.
[29] Consolidants for painting on copper were recently tested by Leonor Oliveira, this acrylic co-polymer resin (in concentration between 15-40% in toluene) was the one with the best performance (Oliveira, 2015).

toxicity levels, and less danger to the original paint layer and the protective coating of Paraloid B72 which had been applied to the loss.

Hardness

The hardness of the WR is an important parameter for comparison with the reference samples. The ASTM test method for measuring the hardness of waxes is D1321 which requires a penetrometer. It was not possible to locate a penetrometer at a Portuguese University however, after a substantial search, a penetrometer was located at the Quality lab of a Portuguese candle manufacturer, Promol, located in Caldas da Rainha. With their kind permission, samples of all the materials to be tested were sent to Promol in June 2016, unfortunately, to date no results have been provided. Therefore empirical tests (see below) were undertaken to assess hardness of the C-PWR, G-PWR reference samples and of the new formulations.

Blooming

Pigmented pastilles (2 cm diameter) of the selected WRs were produced (as well as a pastille of pigmented beeswax). The development of blooming is currently being assessed by regular visual monitoring.

2.6.2 SELECTION OF WAXES, RESINS AND PIGMENTS FOR THE NEW FORMULATION

In principle, in order to reduce variables and thus simplify the evaluation of their performance, both of the primary ingredients (the wax and the resin) should be as pure as possible.

Microcrystalline waxes were chosen based on their melting ranges; the selection involved waxes with a similar or a higher melting range than the wax or waxes used in the infill reference samples. Locating a source of synthetic waxes with a range of melting ranges proved difficult as few of the manufactures contacted returned emails and phone calls. Fortunately, the British company Kerax (www.kerax.co.uk), kindly provided samples for this study which covered the melting ranges required (see Table 8 and Appendix VIII).

Regarding the resins, Laropal A 81 was selected as it was found to be the best option for producing WRs in McIntyre's study because she found that it provided effective adhesive qualities and flexibility to the infill. Laropal A 101 was chosen in addition for this research because it presents a different molecular weight and melting range for comparison with the A 81.

Other low molecular resins, primarily used for varnishing paintings were also included, Regalrez 1094 and 1126. McIntyre eliminated Regalrez 1094 because she found that it made a slightly brittle WR which did not mix well with pigments. In the present study Regalrez 1094 was included because additional microcrystalline waxes were also being tested, and because Regalrez 1094 is reported to have good performance regarding its long-term stability [105-108]. Therefore re-evaluation of this resin was felt to be important. Regalrez 1126 was included, like Larapol A 101, to provide an alternative for testing which offered different characteristics (see Table 9 and Appendix VII).

Robert Gamblin suggested that we use of the successful recipe reproduced in Christine McIntyre's Masters Thesis in relation to his wax resin sticks: 4 parts of wax to 1 part of resin. The guidelines given for the production of the wax resin, were also in McIntyre's work.

For the new formulae, the same proportions of wax to resin were used throughout: 50g wax to 12.5g resin. These materials were weighed on a digital precision balance (Appendix VII). In a double boiler on a hot plate, the wax was melted, and the resin, which had been reduced to powder, was slowly added while stirring.

The limited colour range of pigmented wax-resins available from C-PWR samples, help us to focus our study to just two colours from Gamblin's pallet: titanium white and Burnt umber, for a comparison between these reference samples (see Table 10 and Appendix VII).

TABLE 8 – Microcrystalline waxes selected.

Code	Description	Appearance	melting range (ºC)
KTW1	Techniwax 9211	pastille	84-88
KTW2	Techniwax 9265	pastille	65
KTW3	Techniwax 9300	slab	76
KTW4	Techniwax 9356	pastille	72-78
KTW5	Techniwax 9426	pastille	72-78

TABLE 9 – Synthetic resins selected.

code	Description	melting point (ºC)
R1	Regalrez 1094	95
R2	Regalrez 1126	124
L1	Laropal A 81	80-95
L2	Laropal A 101	95-110

TABLE 10 – Pigments selected.

code	Description	colour index	Chemical description
P1	Titanium Buff	PW 6,7789	TiO_2
P2	Burnt umber, Cyprus	PBr 8,7772	Natural brown earth, contains manganese oxides

2.7 RESULTS AND DISCUSSION

The most noticeable result of these tests was the impossibility of obtaining a mixture of any of the microcrystalline waxes with the two Laropal resins A 81 or A 101. After six hours of mixing and several attempts, a viable wax-resin mixture could not be formed. The resin become turbid and progressively adhered to the walls of the glass till the magnetic stirrer became stuck.

Interestingly these results likely explain the necessity of adding beeswax to the commercial WRs. In fact when beeswax was melted with microcrystalline wax then the Laropal A 81 (3:1:1) were added, the mixture was easily achieved after 25 minutes.

TABLE 11 – Results during the tests concerning melting range, workability and acid number.

Wax-resins	Miscibility of components	Time (minutes)	Range of Workability		workability	Acid Number	Consitency
			Softening point	Melting point (ºC)			
C-PWR			41	68	yes	16,056	2
G-PWR			42	69	yes	11,299	2
KTW1:R1	√	25	41	70	yes	0	3
KTW1:R2	√	40	43	73	yes	0	4
KTW2:R1	√	17	25	50	no	0	1
KTW2:R2	√	17	28	52	no	0	1
KTW3:R1	√	21	24	50	no	0	1
KTW3:R2	√	22	24	52	no	0	1
KTW4:R1	√	18	39	57	no	0	1
KTW4:R2	√	18	40	58	no	0	1
KTW5:R1	√	22	41	64	yes	0	2
KTW5:R2	√	25	41	68	yes	0	2

1. Soft, 2. Medium soft, 3. Medium hard, 4. Hard

Two possible mechanisms could explain why both Laropals mix with beeswax: 1. Beeswax, due to its complex chemistry, may contain natural surfactants[30] that facilitate the mixture with this synthetic resin; 2. Carbonyl groups present in the Laropals may have an affinity for the polar groups present in the beeswax (e.g esters, free fat acid). Regarding the mixture of microcrystalline waxes and beeswax, this is likely due to their chemical affinity (the high presence of hydrocarbons in both) (Appendix VI.2).

In contrast, the mixture of each of the two Regalrez resins with each of the five microcrystalline waxes was very straightforward. All of the 10 different mixtures took 17 to 40 minutes to prepare. This is likely due to the extant chemical affinity between the two non-polar products (Table 11).

In addition, the 10 new formulations for WRs mix very well with pigments and a uniformly coloured WR is obtained, since the pigments remain in suspension in both the liquid and the solid.

It is reported in the literature that the individual products tested, the microcrystalline waxes and both resins Laropal and Regalrez are stable [102-108]. However the resultant mixtures can present differences concerning chemical stability and ageing performance. FTIR analysis were undertaken to characterize the WRs and to identify the functional groups present in the reference samples (C-PWR & G-PWR), in the individual materials alone (waxes and resins) and the new WR formulations.

Preliminary FTIR analyses of the new formulations appear to indicate that the materials will be stable, both, the pure materials as well as the final mixtures. FTIR spectra of the new materials, the microcrystalline waxes and the resins, show the presence of hydrocarbon saturated bonds only (Appendix VIII.1); these are known to be the least reactive bonds found in organic compounds [e.g. 109]. Typical unstable bonds (e.g. double bonds) as well as other functional groups were not identified.

In contrast, the spectra of the reference samples show the presence of functional groups which are chemically more reactive, and could develop free radicals. Of the functional groups, the carbonyl groups are bonded to esters, ketones and aldehydes. The esters are from the beeswax, (present in both C-

[30] Surfactants are amphilitic or amphipathic molecules consisting of a non-polar hydrophobic portion which is attached to a polar or ionic portion (hydrophilic). Beeswax surfactants are used in cosmetic industry in a limited range since synthetic surfactants are chemically more efficient.

PWR and G-PWR); the ketones from the polycyclohexanone resin (present in C-PWR) and the aldehydes are from the Laropal A 81 (in G-PWR). In addition there are unsaturated bonds and hydroxyl groups from the Laropal A 81 (in G-PWR) (see Apendix V.2-4 and Appendix VIII.2, 3).

Based on this information it is likely that the new formulations will prove to be more stable than the reference samples. However it will be important to undertake photochemical accelerate ageing tests on the individual materials alone and in mixtures [110]. The starting materials will all need to be freshly acquired to ensure no previous natural aging has occurred before testing. In addition it is important to note that recent studies undertaken of Laropal A81 and Regalrez 1094, which made use of different and more sensitive analytical instrumentation provide new information about the identification of previously undetected features. In Laropal A81 the presence of polar groups and in Regalrez 1094, of double bonds, could compromise their excellent ageing performance [111]. This requires further research.

Concerning the measurements for the melting ranges it was shown that the 10 new formulations all showed a lower melting point than the pure products alone. This is in accordance with the literature (e.g. 112) which report a common phenomenon known as 'Melting point depression': the melting point of a mixture of two different materials is never the average of the melting points of the two initial products, but is always lower than the melting point of the material present in the greatest amount.

It was also shown in this work (see Tables 8, 9 & 11) that the resin with the highest melting point consistently affects the overall melting point of the mixture by raising it one to three degrees Celsius more than the results with the resin with the lower melting point. As a result six of the new formulations were discarded as their melting range was deemed to be too low, in fact, four of the formulations were very soft and tacky at room temperature. The WRs with the highest melting points, which were all similar to the reference samples were selected: KTW1-R1, KTW1-R2, KTW5-R1 and KTW5-R2. These all consist of mixtures of the microcrystalline waxes Techniwax 9211 (KTW1) and Techniwax 9426 (KTW5) with the resins Regalrez 1094 (R1) and Regalrez 1126 (R2).

Importantly the melting and softening point measurements also showed that the introduction of a pigment increases the melting point of the mixtures by one or two degrees Celsius (Appendix IX).

Regarding the acid number of the reference samples, as expected, because of the presence of beeswax, they proved to be acidic. Not surprisingly the acid number is higher for the WR with the highest proportion of beeswax in its formulation (C-PWR).

In contrast all of the new formulations present an acid number of zero. This is an important advantage for these new products since they are unlikely to interact with the copper support. Unfortunately it was not possible to verify this assumption since the aging chamber was not available during the time of this project.

Characteristics which were assessed empirically: workability and hardness, also revealed interesting results and contributed to the choice of the final two formulations from the four remaining.

Regarding workability, both the reference samples and the final two new formulations were found to have the same application and working parameters: the temperature required for softening was 52ºC (despite the recommendation by Gamblin of 78ºC for application of his product); application was

straightforward and efficient using the 'wax carving pencil'[31] supplied by Gamblin (Appendix VII); the infills were easily levelled with gentle pressure with the tool while the infills were still warm; and it was possible to work the infills at room temperature or by warming and to provide texture using dental tools or a thin bamboo stick.

The removal of excess material in the loss or around the loss area can be carried out mechanically or with solvents. In the first case, most of the material can be gently removed with the sharp edge of a bamboo stick without causing damage to the paint surface. This mechanical removal can be followed by cleaning with white spirit or one of the Shellsols (e.g, Shellsol D).

In addition, it was also found that the new formulations for the wax resins, like the reference samples, can match the gloss of the painting surface by buffing the surface of the WR infill.

The infills were easily covered with a synthetic varnish based on Regalrez 1094 diluted in white Spirit (20g resin to 80 mls white spirit). Nevertheless, since the infill material is sensitive to most solvents and extensive brush application could disrupt or remove the surface texturing, it may be prudent to apply the varnish by spraying.

In order to make a selection from the WRs to achieve the best match in properties to the reference samples, a hardness test was also undertaken: using a scalpel and a needle, the hardness of the different WRs was compared. From the original group of four two were eliminated as they were considerably more rigid than the references. The final selection for the new WR formulation came down to the two already identified from the workability testing: KTW5:R1 and KTW5:R2.

Blooming is evident on both the C-PWR and the G-PWR reference samples, however to date, blooming has not been observed on the surfaces of the new pigmented formulations. Since these are relatively fresh, it would be ideal to follow up by testing these materials for bloom development by natural aging in ambient temperatures with cycles of low and high relative humidity[32].

2.8 CONCLUSIONS

The second part of this thesis encompassed the characterization of two wax-resins formulations used as infill materials for paintings (C-PWR and Gamblin). The characterization of these WR reference samples; the Master thesis by Christine McIntyre; and the important suggestions made by Robert Gamblin; formed the basis for preliminary trials and testing to explore and develop a new wax-resin formulation suitable for infills on paintings with a copper substrate.

The need for an inert material for infilling paint losses on a copper support is particularly important as the range of infill materials currently available are not suitable for a variety of reasons, for use on this type of support.

The characterization of the references proved to be very important for the choice of the raw materials to be used in the new formulations, and as anticipated, highlighted the problem of beeswax as

[31] The application using an unheated spatula was not ideal as it was difficult to maintain a high enough temperature to avoid cooling and hardening the WR fill material before application could be effected.
[32] Dr. Bartl, at Institute of Chemical Technology (Prague), has studied this phenomena in natural ageing modern samples storage at 4ºC for at least 3 years (2015, 2013, 2008).

an ingredient for treatment materials to be applied on copper since the beeswax promotes the corrosion of the copper, as claimed by several studies.

The characterization of the individual materials, and of the new formulations KTW5- R2, made of Techniwax 9426 microcrystalline wax with Regalrez 1126, and of KTW5-R1, made of the same microcrystalline wax with Regalrez 1094, showed that these wax resin mixtures are likely to be chemically stable since they are composed of saturated hydrocarbons only.

However it will be important to design and execute accelerated ageing tests (through photo-oxidation) to monitor for signs of degradation, within the mixtures and in relation to the copper plate. This is an essential step before any claims can be made for the chemical stability of these new formulations.

It is very encouraging that the working qualities of the new formulations were found to be very similar to the reference samples: they are easy to apply and achieve an excellent result regarding the infill of very shallow losses; as well as the application temperatures and subsequent softening points were in the range suitable to use on oil paintings.

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APPENDIX I – PAINTINGS ON COPPER

TABLE I.1 – Information regarding the studied paintings.

Code	Provenance	Date	Punched Mark	Measure (mm)	Thickness (mm)
PINT-B	Spain	17th c.		160 x 130	0,7
PINT-C	Portugal	17th c.		111 x 87	0,8
PINT-E	Portugal	17th c.		220 x 170	1,2
PINT-G	Flanders	17th c.		228 x 173	0,7
PINT-H	Portugal	17th c.		167 x 222	0,6
PINT-J	Portugal	18th c.		152 x 109	0,8
PINT-K	taly	17th/18th c.		360 x 285	0,8
PINT-M	Flanders	17th c.		166 x 219	0,8
PINT-N	Flanders	17th c.		283 x 364	0,9
PINT-O	Flanders	18th c.		220 x 169	0,8
PINT-P	Flanders	18th c.		220 x 170	0,9
PINT-Q	Flanders	18th c.	yes	220 x 170	1,1
PINT-S1	Portugal	18th c.		224 x 38	0,8
PINT-S2	Portugal	18th c.		241 x 39	0,9
PINT-S3	Portugal	18th c.		430 x 50	1,1
PLT-T1		21th c.			1,6
PLT-T2		21th c.			1,6

APPENDIX II – SUMMARY OF HISTORICAL SOURCES

The edition consulted (1979) was originally translated from Latin into English by Cyril Stanley Smith and John G. Hawthone in 1963, and published by The University of Chicago Press. Then, re published by Dover Publications, Inc. in 1979 with some slight corrections. No other English version/translations of this book exist.

The edition consulted (2015) was originally translated from Italian to English by Cyril Stanley Smith and Martha Teach Gnudi in 1942, and published by The American Institute of Mining and Metallurgical Engineers, Inc. In 1959, the translation was revised and slightly corrected by the same translators and publisher. In 1990 and 2015, new unaltered re-editions were published by Dover Publications, Inc. No other English translations of this book exist.

The Dover edition consulted (1950) was originally translated from the first Latin edition of De Re Metallica (1556) by Herbert Clark Hoover and Lou Henry Hoover in 1912, and published by The Mining Magazine. In 1950 an unaltered reprint was published by Dover Publication, Inc. No other English translation of this book exist.

TABLE II.2 – Copper extraction and purification according to historical sources

Source	Sections	Copper Extraction and Purification			
		Preparation	**Roasting**	**Smelting**	**Refining**
Theophilus 12th c.	Ch. 63, 64, 67	Not mentioned	Roast and grind	• Use of bellows. • Fuel: charcoal. • Keep copper melted during a day and night. • Include liquation operation.	• Use of Bellows • Fuel: charcoal • Addition of charcoal ashes. • Removal of lead. • Poling. • Product: *cuprum 'torridum'*
Biringuccio 1540	Book III: Ch. 1-6, 8 Book V: Ch. 3	• Manually separation of ore from rocks • Quench with water, grind and washed (2-3 times)	• Use of an open furnace. • Fuel: Wood and charcoal. • Repeat 2 - 3 times • Useful for eliminating arsenic • Fluxes could be added to soften the ore in order to extract the metals and to purge them of earthiness. Test and try different proportions.	• Use of a blast furnace. • Fuel: charcoal • Bellows are used to evaporate the trace of lead. • Kept molten for a long time • Lead is added (for liquation) • Products: copper Matte (well evaporated and reduced), 'work lead' and slag	• Use of a blast furnace • Fuel: charcoal • Use of Bellows • Removal of lead • Poling – use of chestnut wood • Product: 'very pure and beautiful copper' p. 172
Agricola 1556	Book VIII; IX; XI	Ores are sorted, broken with hammers, burnt, crushed with stamps, ground into powder, sifted and washed.	• 7 - 9 times • Fuel: wood • Use of an open furnace. • Useful for eliminating sulphur, bitumen and arsenical sulphides	• Use of blast furnace: method most used is with the tap-holes always open • Use of Bellows • Fuel: charcoal • Product: copper matte, lead and slag • Use of fluxes • Rotating shift schedule of 12 hours. • Include liquation operation.	• Use of a blast furnace • Fuel: charcoal • Use of Bellows • Removal of lead • Poling • Product: good copper

APPENDIX III - ANALYTICAL INSTRUMENTATION AND CONDITIONS

The analytical instruments used for part 1 of this thesis belong to CENIMAT/I3T-FCT (OM, micro hardness Vickers, SEM/EDS and XRD), Campus Tecnológico e Nuclear Instituto Superior Técnico - CTN/IST- (PIXE) and FCT-DCR (digital camera, x-radiograph and μ-EDXRF). The analytical instruments used for part 2 belongs to DCR (μ-FTIR and FTIR-ATR).

Photographic Documentation

Photographic documentation was performed with a Sony digital camera (DSC-F828, Cyber-shot, Zeiss, Super HAD CCD, 4 colous. 7x opical zoom. 8.0 Mega-pixels.

X-radiograph

X-radiographs were taken using an ArtXRay from NTB electronische Geraete GmbH digital system. This system is composed of a X-ray generator Y.MBS/160-F01, with a directional beam with a focal spot size of 1.9mm, a 40-160kV voltage, 0.2-5.0mA current and a maximum X-ray power of 480W; a manipulator of 4μm/step and 5000steps/revolution resolution; and a camera with 10-160kV radiation sensitive range, 0.083mm pixel size, and 12pixel/mm resolution.

For the X-radiographs the following conditions were used according to the thickness of the plates: 100 kV and 4.2 mA with 100ms/150ms of integration time; 115 kV and 4.2 with 100ms of integration time. The digital images acquired were processed with iX-Pect software.

Sample mounting

Sample were mounted as cross sections in acrylic resin Technovit 2000 polished with SiC abrasive paper (P1000, P2500 grit sizes) and finished with 3 μm diamond paste on a polishing wheel.

Optical Microscopy (OM)

The optical microscope used is a Leica DMI 5000M coupled to a computer with the LAS V2.6 software. The optical lenses of this microscope are set in an inverted position. Samples were analysed with 10x ocular lenses and 50x, 200x and 500x objective. This equipment has a lighting system for bright field (BF), dark field (DF), cross-polarized light (X-Pol).

Energy Dispersive X-Ray Fluorescence (μ-EDXRF)

X-ray fluorescence spectra were obtained using an ArtTAX spectrometer from Intax GmbH. Operating with a molybdenum (Mo) X-ray tube, focusing polycapillary lens and silicon drift electro-thermally cooled detector and a xFlash (Si drift) detector, with 170 eV resolution. The accurate positioning system and polycapillary optics enable a small area of primary radiation (ø ~70 μm) at the painting's surface. Elemental compositions were obtained from the average of three independent spots, analysed with a tube voltage of 40KV and a current intensity of 600μA and live time 100s.

Particle Induced X-ray Emission (PIXE)

The chemical composition of the bulk-metal substrate was analysed by PIXE. These measurements were made with a 2 MeV proton beam extracted in air, from a van de Graaff accelerator, and an acquisition time of 600s. The x-ray detector was a SDD, with filter Mylar 54 μm; and the particle detector used was a RBS, 200 V. Electric current used was 200-300pA. The spectra were analysed by the GupixWin 2.1.4 software, and calibrated with reference standards. A carbon coat was necessary to applied to all samples before analysis.

Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/EDS)

A Zeiss DSM 962 Analitycal Scanning Electron Microscope was used with a backscattered electrons (BSE) imaging modes. The system also has an energy dispersive spectrometer (EDS) detector: an Oxford Instruments INCAx-sight with an ultra-thin window. Samples were covered with a layer of gold. The elemental maps were acquired with a voltage of 15.0kV (high voltage).

Microhardness hardness Vickers

The microhardness was determined in a Zwick-Roell Indentec testing equipment. The mounted samples were indented for 10 s with a low force of 0.2 kgf. At least 3 indentations were made, being considered the average value of several measurements with a relative standard deviation better than 5%.

XRD – Pole Figure

Pole figures analysis was performed using a Bruker X- ray-diffractometer (rotating anode –Cu-Kα radiation(1.5418 Å), 30 kV/100 mA, Texture goniometer (eulerian cradle) with scanning of 2θ= 43.44 and 2θ=50.56. $0<x<69$ ($\Delta x= 3^{o}$) $0<\theta<360$ ($\Delta\theta=3^{o}$)The acquisition time was 1s/point and the conical slip was a few mm^2

Fourier Transform Infrared Spectroscopy (μ-FTIR)

Infrared spectra were acquired using a Nicolet Nexus spectrophotometer coupled to a Continumm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, between 4000-650 cm-1, resolution setting 4cm-1 and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown here as acquired, without corrections or any further manipulations, except for the removal of the CO2 absorption at ca. 2300-2400 cm-1.

FTIR- Attenuated Total. Reflectance (FTIR-ATR)

The FTIR analysis was performed using an Agilent 4300 Handheld FTIR Spectrometer with a diamond ATR head . Spectra were obtained covering the 4000-650 cm-1 range, with spectral resolution of 4cm-1. The collected spectra were obtained with 64 scans before Fourier transform. Data was acquired by MicroLab® software and data was matched by Polymers and Polymer Additives P/N 30002 ATR-FTIR Spectra database, from S.T. Japan (Europe Gmbh).

APPENDIX IV – ANALYTICAL RESULTS

APPENDIX IV.1 – SELECTED RL AND XR DIGITAL IMAGES

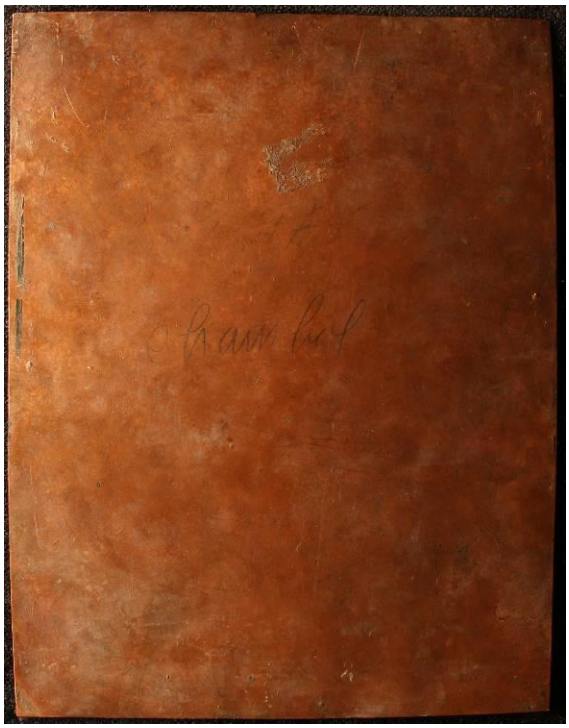


FIGURE IV.1 – PINT-E: Raking light from the left side, back, showing support texture.

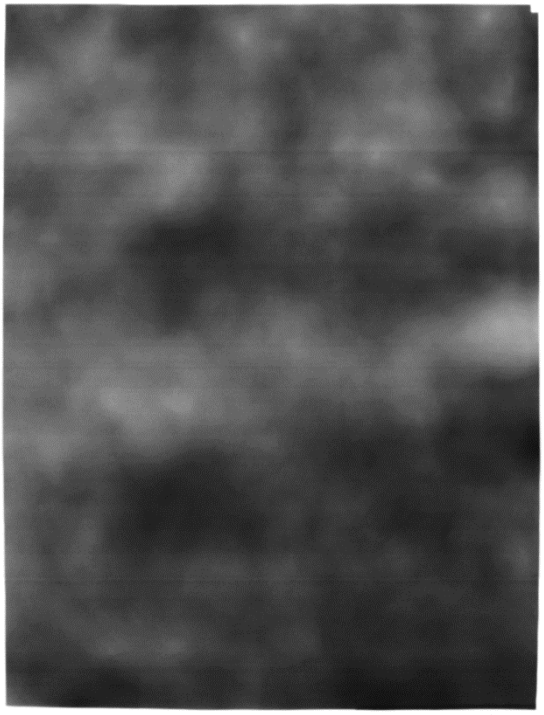


FIGURE IV.2 – PINT-E: X-radiograph

FIGURE IV.3 – PINT-O: Raking light from the left side, back, showing support texture.

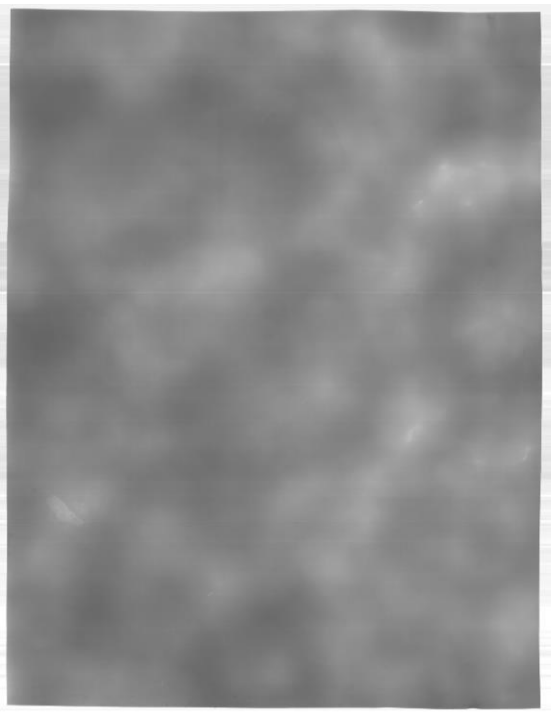


FIGURE IV.4 – PINT-O: X-radiograph

FIGURE IV.5 – PINT-K: Raking light from the left side, back, showing support texture.

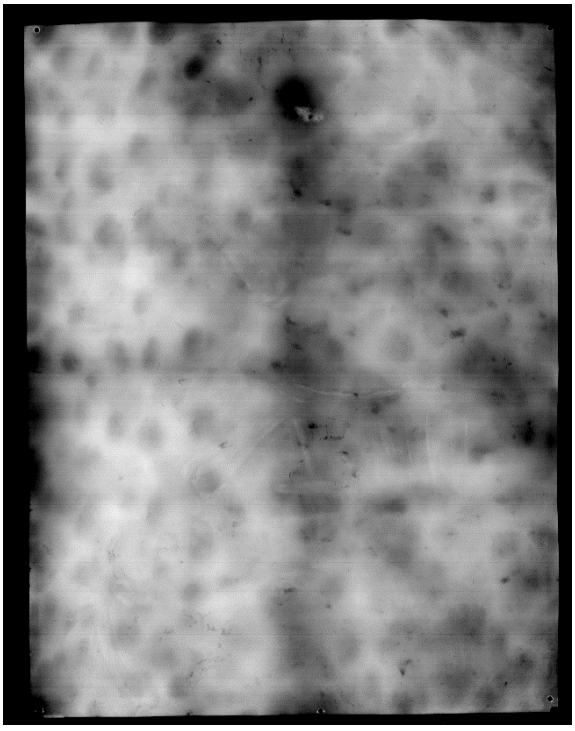


FIGURE IV.6 – PINT-K: X-radiograph

FIGURE IV.7 – PINT-S2: Raking light from the left side, back, showing support texture.

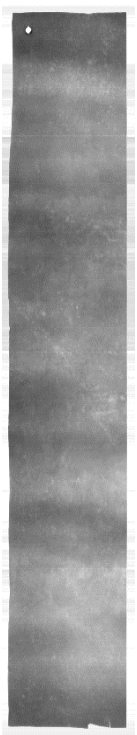


FIGURE IV.8 – PINT-K: X-radiograph

FIGURE IV.9 – PLT-T1: X-radiograph

APPENDIX IV.2 – XRF

Note: mapping and spectrums of all samples were acquired. They are stored at the painting Lab at DCR for further research.

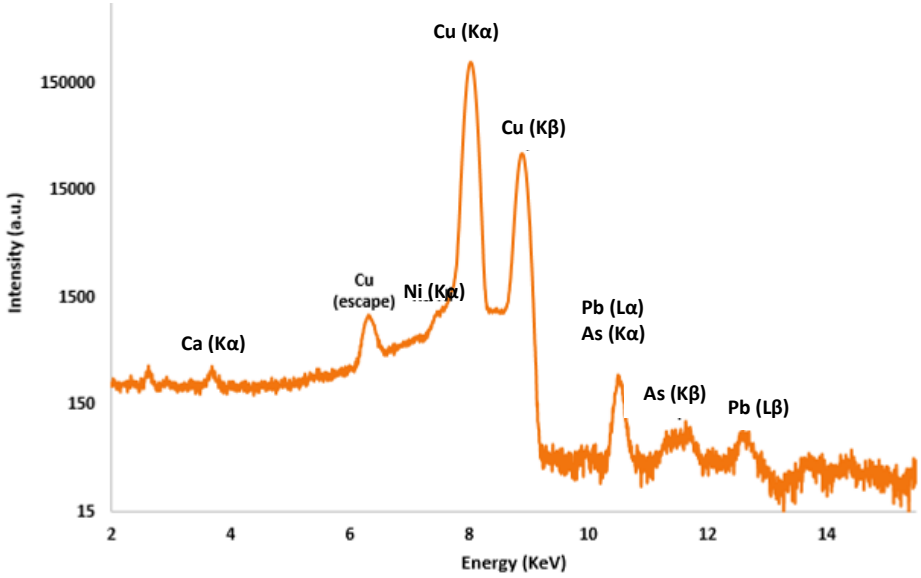


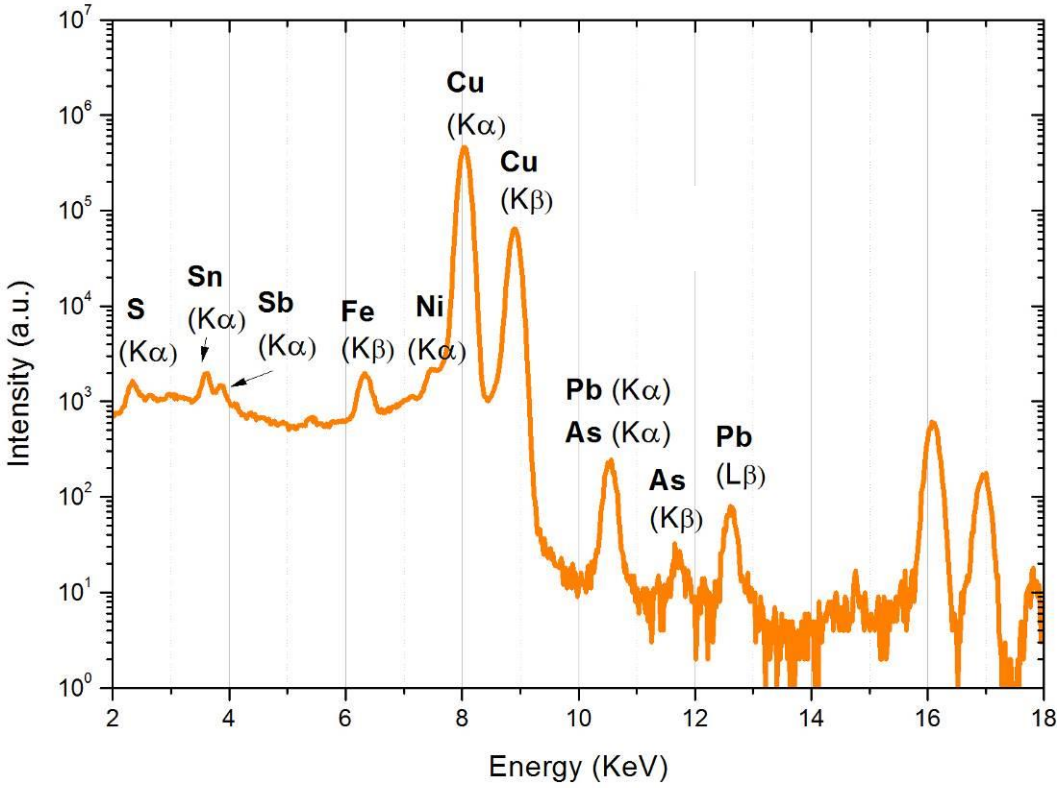
FIGURE IV.10 - Elemental composition of the copper plate PINT-E by µ-EDXRF.

All spectrums acquired are similar to the one shows. The only difference are in samples PINT-B, PINT-Q and PINT-M where peaks of chlorine and mercury can be also detected.

APPENDIX IV.3 – PIXE

FIGURE IV.11 - Elemental composition of the copper plate PINT-N by μ-PIXE .

All spectrums acquired are similar to the one shows.



APPENDIX IV.4 – OPTICAL MICROSCOPY

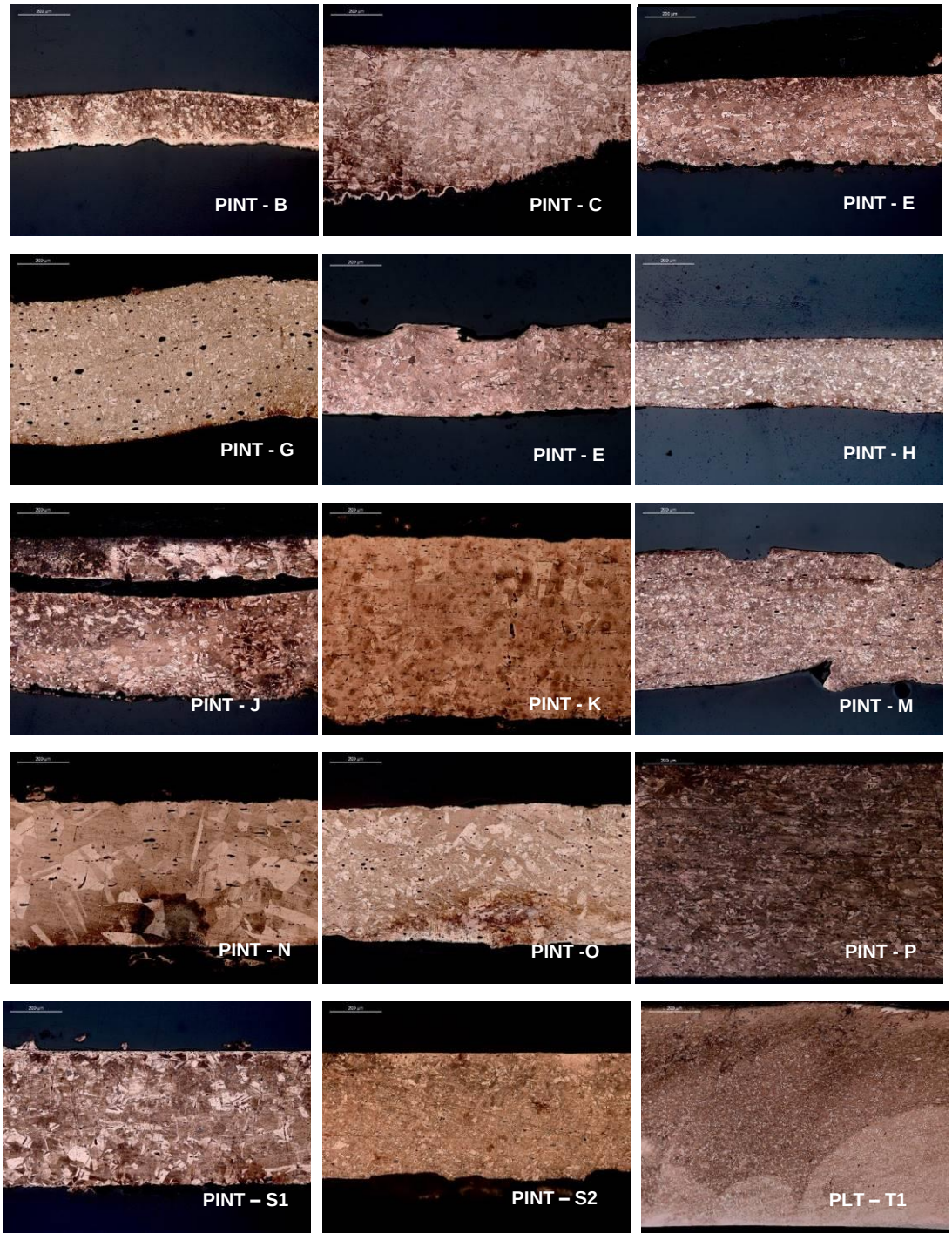


FIGURE IV.12 – OM (10x). Etched samples. Thickness of plates as well as a general grain size can be compared.

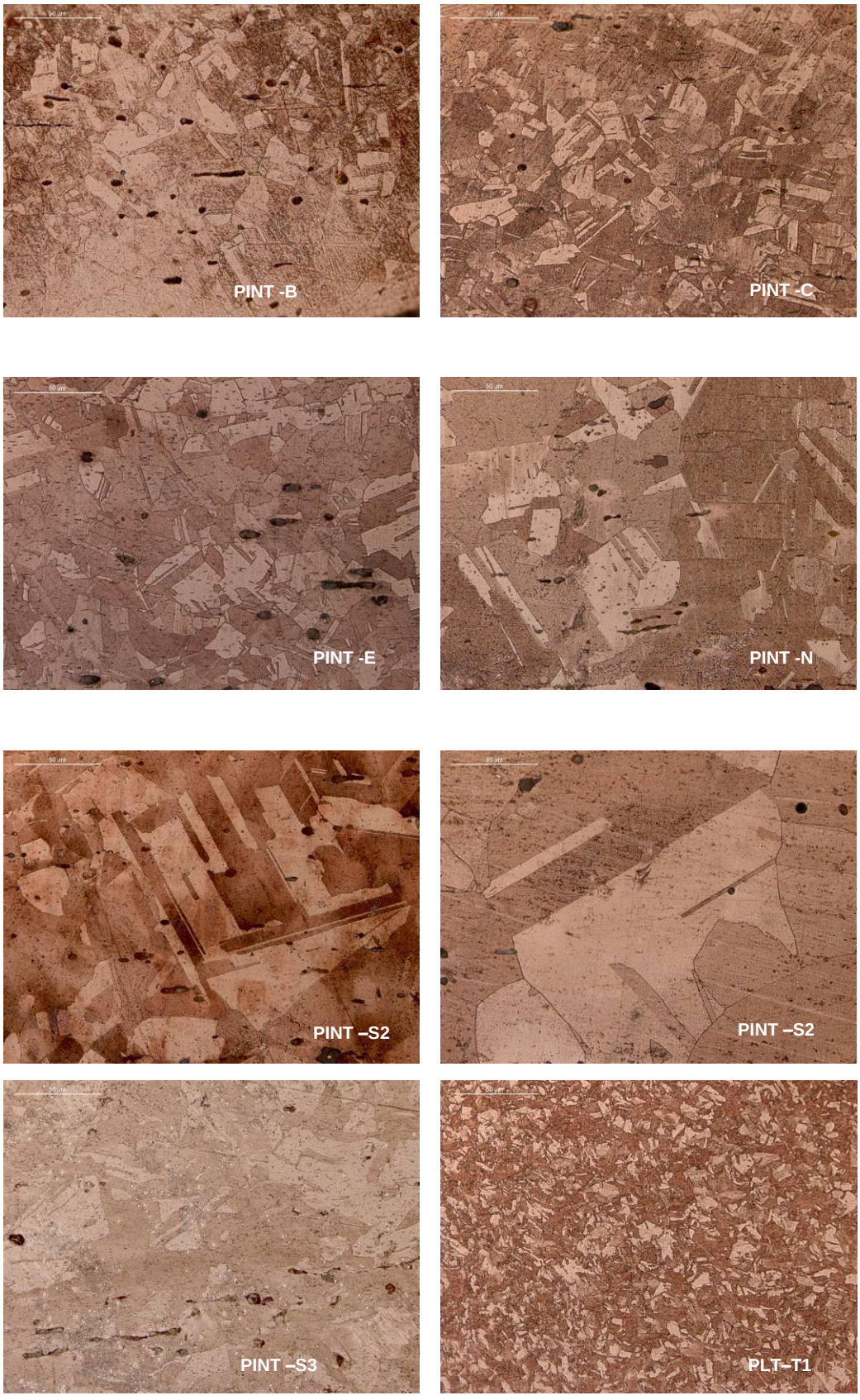


FIGURE IV.13 – OM (50x). Etched samples. Selected imagens where straight and bending twins are identified.

APPENDIX IV.5 - SEM-EDS

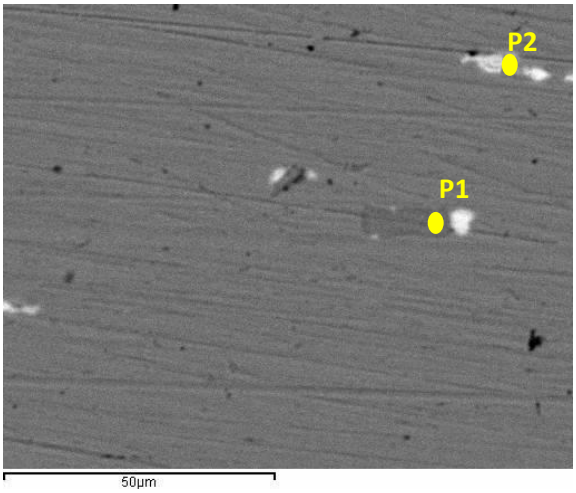


FIGURE IV.14 - PINT H – SEM-BSE image detail showing the identification of two points by EDS; P1 and P2: Pb-Sb inclusions.

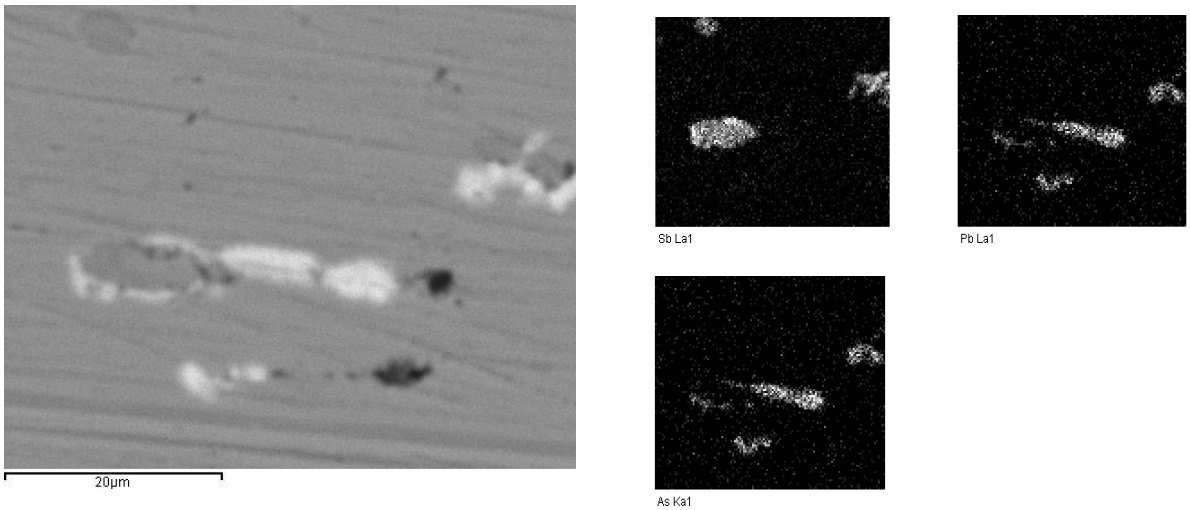


FIGURE IV.15 - PINT H – SEM-BSE image and the corresponding X-mapping of element present in Pb-Sb-As inclusion.

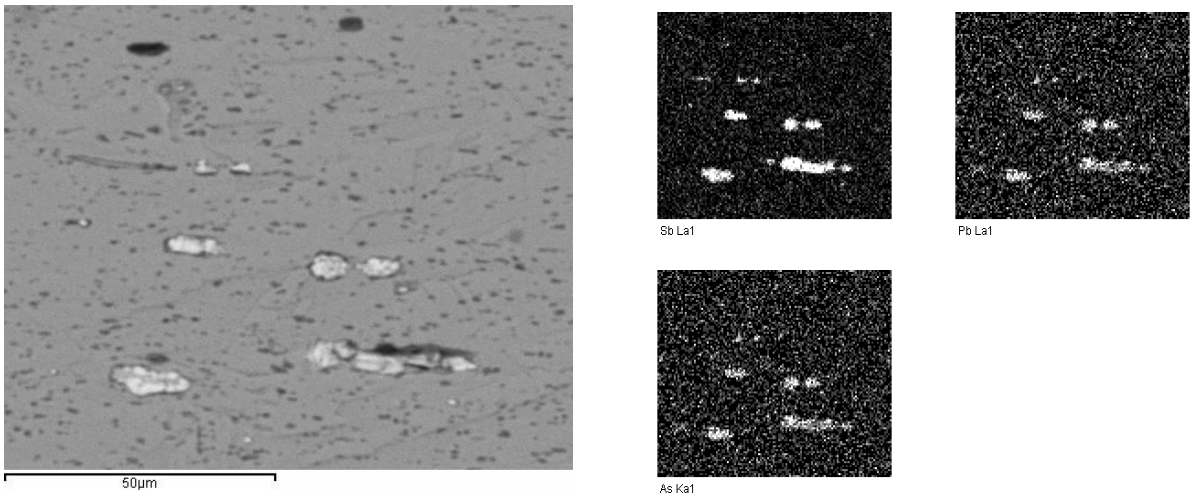


FIGURE IV.16 - PINT Q – SEM-BSE image and the corresponding X-mapping of elements present in Pb-Sb-As inclusion.

APPENDIX IV.6 XRD - POLE FIGURES

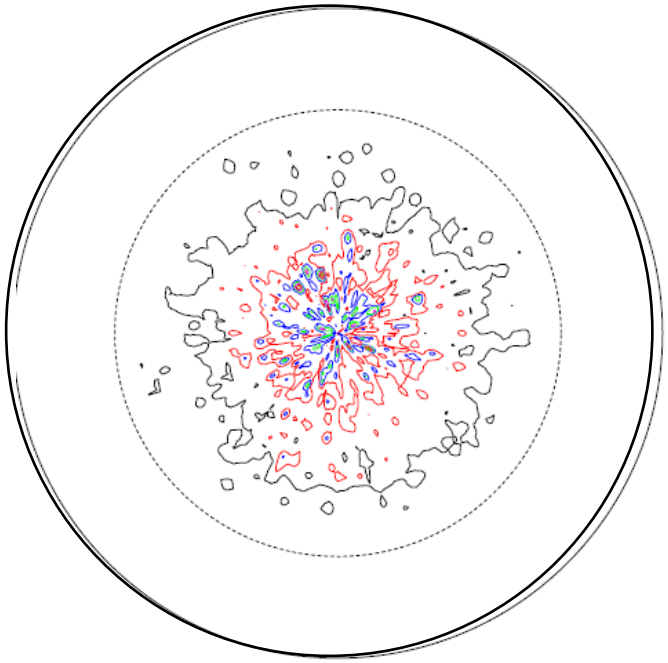


FIGURE IV.17 – PINT-S1 – 111 - Pole Figure showing no preferential direction in the surface. Scanning of 2θ=43.44.

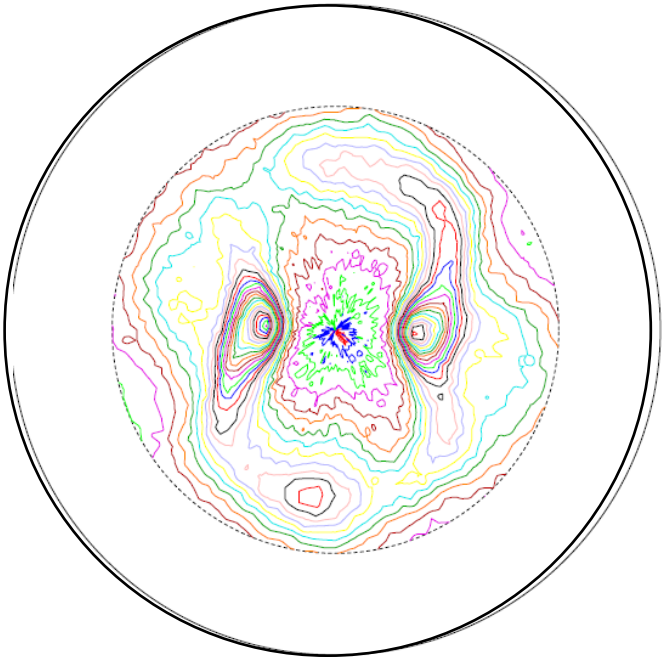


FIGURE IV.18 – PLT-T2 – 111 - Pole Figure with preferential direction in the surface. Scanning of 2θ=43.44.

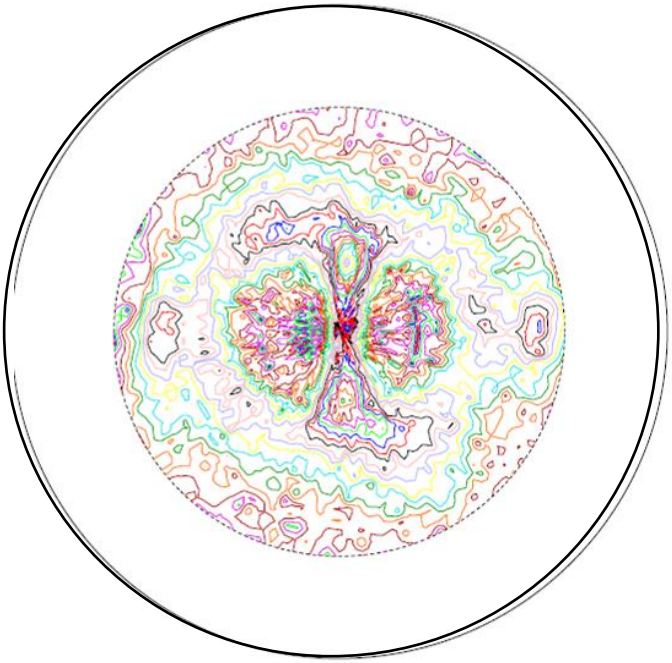


FIGURE IV.19 – PLT-T2 – 200 - Pole Figure with preferential direction in the surface. Scanning of 2θ=50.56.

APPENDIX IV.7 - VICKER MICROHARDNESS

TABLE IV.3 – Vickers microhardness results (HV0.2, 10s)

Applied in three different locations of the artefact (when justified)

	PINT B	PINT-C	PINT-E	PINT-G	PINT-H	PINT-J	PINT-K	PINT-M	PINT-N	PINT-N	PINT-O	PINT-P	PINT-S1	PINT-S2	PINT-S3	T1
grain size	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	100-50	20
HV 0.2	105	106	80	117	100	111	114	112	89	89	101	110	72	75	131	103

APENDICE V – IMAGES

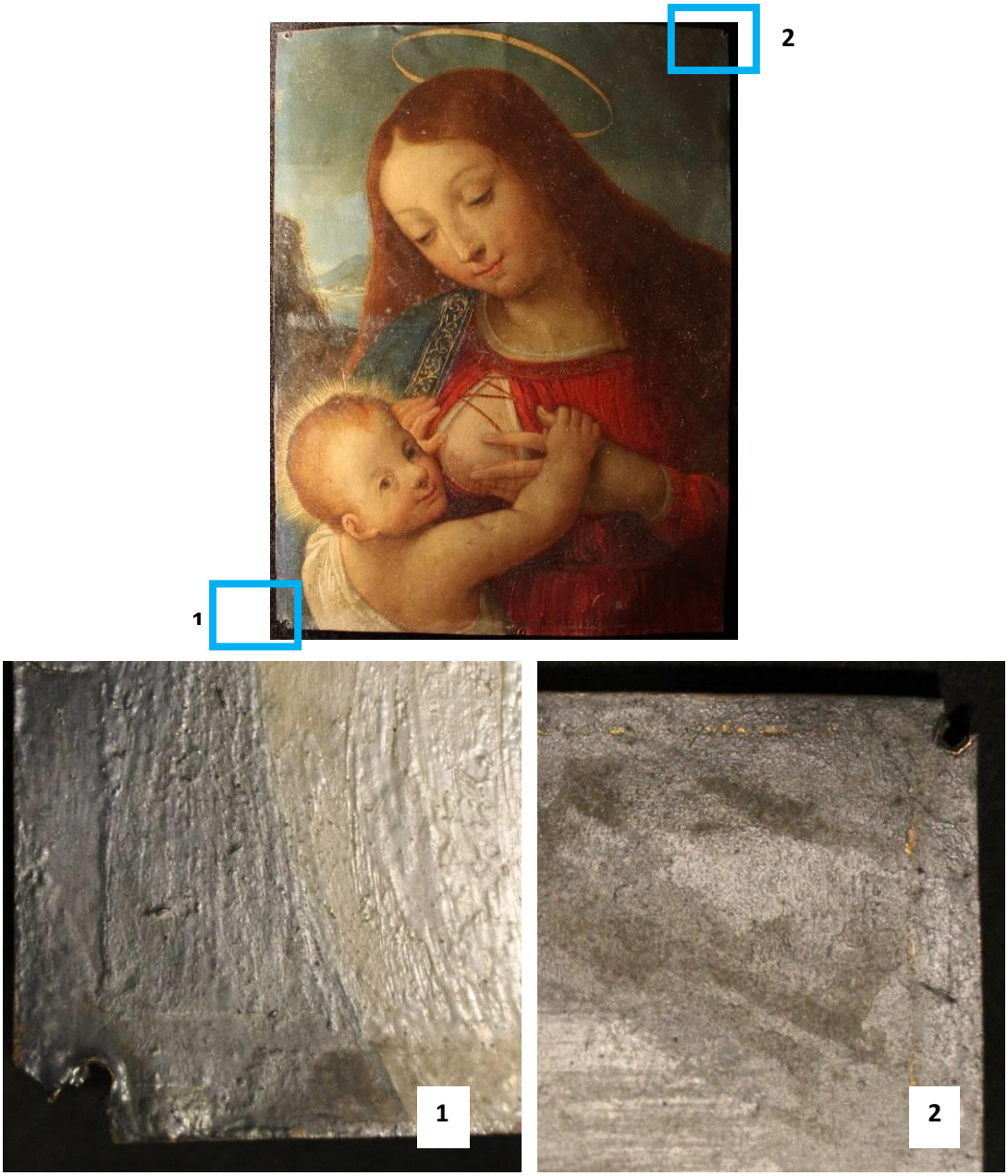


FIGURE V.1 – Sample of support losses in painting on copper PINT-K.

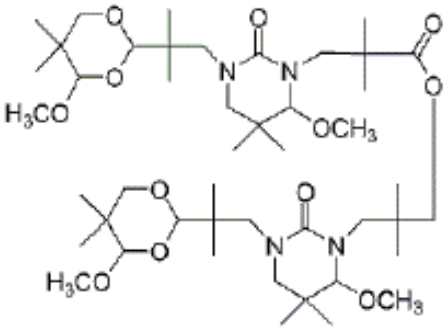


FIGURE V.2 – Proposed molecular structures of Laropal A 81 (Source: Smith, 2008, p. 11)

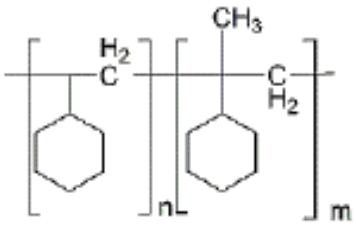


FIGURE V.3 – Proposed molecular structures of Regalrez 1094 (Source: Smith, 2008, p. 11)

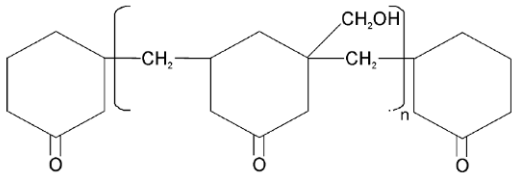


FIGURE V.4 – Proposed molecular structures of Laropa K 80 (Source: de la Rie, 1989, p. 12)

APPENDIX VI – INGREDIENT IDENTIFICATION FROM TABLES 6 & 7

Commercial products:

The following commercial products were not identified by the authors. Although it may be possible to identify the current ingredients this does not necessarily correlate in any way to the products as used at the time of publication since manufactures are free to alter their formulations at any time.

Fine Surface Polly Filla; UVS Retouch Varnish; Rowney Acrylic, Liquitex Acrylic Gesso, Modostuc, Lefranc & Bourgeois Gel Relief, Lascaux Hydrogrund 750**,** tempera paint.

Conservation products:

- **Mowilith 20:** PVA resin based on low molecular weight solid VA homopolymer [1]
- **PB72:** Paraloid B72, Thermoplastic acrylic resin based on ethyl methacrylate/methyl acrylate (EMA/MA) copolymer (70:30) [2]
- **PB48:** Paraloid B48, Thermoplastic acrylic resin based on butyl acrylate/methyl methacrylate (BA/MMA) copolymer (22-44%BA) [2]
- **BTA:** Benzotriazole; ($C_6H_5N_3$), a nitrogen heterocyclic derivative [3]
- **Plextol B500:** Acrylic dispersion [4] based on copolymer EA/MMA (66% EA) [2]
- **Beva 371:** Resin based on copolymer ethylene/VA. (1) Composition: 60% solvents: toluene and naphta + 40% solids: two ethylene vinyl acetate copolymers (Elvax 150 resin, and A-C Copolymer 400), an aldehyde ketone resin, phthalate ester of hydroabietyl alcohol (Cellolyn 21) and paraffin wax [5]

References:

[1] Kremer product information sheet for “Polyvinyl Acetate 20”.

[2] Down, J. 2015. The evaluation of selected poly(vinyl acetate) and acrylic adhesives: A final research update. Studies in Conservation, 60(1): 33-54.

[3] Sease, C. 1978. Benzotriazole: a review for conservators. Studies in Conservation, 23(2): 76-85

[4] Horie, C. V. 2010. Materials for Conservation: Organic Consolidants, Adhesives and Coatings, 2nd ed. Oxford: Butterworth-Heinemann

[5] http://www.conservationsupportsystems.com/system/assets/msds/New_Beva_Formula

APPENDIX VII - EQUIPMENT AND SUPPLIERS

Equipment

- Digital precision balance: Precisa®, model 500M 2000C
- Magnetic Stirrer with Heating: Heidolph®, MR Hei-Standard
- Wax carving pencil: Wax carving pencil is commercialized by Gamblin, America. https://www.gamblincolors.com/conservation-colors/
- Reichert Thermovar HT-1 B11 polarising microscope.

Suppliers

Product	Suppllier	Date of Receipt
Techniwax 9211	Kerax® www.kerax.co.uk	Received 2015
Techniwax 9265	Kerax® www.kerax.co.uk	Received 2015
Techniwax 9300	Kerax® www.kerax.co.uk	Received 2015
Techniwax 9356	Kerax® www.kerax.co.uk	Received 2015
Techniwax 9426	Kerax® www.kerax.co.uk	Received 2015
Gamblin PWR	Gamblin Conservation Colours www.gamblincolors.com/conservation-colors	FCT-PNT stock and Purchased 2015
Regalrez® 1094	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015
Regalrez® 1126	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015
Laropal® A 81	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015
Laropal® A 110	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015
Paraloid™ B-72	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Pigment Titanium White	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015

Burn umber	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	Purchased 2015
Potassium hydroride BioXtra, ≥85% KOOH basis (P5958 *FLUKA*)	Sigma-Aldrich www.sigmaaldrich.com	FCT Scientific lab Stock
Phenolphthalein ACS reagent (105945)	Sigma-Aldrich www.sigmaaldrich.com	FCT-PhotoChemistry (PC) Stock
96% etanol Puriss. P.a., ACS reagent, reag. Ph. Eur., 96% (v/v) (32294 *RIEDEL-DE HAËN*)	Sigma-Aldrich www.sigmaaldrich.com	FCT-PC Stock
Hydrochloric acid ACS reagent, 37% (320331 *FLUKA*)	Sigma-Aldrich www.sigmaaldrich.com	FCT-Scientific lab stock
Xylene Reagent grade (214736 *ALDRICH*)	Sigma-Aldrich www.sigmaaldrich.com	FCT-PNT Stock
Copper plate	CENIMAT	FCT CENIMAT Stock
Jewellers saw blades 3/0, Glardon® Vallorbe	Jewellry Store Lima & Teixeira, Lisbon, Portugal Tel. 21 847 53 91	Purchased 2015
Fine sable-haired brush Winsor & Newton Cotman Watercolour Round III Series	FCT-PNT Stock	FCT-PNT Stock

APPENDIX VIII – FTIR ANALYSIS

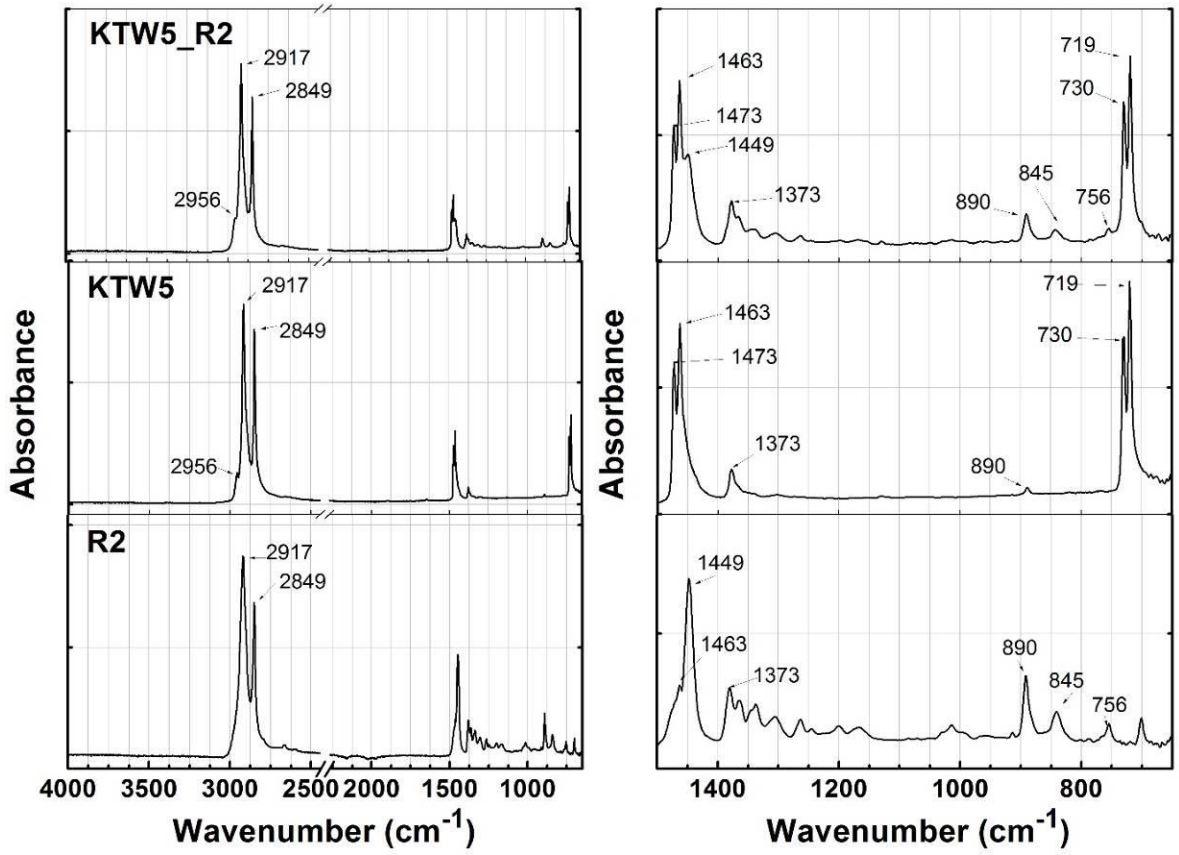


FIGURE VIII.1 – μ-FTIR spectrum of the wax resin KTW5:R2 and of pure materials, the microcrystalline wax KTW5 and the Regalrez 1126 (R2). Showing only the presence of hydrocarbon bonds.

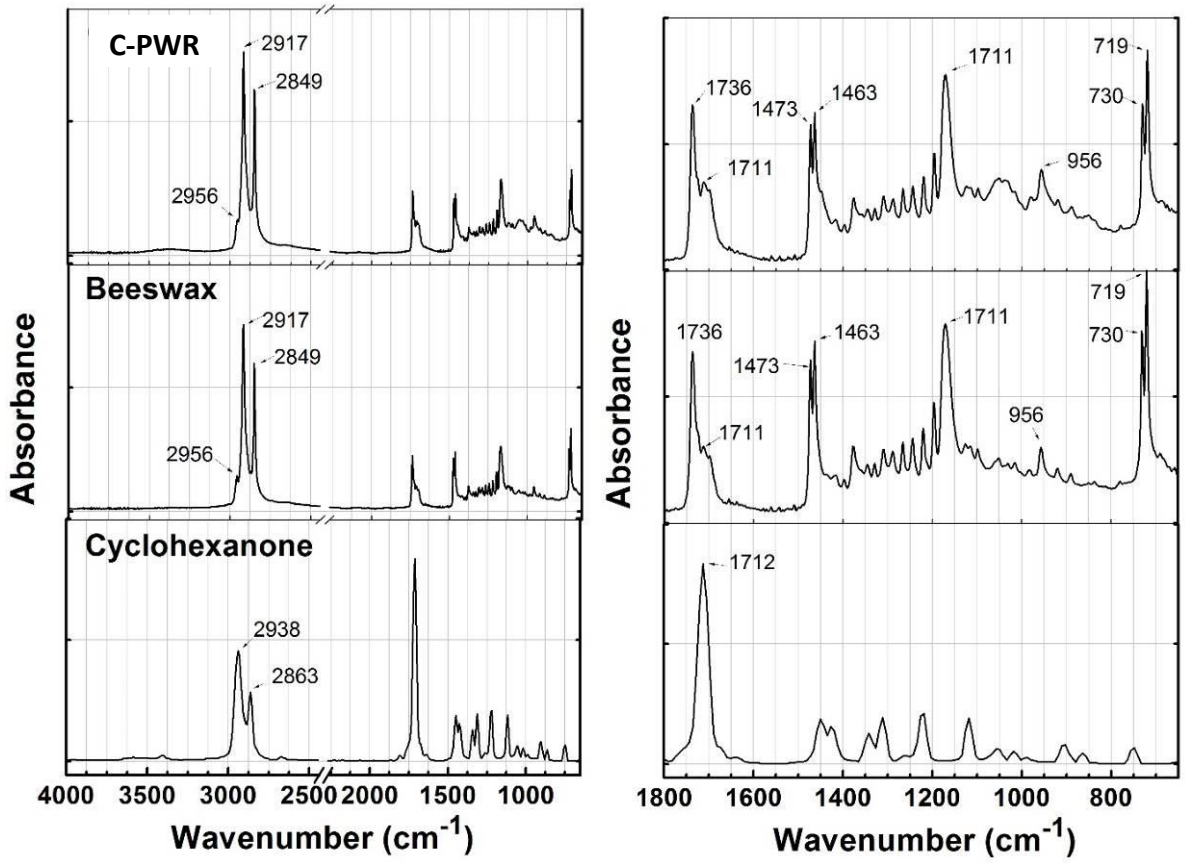


FIGURE VIII.2- µ-FTIR spectrum of the C-PWR and reference spectra of beeswax and of cyclohexanone resin. Showing the presence of carbonyl groups associated to ketones (in poly cyclohexanone) and esters (in beeswax)[33].

[33] As samples of cyclohexanone and beeswax originally used in the formulation of C-PWR, reference FTIR spectra were used for comparison.

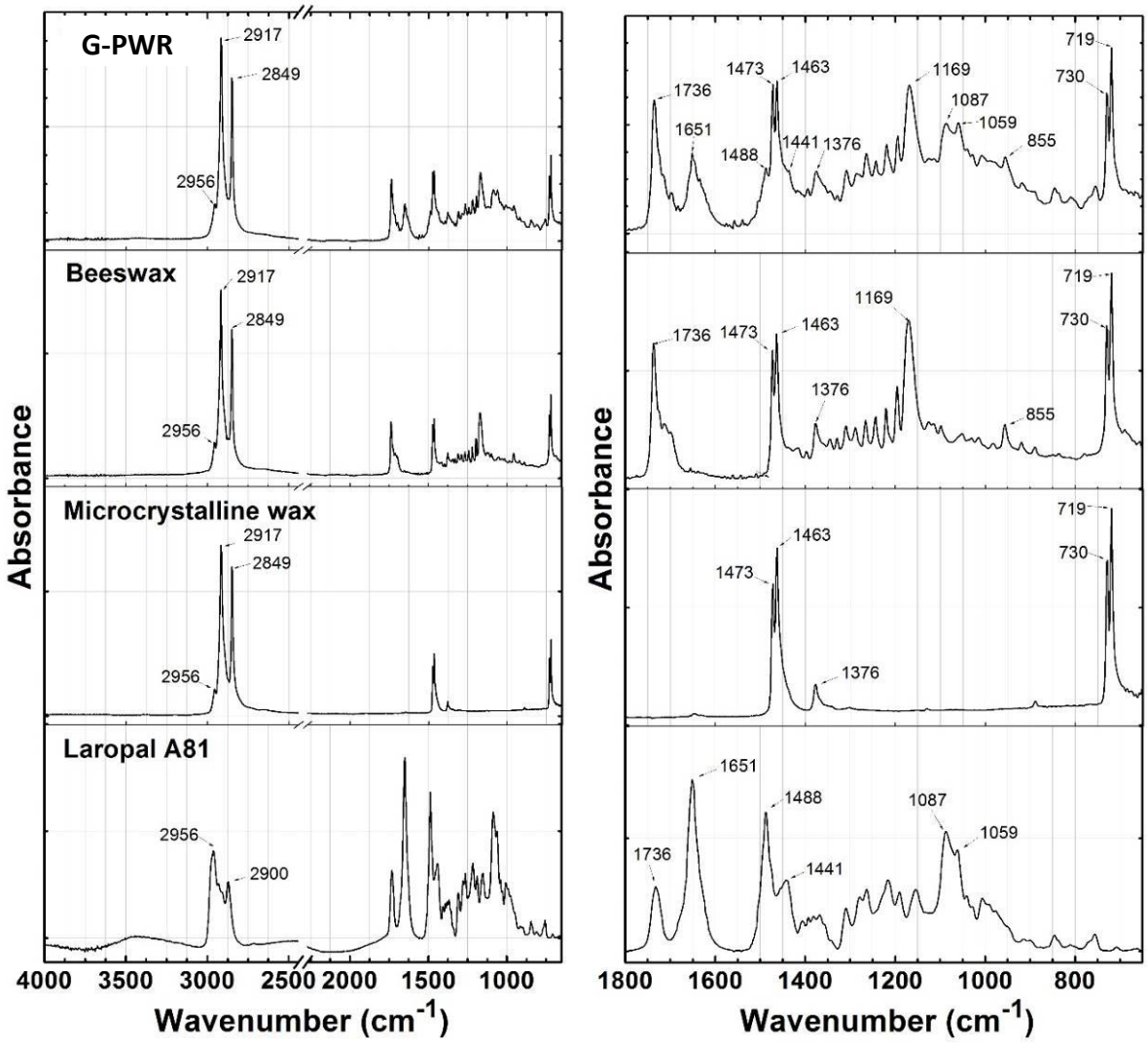


FIGURE VIII.3- µ-FTIR spectra of the G-PWR, reference spectrum of beeswax, spectrum of microcrystalline wax KTW5 (for comparison) and of Laropal A81, showing the presence of carbonyl groups associated to aldhydes (in Laropal A81) and esters (in beeswax); as well as unsaturated bonds (in Laropal A 81).

APPENDIX IX – TEMPERATURE MEASURED FOR THE PIGMENTED WAX-RESINS

Table IX.4 – Temperature range of workability for the pigmented Wax-resins.

blend	pigment	melting range	
		softening	melting
C-PWR	t.w	**42**	**69**
	b.u	**42**	**69**
G-PWR	t.w	**42**	**70**
	b.u	**42**	**70**
KTW1:R1	t.w	**42**	**71**
	b.u	**42**	**70**
KTW1:R2	t.w	**43**	**74**
	b.u	**43**	**74**
KTW2:R1	t.w	**26**	**52**
	b.u	**26**	**51**
KTW2:R2	t.w	**29**	**54**
	b.u	**29**	**54**
KTW3:R1	t.w	**25**	**51**
	b.u	**25**	**51**
KTW3:R2	t.w	**25**	**54**
	b.u	**25**	**54**
KTW4:R1	t.w.	**40**	**58**
	b.u	**40**	**58**
KTW4:R2	t.w.	**41**	**60**
	b.u.	**41**	**59**
KTW5:R1	t.w.	**42**	**66**
	b.u.	**42**	**67**
KTW5:R2	t.w	**42**	**69**
	b.u	**42**	**70**

t.w.: titanium white; b.u.: Burnt umber

APPENDIX X- STANDARD TEST METHOD FOR ACID NUMBER (EMPIRICAL) OF SYNTHETIC AND NATURAL WAXES

The norm D1386[34], published by the American Society of the International Association for Testing and Materials (ASTM), was followed for this test.

Scope:

- This test method covers the determination of the acid number of synthetic waxes and natural waxes. The number is obtained by direct titration of the material and indicates the amount of free acid resent.
- This test method, using an ethanol-xylene mixture, is applicable to all natural waxes, including carnauba. The test method is also applicable to oxidized microcrystalline waxes, oxidized Fischer-Tropsch, oxidized polyethylene, and montan esters.
- The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

Terminology

Acid number or acid value – The number of milligrams of postassium hydroxide necessary to neutralize 1 g of the sample

Significance and use

This test method is used to determine the property of acid functionality. Acid functionality determines the utility of the wax as well as being a significant Quality Control test.

Reagents and materials

- ***Purity of Reagents –*** Reagent-grade chemicals or equivalent, as specified in Practice E200, shall be usedin all tests.
- ***Ethanolic Potassium Hydroxide, Standard Solution –*** Dissolve approximately 5.6 g ofpotassium hydroxide in 5.6 g pf distilled water. Dilute with USSD3A denatured ethanol or 96%ethanol to 1000 mL. Standarize with 0.1 *N* hydrochloric acid.
- ***Phenolphthalein Indcator Solution (10g/litre) –*** Dissolve 1 g of phenolphthalein in 100 mL of USSD3A, denatured ethanol or 95% ethanol.
- ***Xylene***

Procedure

1. Transfer1 to 2 g of the sample, weighed to the nearest 0.001 g to a 250-mL acid-value flask. Add 40 mL of xylene. Heat on a hot plate or water bath to put the sample into solution. Occasional swirling may be necessary.
2. Add 3 to 5 drops of phenolphthalein indicator solution and titrate the hot solution to the first persistent pink colour. The end point is taken when the pink colour remains for at least 10 s. Swirl the flask vigorously during the titration. If precipitation of waxes occurs during titration, reheat the sample. The titration should be carried out as quickly as possible. Record the number of millilitres of standard alkali solution used. Warning - to avoid saponification, do not reheat the solution during this operation.
3. Determine the blank titration value by repeating the procedure of and without the addition of sample material.
4. Run a total of three titrations of sample being tested and one blank

[34] The edition used was approved and published in October 2015. Originally approved in 1955 as D1386-55T. Last previous approved in 2010 as D1386.

Calculation

Calculate the acid number as follows: **Acid number = (*A* – *B*) x *N* x (56.1)/*C***

***A* =** millilitres of alkali solution required for titration of the sample,
***B* =** millilitres of alkali solution required for titration of the blank sample,
***N* =** normality of the alkali solution, and
***C* =** grams of sample used.