A LOOK INTO SOME FACTORS INFLUENCING THE FILM FORMING PROPERTIES OF OIL PAINT FILMS IN COPPER PAINTINGS AND THE EFFECTS OF ENVIRONMENT IN THEIR STRUCTURAL BEHAVIOUR

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Introduction

The treatment of paintings on metal plates represents some of the most challenging situations in easel paintings conservation. Differences induced in the film forming and aging properties of the oil paint film by the presence of a metal support require a comprehensive conservation approach that considers not only the characteristics of the paint film and the specific nature of the metal plate but also the interface formed in-between them. Despite having different metal plates used as painting support throughout history (i.e. copper, lead-tin, silvered copper plates, etc.) (Wadum 1998, 1999; Komanecky 1998; Horovitz 2013; Cross et al. 2013) this paper will briefly address some issues dealing specifically with paintings on copper plate.

Recent studies have pointed out some of the aspects that might have contributed to the pristine condition that many copper paintings of the collections worldwide present nowadays (Horovitz 1998; Pavlopoulou et al. 2006). The absence of a size layer, the non hygroscopic support and the chemistry involved in the reaction of the free fatty acids of the oil with the metal cations from the plate are some of the main issues addressed in literature to explain the exceptional condition usually presented by paintings on metal plate in comparison to the degradation experienced by canvas and wood panel paintings of similar age. However, some times severe damage can be found in form of disruptions, cracking or flaking. Many damages are simply mechanical in nature such as bending the copper plate etc., but the study of other structural aspects can add some understanding to the failure mechanisms observed in copper paintings.

The drying and film forming process of oils on copper plate

From ancient treatises to more recent scientific texts, literature refers to the multiplicity of materials and techniques used throughout history to produce flat and stable paintings on metal plate. The predominance of oil grounds in the production of copper paintings has been extensively reported. Paintings on copper plate produced from the 16th century onwards usually present thin oil grounds made of lead white and earth
ing continuous paint hydrolysis to form increased amounts of metal carboxylates (Erhardt et al. 1990), which has a direct relationship to the mechanical properties of oil paint films (Mecklenburg et al. 2005; Erhardt et al. 2005). Driers containing metal ions can be added to paints in a ratio of 0.005 to 0.2 per cent metal based on the solid binder (oil). Some metal ions can also be extracted by the oil from the bound pigment which can have significant implications in the mechanical and dimensional properties of the resulting paint film (Mecklenburg et al. 2013; Fuster et al. 2016 a, b).

A third source of metal ions can be obtained directly from the metal substrates themselves. Research has shown that metals such as copper interact with the free fatty acids of the oil paint film. The extent of copper the free fatty acids of the drying oil are putting into solution depends on the type and refining of the oil. In 1996 Horovitz observed the reactions of different oils (linseed, poppy and walnut oil) after being in contact with a copper plate for ten days (Horovitz 1996). Broers ran a similar experiment with different combinations of cold pressed linseed oil applied under copper plates subjected to different surface treatments including artificial ageing (Broers 2003). Similarly, in figures 1a and 1b it is possible to observe how the fatty acids in the oil seem to be putting some of the copper into solution. Over time, the copper ions are reacting with the oil to form the green compound (where carboxylates have usually been identified) and that can be observed as a green transparent layer as reported by several authors (Horovitz 1996; Gunn 2002; Broers 2003; Gates 2006; Pavlopoulou et al. 2006). In about eighteen hours a green tint was observed (Figure 1a).

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There are several circumstances where metal ions are present in paintings. Some authors suggest that large amounts of metal ions from pigments or a drier can react with the fatty acids that are produced dur-

Fig. 1 (a, b). Copper ions from a copper plate reacting with different drying oils

pigments, generally umbers. Red earths, and carbon black and even calcium carbonate have also been found in the literature (Horovitz 1986, 1999; Broers 2003). In some occasions an extra oil priming was applied to the metal plate in addition to the pigmented oil ground and in other cases lead white in linseed oil was applied to both faces of the metal plate to prevent corrosion (Pavlopoulou et al. 2006).

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strates in the drying of linseed oil. As it can be observed, the maximum oxygen uptake for linseed oil applied on a lead plate takes place eight times faster than when that same oil is applied on an inert substrate such as polyester that does not provide any metal ion. Copper and brass (a copper and zinc alloy) also accelerate four times the drying of the oil film. Hard oil films were formed on all the metal plates whereas the pure oil on the inert substrate remained tacky.

b) The adhesion of the paint layers to the underlying substrate: A faster drying of the oil paint film on a copper substrate is not necessarily directly related to improved mechanical properties. Nevertheless in the case of paintings on copper, the drying and film forming properties of the oil paint film can be explained as a function of the ion migration mechanism.

Mecklenburg et al. have studied the influence of pigments, metal ions and the mixing of paints and ion migration mechanisms on the stability of oil paints and suggested that metal ions are not only capable of migrating throughout a given paint layer but also sufficiently mobile to migrate from one paint layer to an adjacent one in a painting enhancing (i.e. lead ions) or degrading (i.e. zinc ions) the adjacent paint layers. Those paintings that do not have the benefit of metal ions contributing to the durability of adjacent layers (i.e. earth grounds) are typically easily damaged by high environmental moisture levels and cleaning solvents (Mecklenburg et al. 2013; Tumosa et al. 2013). This suggest that adhesion in-between the metal support and the paint layers is enhanced when lead and copper ions are involved. Oil paint films on lead and copper plates are therefore expected to present good anchorage to the substrate.

On the contrary, adhesion problems can be expected in some specific alloys (i.e. brass) and coated plates (i.e. tinned plates). Metal plates were commonly coated with zinc, lead, tin and also lead-tin alloys in the past (Horovitz 1996). For example, tin-plated iron supports are said to be susceptible to high humidity, oxygen and pollutants (Cross et al. 2013). Some reference to the presence of adhesion failure in tinned plates has also been reported in literature. Previous research has shown that the presence of tin accelerates the oxygen uptake and drying of a lead-tin yellow in cold pressed linseed oil paint film in a similar way a siccative such as litharge would do (Figure 3a). Figures 3b and 3c also show that the paint film formed gets stiff and brittle in quite a relative short period of time, being prone to premature cracking (Mecklenburg et al. 2008). Having a tinned support contributing in such a way to the durability of the upper paint layers could explain the adhesive failure in form of recurring delamination, cleavage and cracking that sometimes is observed in paintings on tinned plates.

c) The durability of the paint film: that the underlying substrate is contributing (or not) to the upper layers has also an influence in how the paint layers will resist to environmental moisture and cleaning solvents. This can have dramatic consequences in the dark areas where earth pigments are predominant, since the hydrolysis they experience in the early stages of their drying process not only causes the degradation of the mechanical properties but increases their vulnerability to atmospheric moisture and cleaning solvents.
the 1980's demonstrated that in a wide range of relative humidity conditions (20-70 per cent RH), the primary force in canvas paintings is in the size layer given the stiffness (high elastic modulus) and strength development of animal glues over most of the RH range (Mecklenburg 1982, 2007; Hedley 1988). In such circumstances, the glue size provides support to the entire painted structure. As a result of stretching and as a consequence of environmental fluctuations different forces act in each layer of canvas paintings. This does not happen in copper paintings (where – in structural terms – the copper constitutes the support), which has relevant implications in conservation terms (Mecklenburg 1982).

b) The mechanical and dimensional properties of the resulting paint film and its response to environmental fluctuations.

b.1. The structural behaviour of copper paintings and the effects of Relative Humidity (RH)

Copper plates are not hygroscopic and therefore they are not expected to experience any change in dimensions due to RH fluctuations. Also, being the painted structure a restrained system, the absence of a glue size prevents the painted structure from most of the humidity-related damage typically found in canvas paintings since the animal glue is the material that shrinks the most in dessicated conditions (developing very high stresses) and that loses all its adhesive an cohesive properties with RH levels above 80 per cent, (Mecklenburg 1988, 2007; Mecklenburg et al. 1991; Roche 2003, 2005). Moreover, the lack of shrinkage in copper substrates in high RH environments prevents the paint layers from experiencing compression, thus damage in the form of tenting is not expected to be found in paintings on copper plate (Andersen et al. 2016).

Nevertheless, that copper plates are not moisture-sensitive and have no glue sizing does not mean that they cannot experience any damage when subjected to different levels of relative humidity. Several authors have referred to the presence of microfissures in the dark earth colors (Horovitz 1996). Despite that the presence of lead white in the ground and a metal substrate should be expected to enhance the durability of an earth oil ground to some extent, in some severely damaged studio cases, most of paint disruption usually took place in the darker areas of the paint film. Even having a metal plate contributing ions to upper layers

Aspects influencing the structural behaviour of paintings on copper plate

There are several aspect that help explain the type of damage that can be found in paintings on copper plate.

a) Alternative forces

In the traditional canvas painting where glue size is present, that size actually acts as a significant support to the paintings design layer. The research carried out in
the fact of darker areas being more prone to disruption that the lighter ones could be the consequence of several encountered circumstances.

First, copper plates can be severely damaged in adverse environments since high relative humidity could promote the corrosion as well as enhance other specific chemical processes in the mid-to-long term to the metal plate as it has been reported elsewhere (Horovitz 1986; Broers 2003; Pavlapoulou et al. 2006). Even if the possibility of being subjected to the extreme conditions that promote the corrosion of copper supports could seem rare in those artworks preserved indoors, condensation as well as moderate RH fluctuations could be a reason for paint disruption.

Second, and as mentioned in the precedent section, the understanding of pigments’ role in oil paint film forming process is crucial to understand the type and extent of damage found in paintings. In copper paintings this becomes especially relevant since earth pigments are a typical component in oil grounds, together with lead white and carbon black (Horovitz 1986). Research has shown that the clay content induces severe swelling in earth based paint films making them become extremely weak and dimensionally
responsive to moisture and therefore vulnerable to humid environments as well as to solvent action (Figures 4 a, b). Such dramatic swelling also cause the paint to shrink and crack with desiccation as the swelling causes plastic deformation. The fact of being slow driers is also responsible for a more significant dimensional response to changing RH in comparison to stiffer paints such as lead whites, that have shown to be less dimensionally responsive to RH (regardless the drying oil used in the oil paint film formulation) (Figure 4c).

The hygroscopicity of earth pigments could also contribute to retain moisture in the painted structure promoting other chemical reactions that, together with the hydrolysis experienced by earth oil paint films in the early stages of their drying process, could contribute to paint softening and plasticity (Figure 4d).

Finally, cracking and flaking has been traditionally associated to the movement of hygroscopic supports such as wood or fabrics. Therefore no RH-induced crack should be expected in those paintings where the substrate is non-responsive to RH such as copper plates. However there has been significant misunderstanding in the way paint cracking takes place. The study of the dimensional and mechanical properties of single painting materials and their response to environmental fluctuations provides a deeper understanding on the behaviour of more complex multiple-layered structures. On the one hand, different materials swell and shrink in a different magnitude depending on the material for a same given RH range. On the other hand, not being copper responsive to RH, any hygroscopic material applied to it (i.e. priming, paint layer, etc.) will experience significant internal stresses if environmental oscillations take place, since the metal support will be acting as a restraint to the upper layers when these attempt to shrink upon dessication (Mecklenburg 1982; Hedley 1988). The inability of the design and paint layers to contract when the ambient is dessicated will turn into significant stresses that will be dependent of the magnitude of the RH changes, the coefficient of the expansion of the material (and therefore the materials’ attempt to contract), as well as on the elastic modulus of the materials. It is because the support does not move that the upper layers will fail (crack) if 0.5 per cent strain is exceeded.

b.2. The structural behaviour of copper paintings and the effects of temperature
As observed in panel paintings, paintings on copper are not prone to temperature cracking. Copper has a very low thermal coefficient (0.000017) which means that it does not experience significant changes in dimensions as a function of changes in temperature. The average thermal coefficient of expansion for oil paint films is five times higher (0.000083), but these are still very small numbers especially when compared to moisture coefficients. Figure 5a represents the free swelling strains for pines as a function of temperature and figure 5b represents the free swelling strains of different oil paint films in linseed oil naturally aged for 22 years. As it can be seen, all of the oil paints follow a similar trend which is an indication of the binding medium governing the behaviour of these oil paint films in a broad range of temperatures regardless the pigment used in their production. Considering copper’s thermal coefficient of expansion and the information showed in figure 5b, a drop of temperature from room conditions (22°C) to 5°C would make copper shrink 0.05 per cent, a negligible value compared to the dimensional changes induced by moderate RH in hygroscopic painting materials. The only possibility for temperature having a significant effect in the cracking of oil paints is when it drops below oils’ glass transition temperature, since the paint film will become extremely brittle and will crack irreversibly.

Conclusions

In the last twenty years there has been a significant and gradual increase in the information available around the production, degradation and conservation of paintings executed on metal plate. Whereas art technological studies have showed the historical, economical, aesthetic and technical reasons that brought artists to evolve to what was thought to be a more stable and gentle support, conservation science is providing a deeper understanding of the chemistry and mechanics of painting materials. Even if artists were probably not aware about the changes that the interaction between the painting materials and the novel metal substrate would take place in the course of time in their artworks, the stiffness, portability, easy preparation absence of cracks or tears and stability against biodeterioration in combination with a more refined, smooth, bright and precious appearance enticed artists into experiencing with metal plates to produce new paint effects.

In this paper some factors influencing the film forming properties and behaviour of oil paint films in copper paintings were discussed. This paper built up on previous research and focused on the behaviour of the painted layered structure and the effects of relative humidity and temperature in its long term performance. Given the structural and chemical complexity of paintings on metal plate, the understanding of the role of metal supports and their interaction with the upper paint layers in the mechanical and dimensional stability of the painted structure is crucial for the development of appropriate conservation strategies and the selection of the materials and methods that guarantee their structural stability in time.

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and other metal plates
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Cross section of a painting on copper from the collection of the Musée des Beaux-Arts de Liège (BAL).
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