DELAMINATION OF OIL PAINT FROM ACRYLIC GROUNDS

by

Yonah Maor

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Abstract

Many modern artists paint in oil or oil-modified alkyd paints over acrylic grounds. In some cases the oil-based paints do not remain adhered to the ground. In a set of composite samples of oil or alkyd paints, over acrylic grounds, naturally aged for nine years, some of the samples delaminated. Samples were analyzed with X-ray fluorescence (XRF), inductively coupled plasma (ICP), Fourier transform infrared - attenuated total reflectance (FTIR-ATR), scanning electron microscopy (SEM), pyrolysis gas-chromatography mass-spectrometry (PY-GC/MS), laser desorption/ionization mass-spectrometry (LDI-MS), atomic force microscopy (AFM) and other methods, in order to find what the delaminating ones have in common. In addition, two examples of severely delaminating paintings were examined, to confirm the results from the laboratory-prepared samples. Results indicate the main cause of delamination is metal soaps in the oil paint and particularly zinc soaps. There is some evidence that metal soaps were more concentrated at the interface between the layers and this disrupted the adhesion. The ground is a minor consideration as well, rougher grounds providing better adhesion than smooth ones.

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Chapter 1

Introduction

Painting in oil or alkyd over acrylic is usually considered a safe practice, despite the fact that there is no chemical bond between the layers. In some cases, however, there is severe delamination within just a few months or a few years of painting a work of art. For example, Marc Hanson found that four years after painting the sketch in figure 1, the oil paint layer could be easily scratched off. He reports “it is an oil, painted alla prima with no medium on Frederix-Red Lion "Polyflax", and has a factory Acrylic primer as ground. I'll add that it isn't the primer that isn't adhering to the poly, it's the oil that isn't adhering to the Acrylic Primer.” (WetCanvas.com post). This project aims to investigate the cause behind such delamination.

Figure 1: Left: Marc Hanson, sketch, oil on artificial canvas primed with acrylic, 8"x12", c. 2000. Right: Detail of delaminated area. Images from 2004 (WetCanvas.com post).

Unfortunately, it was not possible to examine Marc Hanson's painting; however, a couple of other artists with similar problems, were happy to have their work analyzed. Figure 2 is an example of a painting completely destroyed by delamination. The first image was taken shortly after the painting was completed; the second is a detail showing its current condition, where most of the blue paint has flaked off and some of the green

paint is missing as well. The second painting analyzed is referred to as the ‘brown/grey painting’ and a section of it is shown in figure 3. While the delaminating paint in that work is holding together and not crumbling as in the first two examples, it is not adhered at all to the white layer beneath it, and large pieces detach at the slightest mechanical stress.

Figure 2: Michael Skalka, ‘Colorado Lagoon’, Long Beach, CA, Oil and alkyd on canvas, 12”x16”, 2006. Photo taken immediately after painting. Detail of delamination with ground showing, taken Nov. 2007

Figure 3: A section of the ‘brown/grey painting’ with large paint flake on top.

This research will make use of samples prepared in 1999 by Marion Mecklenburg at the Smithsonian Institution. He constructed the samples after an artist sent him a painting where the oil paint was only resting on the ground and not adhered at all. Since no problems appeared once the 1999 samples had been dry for some time, the samples were put aside for seven years until Mecklenburg noticed that many of the samples were delaminating.

To understand the problem, it is best to begin with understanding the purpose and history of painting over a ground layer. Ground is a necessary preparation layer, between the support and the paint. The ground serves a number of functions: it absorbs excess paint media and provides a surface to which the paint can adhere. Grounds can be used to create different textures for various aesthetic purposes. When used under oil paintings, the color of the ground becomes important as well, since the oil paints become transparent with age and the ground shows through.

Early panel paintings were prepared with gesso, CaSO_4 or CaCO_3 bound in animal glue¹. When canvas became the more popular support, artists found the gesso too brittle. From the 16th century, oil or oil and glue emulsions became the favorite form of preparation for not only canvas but panel paintings as well.

The traditional priming for the past few centuries has been lead white oil ground over animal glue sized linen. Since the 1950s this practice has mostly been abandoned in favor of titanium white in acrylic or oil-modified alkyd grounds. The acrylic grounds are used for both oil and acrylic paints and can be applied without sizing (Perry and Hackney 1992). The modern, synthetic media are preferred over the oil because they are cheaper and dry much faster. The lead white pigment has fallen from use because of its toxicity. Many oil painters today paint on canvases pre-primed with acrylic grounds.

There is no chemical reaction between the acrylic and oil media. The bond between an acrylic ground and an oil paint is of a mechanical nature: the oil paint enters crevices in the rough acrylic ground and interlocks as it dries. A manufacturer of acrylic grounds, Golden Artist Colors, reports that they have tested their grounds with oil paints, and no

¹ Strictly speaking, gesso is the Italian term for gypsum, so it should only be applied to the calcium sulfate ground

adhesion problems were detected; however, Golden conducted the tests on samples that were no more than a few months old (Berthel 2007) and the delamination may not start until the paint has cured for several years.

Through discussion with conservators, conservation scientists, paint manufacturers and artists, several possible reasons for delamination were suggested. A common suggestion was that the artists had used a prepared canvas that had been in inappropriate storage for some time and was not clean. Dirt, dust and grease can prevent the paint from completely wetting the ground and this lowers the adhesion (Pavlopoulou and Watkinson 2006). This option, however, is certainly not relevant for the 1999 samples. These samples were prepared identically and stored in a controlled environment, narrowing down the list of possible culprits.

First, the option that poor quality materials were at fault, while clearly not the only factor (based on a cursory examination of the 1999 samples), was found to have some merit. Smith (2006) suggested that additives, such as surfactants, migrating to the surface of the acrylic ground, create a “release layer”. Interestingly, when Bronwyn Ormsby at Tate examined the surfactant build-up on acrylic grounds she found that on the Fredrix canvas, the same company that produced the canvas in Marc Hanson’s aforementioned painting, there were no surfactants on the surface (Ormsby 2007). Surfactant build-up was tested here.

Based on the initial survey of the 1999 samples, the main theory was that zinc, or possibly zinc and lead, in the oil paint was the most important factor in causing delamination. A great part of the following work, deals with testing and explaining this possibility.

Chapter 2

Literature Review

Since very little research has been published on delamination of paint and ground or on compatibility between the various paint media available today, this literature review starts by looking at each component separately. By studying the composition of acrylics, oils and alkyds, how they dry and some of their physical characteristics, a better understanding of the possible reasons for delamination is obtained. At the end of this section there is a review of literature on adhesion, both in the conservation field and in the coating industry.

2.1 Acrylics

The term acrylic ground, in this paper, refers to aqueous acrylic dispersions. This distinction is important since the acrylic could also be used in a solution with an organic solvent. The acrylic polymer is usually a copolymer of either ethyl acrylate (EA)/methyl methacrylate (MMA), or n-butyl acrylate (BA)/methyl methacrylate (see monomers in figure 4). Copolymers for paint can also be formed with a vinyl type molecule (containing C=C double bond), such as vinyl acetate or styrene. These are more common in cheaper house-hold paints (Learner, 2004). Moreover, previous research (Kaukovalta 2002) showed that many products advertised as acrylic gessoes are not actually acrylic-based. Acrylic dispersions are often (incorrectly) called acrylic emulsions. They are, in fact, a dispersion of solid, amorphous, polymer suspended in water with many additives, including pigments, surfactants, buffers and preservatives.

Figure 4: Likely monomers in acrylic copolymer dispersions

The acrylic particles in the dispersion are typically spherically shaped, ranging in size from 0.01 to 1.0 μ . Each sphere contains many molecules. The polymer molecules can be very large; even a molecular weight of over 1,000,000 is not unusual. This is possible, because the liquid phase of the dispersion (water) gives the paint or ground its viscosity, independently of the particles in it (Learner 2004).

In the initial phase of drying, water evaporates from the dispersion, so that the particles are more closely packed. This phase depends on the vapor pressure and diffusion of the water. In the second phase, the round polymer particles deform, changing to polyhedra, and coalescing to a continuous film. There are several possible theories about the particulars of this process. For instance, do the particles begin to deform while there is still some water present between them, or only once they are actually in contact with each other? One suggested mechanism relies on surface tension considerations, forcing the particles together (this would occur after complete evaporation). Other mechanism options are capillary forces and mutual diffusion which would occur while there is still water present. It is most probable that all three mechanisms take place together (Learner 2004). A summary of the process is shown in figure 5.

Figure 5: Film formation process in an acrylic dispersion (Learner 2004).

Many factors affect the film formation of dispersion. Small particles, properly dispersed, will pack more tightly before the film coalesces, thus producing a better film. Lower temperature, high relative humidity (RH) and low substrate porosity can increase the time it takes the water to evaporate. Slow evaporation produces a more coherent film. Of course the temperature can't be too low; if it is below the acrylic's T_g , the particles will be glassy and will not deform or coalesce.

Once a film is formed, it is insoluble in water. In fact, it is very difficult, or even impossible, to dissolve dry acrylic films even in strong organic solutions. This could be

due to some cross-linking that occurs (Learner, 2004). Certain inorganic components (pigments or extenders) can catalyze photo-oxidative cross linking reactions in acrylic paints (Chiantore, Scalarone and Learner 2003; Scalarone et al. 2005). Some evidence of cross-linking was found in unpigmented acrylic films as well (Smith 2007). Acrylics are swollen by organic solvents and even water can cause some leaching (Learner 2004). This fact poses many concerns for conservators interested in cleaning acrylic paintings (Ormsby et al. 2007). It could also be important when considering an oil layer applied over an acrylic.

BA-MMA paints tend to cross-link more than the older, EA-MMA films because oxidation of butyl groups forms hydroperoxides, which immediately photolyse to alkoxy radicals. The radicals then initiate cross-linking reactions. Cross-linking is likely the cause of decreased solubility in BA-MMA films; however, in EA-MMA films, photo oxidation can cause more chain scission than cross-linking. In those cases, a decrease in solubility could be due to chain entanglements (Scalarone et al. 2005; Chiantore et al. 2000; Learner et al. 2002)

Tumosa and Mecklenburg (2003) studied the weight change of acrylic dispersions over four years. They found that while the bulk of the weight loss occurred during the first four months, the weight was still decreasing slowly at four years. The loss of volatiles was different in paints from various manufacturers. They concluded that painting an oil layer over an acrylic ground could be problematical, since the water and antioxidants being slowly released from the acrylic layer could alter the drying process of the oil. Surfactants could also interfere with adhesion of the paint layer and other compounds, such as glycols, could diffuse into the oil layer, changing its mechanical properties.

Acrylics remain fairly flexible as they age, unlike oil paints. In an artificial aging experiment on Rophlex AC-2235, a BA-MMA copolymer dispersion used as the base for many artist paints, the glass transition temperature (T_g) of the films was measured (Smith 2007). The T_g represents the transition of a polymeric material from a rubbery state to a glassy state. Since acrylic paints and grounds dry under ambient conditions, their T_g has to be around room temperature. The results of the experiment showed the T_g remained around 15 °C throughout the aging regime, maintaining its flexibility.

The surfactants are an important additive, as they hold the insoluble acrylic micelles suspended in water. Surfactants have a hydrophobic section, usually a long hydro-carbon chain, and a hydrophilic end that can attach to the water. Typically, both anionic and nonionic surfactants are used (cationic surfactants may interfere with the activity of the polymerization initiators). Nonionic surfactants are often alkyl phenol ethoxylates, and examples of anionic surfactants are sodium lauryl sulfate or dodecyl-benzene sulfonate. Usually surfactants are added at 2%-6% by weight (Learner 2004).

Another common additive is the polyethylene oxide (PEO) family, also called polyethylene glycols (PEGs). These non-ionic surfactants serve as wetting and dispersing agents and stabilize the polymer in the aqueous phase. The PEOs remain relatively mobile, even once the acrylic has dried and can migrate to the air interface or to a porous substrate. When the surfactants accumulate on the surface, they may affect the adhesion of subsequent layers. This process may also affect dirt pick-up, permeability, gloss and the mechanical properties of the acrylic film. The PEOs tend to form round shapes of crystal-like material, usually centered on dust particles (Digney-Peer et al. 2004).

PEOs can be identified with Fourier transfer infra-red (FTIR), where they have characteristic peaks at 2889, 1343, 1110 and 964 cm^{-1} . They have also been identified with matrix assisted laser desorption/ionization – mass spectrometry (MALDI-MS); in this technique they are characterized by mass increments of 44 amu which are due to $\text{C}_2\text{H}_4\text{O}$ groups (Digney-Peer et al. 2004).

In previous research, more PEOs were found to accumulate on the surface when aged in the dark. This is probably because UV light breaks the ether bond of the PEOs. In the bulk of the film, the acrylic matrix or the pigment protect the PEOs from UV light, and these continued to migrate to the surface even after a year of natural aging. In Smith's (2007) research of Rophlex AC-2235, the surfactants exuded to the surface did not break down with exposure to UV light, suggesting that pigments or other additives catalyze the degradation and volatilization of the surfactants in acrylic paints. Learner et al. (2002) did find that while the surfactant IR peaks were reduced with exposure to light in all the paints they tested, it was difficult to observe the change in cadmium red and titanium white paints, because of pigments or extenders that absorbed in the same region.

More surfactants were found on the surface of samples on non-porous substrates. Presumably, the absorbance of water into the porous substrates facilitates migration of

surfactants in that direction instead of up to the surface. Acrylics from certain manufacturers showed significant build-up of PEOs on the surface, while others did not. This could be due to variation in type or quantity of the surfactant, or other variations in the acrylics formulation, which influence surfactant migration. (Digney-Peer et al. 2004 and Boon et al. 2007).

Scalarone et al. (2005) found no difference in surfactant migration on EA-MMA based paints and BA-MMA paints; however, they were not attempting to quantify the surfactant build-up. Ormsby (2007) found that more surfactants build up faster on EA/MMA acrylic paints than on BA/MMA paints.

In the delaminating paintings, part of the problem could be related to dirt or grease that had built up on the ground surface before the paint was applied. Acrylic films are porous which allows for the passage of moisture. This can cause environmental pollution and dirt to be trapped in the paint. Dirt pick-up could be increased by a number of factors. If the paint is particularly soft, because of the high Tg of low MW components for example, the surface could remain tacky. Since acrylics are non-conductors, films could accumulate static charge, which would then attract dirt. In addition, surfactants on the acrylic surface could attach and imbed dirt particles (Jablonski et al. 2003).

2.2 Oils

Oil paints are based on drying oils, which are a mixture of fatty acids and dry by an oxidation reaction. Though the oxidation slows down once the film has hardened, it does continue, causing the film to become brittle over time; this increases the likelihood of cracking (Jones, Mao, Ziemer and Xiao 2005). The drying process of oils is very complex, and even after centuries of study, some aspects are still not understood. Wexler (1964) wrote an extensive and detailed review of the polymerization of drying oils; however, some new information has been discovered since then. Van de Weed et al. (2005) wrote an excellent summary of current understanding of this process. The following description is based on their paper, as is the reaction scheme in figure 6.

Figure 6: Simplified model of the early reactions taking place during the drying of oil. Taken from Van de Weerd et al. (2005).

The drying process begins when a hydrogen atom is eliminated from an unsaturated fatty acid, forming a free radical. Free radicals are only formed when the hydrogen is eliminated from specific locations (a methylene group in α -position to a double bond or a methylene group between two unsaturations), which allow the molecule to be stabilized by resonance. Drying oils also contain some anti-oxidants, which react with the radicals, essentially deactivating each other. This causes an induction time, before the oil paints begin to dry. Once all the anti-oxidants are used up, any new radicals formed can start the drying process.

Theoretically a radical can undergo an addition reaction with a double bond on an adjacent fatty acid or even on the same fatty acid. This reaction is slow, and usually only occurs when the oil is heated in the absence of oxygen, as in heat-bodying of oil. In a normal drying process, the presence of oxygen causes the formation of peroxides. Then a hydrogen atom can be added, forming a hydro-peroxide. Oxygen atoms are actually added and eliminated several times. In the process, most of the molecules convert from the *cis* formation to the more energetically favorable *trans* double bond.

The hydro-peroxides are not very stable and eventually break into peroxy ($\text{ROO}\cdot$) and alkoxy ($\text{RO}\cdot$) radicals. These radicals can then cause polymerization, termination or degradation reactions. In a polymerization reaction, the radical attacks the double bond in a fatty acid. In a termination reaction, two radicals condense, creating a dimerization of two fatty acids. In a degradation reaction, the radical breaks apart the fatty acid on which it sat, forming smaller alcohols and aldehydes. The smaller molecules formed by degradation of fatty-acid radicals can act as plasticizers. Eventually, they oxidize and then evaporate, contributing to the hardening of the paint.

This description skipped many factors, including the role of catalysts in various stages and the contribution of photo-oxidation to the formation of hydro-peroxides. All the reactions that cause the paint to dry continue long after the paint film has hardened. The polymerization reaction takes the form of cross-linking between polymer chains. Unsaturated fatty acids undergo oxidation and glyceride bonds can be severed by hydrolysis (Erhardt et al. 2005). These processes can slowly begin to degrade the paint. The work of van den Berg et al. (2001) indicates that hydrolysis continues even decades after the paints dried initially.

These reactions cause oil paints to become more brittle as they dry, while acrylics, as mentioned, do not change significantly. Mecklenburg has done tensile tests on the paints and grounds used in the samples examined in this project. Figure 7 shows that after just seven years of natural aging, both the titanium white and the lead white oil paints are more stiff and brittle than the acrylic grounds. Ground A is weak and would also be expected to exhibit brittle behaviour (Mecklenburg and Fuster-Lopez 2008). If the acrylics bend while the oil on top does not, the likelihood of delamination increases.

Figure 7: Seven year old paints and grounds (Mecklenburg and Fuster-Lopez 2008).

Photooxidation and the resultant decomposition products can cause changes in the density of the paint film as well as shrinkage. This can lead to cracking or chalking of the paint film. If a painting is exposed to high RH, water will be absorbed into the painting, increasing hydrolysis (Pavlopoulou and Watkinson 2006). Water may also accumulate between paint layers, or at the interface with the substrate, and destroy the adhesion, either by increased hydrolysis or by mechanical action (van den Berg 2002).

Since all the 1999 samples of oil paint over acrylic have the same basic degradation processes occurring, but only certain paints are delaminating, it seemed likely that the problem had to do with pigmentation or other additives. One possibility is that all the paints that failed to adhere contain zinc (Mecklenburg 2006) and this theory was tested here. Zinc inhibits the initial drying of oil paints and allows oxygen to enter the lower levels of the paint layer, thus eventually creating a paint layer that is drier throughout (McGlinchey 1990; Rhodes and Mathes 1926). In McGlinchey's research, paint films with different white pigments were compared, and it was discovered that the zinc-white had the weakest secondary transition. This concept is described next.

Materials are often characterized by their melting point or T_g and it is known that these temperatures relate to the material's mechanical properties. Polymers are expected to be brittle below their T_g . It is not always recognized that most polymers have additional transitions above and below T_g . These transitions are seen in the results of all methods

used to examine a material's behavior over a range of temperatures and frequencies, whether it is an electrical, electromagnetic or dynamic-mechanical method. Material scientists have researched the transitions of many polymers and the general principal that arises is that the T_g represents the motion (or lack thereof) of a large number of attached atoms, usually the main polymer chains. The transitions at lower temperatures, or secondary transitions, represent motion in side groups or shorter side chains. The secondary transitions generate more free-volume in the glassy state, and represent different types of motion, giving the polymer better impact strength and higher yield stress (Boyer 1968; Chen et al. 1999; Xiao et al. 1994).

The correlation between molecular motion, mechanical properties and the secondary transition has never been investigated in oil paints; however, it is reasonable to assume that the results of such a study would be similar to the work conducted on other polymers. In other words, the lack of a secondary transition in the zinc-containing paint film could mean it is not able to relieve physical stress, which explains why zinc-white films were found to be the most brittle.

Zinc, like other heavy metals and alkaline earths, can combine with monobasic carboxylic acids to form metal soaps. Metal soaps usually contain seven to 22 carbon atoms in the carboxylic chain (see example in figure 8). Certain metal soaps are known to work as driers for oil paint (Robinet and Corbeil 2003).

Figure 8: Palmitic acid and a metal ion can form a metal soap.

Zinc, in metal dust form, is used in priming layers for the coating industry, to control corrosion. Hare (1998, 1998 and 1986) reports that topcoats based on fatty acid esters, including oils and alkyds, often lose adhesion to zinc rich primers within 18 months of application. In the industrial context, Hare suggests that the problem could be due to metal soaps attacking the metal substrate or related to weathering or to zinc salts forming at the interface between the paint and the primer. Paints based on epoxy-esters or oil

modified urethanes, which are more alkali resistant than oil paints; do not suffer from this delamination problem².

Aluminum and zinc stearates were patented and added to oil paints as dispersing agents since the 1920s. In the mid 20th century, paint manufacturers were adding 1-5 percent by weight metal soaps to the oil paints to help disperse pigments and increase the viscosity of the paint. Basic pigments, such as lead white and zinc oxide do not require such additions since the pigments form metal soaps with free carboxylic acids from the oil paint. Aluminum oxide (Al_2O_3) can also be added as a dispersant (Burnstock et al. 2007).

A study by Burnstock et al. (2007), studied these additives and others in relation to water sensitivity of modern oil paints. Crystal-like structures containing aluminum were found on the surface, and it was postulated that they are degradation of aluminum stearate, which migrated to the surface.

Robinet and Corbeil (2003) synthesized metal soaps of lead, zinc and copper (the metal ions most likely to form in paintings) with palmitic, stearic, oleic and linoleic acids. The study characterized the materials with X-ray diffraction, FTIR and Raman spectroscopy. Only copper, lead and zinc oleate and zinc linoleate crystallized to a solid form. Copper soaps were proposed to have a bridged structure, with two copper atoms connected by four carboxylic acids. This structure, which is quite different from zinc and lead soaps, is likely to indicate different behavior when formed in a paint layer. The soaps are easy to identify in FTIR by the bands attributed to COO^- asymmetric stretching, around 1550 cm^{-1} , and symmetric stretching, around 1400 cm^{-1} . The exact position of these peaks can differentiate between soaps of the different metals. The researchers examined a number of case studies and found that they could not always determine which metal soaps had formed.

Van der Weerd et al. (2005) studied how various pigments influence the drying of oil paint, by studying the FTIR spectra of naturally aged paints, including samples 60 and even 90 years old. They attributed a peak at $\sim 1707\text{ cm}^{-1}$ to carboxylic acids. It was observed that in certain paints (Naples yellow, lead white, zinc white and red lead), the carboxylic acid peak was absent (or almost absent), and instead they found peaks

² Hare mentions that if the zinc-rich layer is the top layer, it is unlikely to delaminate because, as a corrosion protection layer, it is formulated very near critical pigment volume concentration (CPVC) and so has relatively low cohesion, so the balance between adhesion and cohesion favors adhesion.

attributed to metal soaps, indicating that the carboxylic acids had undergone an additional reaction with the lead or zinc ions from those pigments.

From the zinc white paint spectra, van der Weerd and his colleagues concluded that the pigment stimulated the formation of alcohol moieties, catalyzed the hydrolysis of the glycerol esters and then zinc formed metal carboxylates with the carboxylic acids. The zinc carboxylate caused a clear and broad absorption at 1589 cm^{-1} , which indicates the presence of zinc-soaps other than stearate and palmitate (that absorb at 1540 cm^{-1}). In the lead white paint spectra, they found the metal carboxylate absorbed at $\sim 1540\text{ cm}^{-1}$. It was noted that samples with a lower lead white pigment concentration had more oxidation products.

Rhodes and Mathes (1926) aged zinc white paints, made with pigments of different quality, in pure oxygen. They found that pure zinc oxide had no effect on oxygen uptake, but lead impurities increased the rate of oxidation. They also found that soluble zinc compounds, such as zinc linoleate, which can of course form naturally in a paint film, or zinc sulfate, caused the oil paint to solidify at an early stage of aging. The resulting paint film was harder and denser. Hess (1965) recommended the use of lead-free zinc oxide to prevent the paint becoming too brittle.

When zinc white is used on its own, the paint film can be too brittle and crack easily. This is one of the reasons that the pigment never gained the same popularity as lead white and titanium white. In addition, zinc white does not have the same hiding power as the other white pigments, since it requires more oil to disperse it. The pigment does have a few distinct advantages. Paints with zinc white yellow less, probably because the pigment absorbs UV light. Zinc has mild antiseptic quality and is used to prevent fungi and bacteria growing in the paint. In addition, adding small amounts of zinc white to lead white or titanium white improves their handling and mechanical properties. Today, almost all commercially available lead white and titanium white paints include a significant amount of zinc white. Zinc is also added to some colored paints, to produce lighter hues (Sullivan 1994 and Kühn 1986).

Normally zinc white has very small, round particles; however, it can be produced in a more crystalline, needle shape. This acicular form has larger particles and forms more durable paint films. Apparently the acicular form is less reactive (Jolly 1944 and Morgans 1982).

The Federation Series on Coating Technology, states that “lead soaps add flexibility, water resistance, adhesion and crack resistance to paint films” (Madson 1967, p. 7). Morgans (1982) says the lead soaps add elasticity and protective qualities to a paint film. Lead compounds are used as driers. According to Morgans, the lead catalyzes the polymerization, making it a ‘through’ drier. The film sets faster, but the surface may remain tacky for a relatively long time.

A problem with both zinc and lead soaps is that they can migrate and form soap aggregates. The soap inclusions can grow and protrude from the surface. The lead soap inclusions appear to be a very common phenomena in 16th and 17th century painting (Noble and Boon 2007; Townsend et al. 2007). Zinc soaps have been noted in 19th century art work (Osmond et al. 2005; Van der Weerd et al. 2003). While the delaminating samples and paintings studied here are too young to have significant soap agglomerates, the fact that the soaps can migrate could be related to the delamination problem. Osmond et al. (2005) noted that zinc white paints, which have a high oil concentration, are likely to have a significant mobile fraction. It was also suggested that high RH increased the mobility of the metal soaps.

The MOLART group, headed by Boon, researched the rate of hydrolysis. They concluded that if the system was indeed held together by cross-linking (covalent bonds) as explained above, the hydrolysis they had noted should bring about complete failure of the paint layer. Since that doesn’t happen, a ‘repair mechanism’ was suggested. Lead or other metals bind the loose ends in a metal coordinated network with stronger, ionic, bonds³. Diacids allow the formation of a three dimensional structure and monocarboxylic acids are chain terminators (Boon, Hoogland and Keune 2007; van den Berg 2002). Figure 9 illustrates this coordinated system. They found some experimental evidence to support this theory (NMR, FTIR and SIMS). This could explain why researchers found paints with lead soaps were stronger (Stewart 2005). That zinc catalyses hydrolysis, as mentioned, could explain why zinc paints could become so strong that they pull apart from the ground.

³ A metal coordinated system could be termed a type of ionomer. An ionomer is a polymer that includes both covalent and ionic bonds (Tumosa et al. 2005).

Figure 9: Proposed structure of metal coordinated oil paint with intact pigment particles (Boon, Hoogland and Keune 2007).

Contrary to the MOLART findings, Mecklenburg and his colleagues (2005) found that extensive hydrolysis takes place early in the life of the oil paint (tested after 12-14 years), but that only a small percent of the free fatty acids converted to metal soaps. They found the following correlation: paints with more hydrolyzed fatty acids were more flexible. Zinc white and lead white paints had the least hydrolysis and were the stiffest paints tested. They concluded that any major changes to stiffness or strength occur early in the life of the paint (Erhardt et al. 2005).

Van den Berg et al. (2001) used a different method for determining the degree of hydrolysis. Their results showed that lead white paints showed the least hydrolysis of the paints tested; however, they could not explain this phenomenon.

One argument against the metal coordination theory is that the excess of pigment in relation to oil in a dry paint film would mean that a metal ion would not be likely to react with more than one carboxylate group. Thus, metal soaps would not be a significant

factor as bridges, or cross-links and would not make the paint stiffer or stronger (Tumosa et al. 2005).

Stewart (1950) examined photomicrographs of lead and zinc metal soaps. The lead soaps formed an interwoven pattern he described as ‘fibers in a cloth’, which could reinforce a paint film. The zinc soaps, on the other hand, formed amorphous, disassociated shapes. It is not mentioned how these samples were prepared. Jacobsen (1941) observed zinc soaps formed within a few hours, by mixing zinc oxide in linseed oil, and described the soaps as spherulites. Boon (2008) on the other hand, reported that lead soaps form nodules, while zinc soaps tend to form horizontal streaks that appear to facilitate the delamination. When zinc white and lead white were used together, Boon found lenses of zinc soaps with small lead white crystals outlining the soap masses.

Rasti and Scott (*European Polymer Journal* 1980) studied the influence of verdigris on oil paint. Verdigris is a mixture of copper acetate hydrate and basic copper acetate. When dissolved in the free fatty acids in linseed oil, it creates a green paint. They found that verdigris cuts the induction period at the beginning of the drying process. This is due to redox reaction between copper carboxylates and hydroperoxides. Verdigris also retards photo-oxidative degradation, but in the retardation process, a dark colored material is formed, causing the paint film to change color as it ages. Osawa (1988) found that it was specifically copper stearate which has a radical scavenging function and absorbs UV light, thus protecting against photo-oxidative degradation. Rasti and Scott also compared the effects of several other pigments on the photo-oxidation of oil paints (*Studies in Conservation* 1980); however, since they used an unrealistic mixture of 1% pigment in linseed oil, their results are not necessarily relevant to actual paint compositions.

Gunn et al. (2002) studied the reactions between verdigris and oleoresinous media. They found that acetate, carbonato and hydroxo ligands in the copper acetate and copper carbonate are gradually replaced by carboxylate groups. Copper carbonate was much slower to react than copper acetate, which is usually the main component in verdigris. Gunn and his colleagues conducted IR and Raman studies which suggested either a binuclear or polymeric structure for the copper carboxylate compounds. Only copper stearate is a mononuclear compound.

Pavlopoulou and Watkinson (2006) reviewed literature on adhesion between oil paint and a copper substrate. Some of the processes observed in that combination could occur

in a painting with oil and a copper pigment, over an acrylic ground. A number of researchers agree that carboxylic acids, such as those produced by paint oxidization, react with free metal ions to produce mobile species which weaken the bond of paint and metal substrate. It has been suggested that the mobile copper soaps can form aggregates; however, this has not been identified as extensively as zinc or lead soap aggregates.

2.3 Alkyds

The word ‘alkyd’ is a combination of *alcohol* and *acid*, reflecting the polyester’s basic components: a polyhydric alcohol (also called polyol) and a polybasic carboxylic acid (or poly acid). The poly acid has to have at least two acid groups ($-\text{CO}_2\text{H}$) and the polyol must include at least three hydroxy groups (to allow branching, instead of a linear polymer). If only these two components are used, the result is a very hard, cross-linked, thermosetting polymer. A manageable paint is produced by adding a monobasic fatty acid, which impedes cross-linking. In artists’ paints, the source of the monobasic fatty acid is usually a drying oil. These paints are known as ‘oil-modified alkyds’. (Learner 2004, p. 18)

The polyol is usually either glycerol (propan-1,2,3-triol), or pentaerythritol (2,2-bis(hydroxymethyl) 1,3-propanediol). The poly acid in almost all alkyd paints is phthalic anhydride, which behaves as ortho-phthalic acid (1,2-benzenedicarboxylic acid). The most common source of fatty acids for alkyd house-paints is linseed oil or soy oil. Linseed dries better than soy, but it yellows, so is not used in white paints. The amount of oil added to the alkyd determines the “oil length”. Artists’ paints and house paints are all “long oil” alkyds, i.e. they contain more than 60% oil by weight. The large oil content makes it possible to thin the paint with aliphatic mineral spirits instead of aromatic hydrocarbons. Many other additives are used in alkyds to produce paints with various properties. Figure 10 shows an idealized alkyd molecule composed of one mole phthalic anhydride, one mole glycerole and one mole linoleic acid (Schilling et al. 2004).

Figure 10: Idealized alkyd molecule.

For specific purposes, changes are sometimes made to the normal formulation described above. For example, phthalic anhydride can be replaced with isophthalic acid, a meta-isomer of phthalic acid, to improve outdoors durability. It may also be partially replaced by maleic anhydride or fumaric acid which will shorten drying time and improve hardness, color, adhesion and water resistance. Flexibility can be improved by using an aliphatic acid instead of the aromatic phthalic anhydride. For the polyol, pentaerythritol (PE) is usually preferred over glycerol, because the additional hydroxyl group improves most of the paint's properties. Glycerol is mostly found in short or medium oil alkyds, as in those cases PE would cause the paint to gel too quickly. Alkyds can also be modified with additional monomers, such as vinyl resins (including styrene, vinyl toluene, and acrylics), silicone, urethane, epoxy and chlorinated rubber (Schilling et al. 2004).

Fast drying alkyds are very popular for house-hold paints and in industrial applications; however, Winsor and Newton (W&N) are the only company manufacturing a full line of alkyd artists' paints (Griffin). Many companies do use alkyds in their oil grounds. In addition, many artists choose to paint with the cheaper house-paint (Learner 2004). Griffin alkyd paints are usually made from phthalic anhydride, pentaerythritol and soya oil (Schilling et al. 2004).

Since alkyd paints contain so much oil, the drying process is very similar to oil paints, depending on the oxidation of unsaturated fatty acids. The polyester component dries by

solvent evaporation. In the case of alkyds, much of the polyester component is already cross-linked; therefore, fewer oxidation reactions are necessary for the paint to dry and the process is much faster. A greater degree of cross-linking can make films stiff and brittle. As in oils, the degree of unsaturation in the fatty acids influences drying rates. For “long oil” alkyds, drying (to the touch-dry phase) takes longer than in “short oil” alkyds because the smaller number of aromatic groups lowers the T_g. This longer drying period allows more oxygen to enter the film, before the surface hardens, allowing cross-linking throughout the paint film. Even once the alkyd has fully dried, some carboxylic acids and hydroxyl groups always remain unattached. (Learner 2004 and Schilling et al. 2004)

Zinc soaps have been observed in alkyd paints as well. The soaps had formed protuberances on the surface, which caused the paint to appear less glossy. The problem was worst in paints with a high content of oleic acid and saturated esters (Robinet and Corbeil 2003). This is unlikely to be a big problem in artist paints, since W&N do not use zinc in any of their alkyds, but it could be an issue with other alkyds.

2.4 Adhesion

In a composite system, such as a painting, each layer has cohesive forces keeping it together and adhesive forces maintain the association between the layers. These forces must be strong enough to withstand any stress, brought about by internal or external conditions, for the system to remain whole. If the cohesion in any of the layers, or the adhesion between any two layers, is weaker than an applied force, the system will fail. Since it is a jointed system, if the force is strong enough, stress can travel throughout the system, so the weakest element of the system will be the first to fail. If the failure is in the cohesion of a single layer, the result could be cracking. If adhesion fails, the result is delamination (Hare 1986).

Internal stresses stem from changes to the different layers as they dry, such as the paint layer shrinking or becoming brittle. External stresses can be caused by swelling and shrinking due to relative humidity (RH) or temperature changes, vibration, bending or other mechanical deformations. When oil paints are applied, they have excellent adhesion and low cohesion. This is due to the paints’ low molecular weight and low surface energy

(they can easily wet almost any surface). As the paint oxidizes and cross-links, the cohesion forces grow and can become stronger than the adhesion forces. If this happens, and the system is put under stress, instead of cracking, the now strong paint layer may pull apart from the layer beneath it (Hare 1986).

Hare (1986) reports that oil-modified alkyds have reduced wetting capability when compared to oil paints. The alkyds also have stronger cohesion than young oil paints and so could be more likely to delaminate. This was a generalization about industrial coatings and is not necessarily true about the long-oil alkyds specially formulated for artists, or even for house-hold use.

As mentioned already, the adhesion between acrylic and oil layers is of a mechanical nature. It could be that the adhesion failed because one or both of the layers were too smooth and did not interlock properly. As the paints age, the oil paints become stiff while the acrylic ground and canvas remain flexible, so that even slight vibrations in the support layer could cause the delamination. The smoothness of the film could be influenced by a number of factors: the substrate, the application method, the media, the pigment volume concentration (PVC), the type of filler and other variations in the formulation. As the substrate and application methods were identical in all the 1999 samples, their influence can be ruled out; however, the differences in materials may have caused variations in texture between the various samples that are significant in explaining why certain samples are delaminating.

Instead of stating that there is no chemical bond between the acrylic and oil, it would be more accurate to state that there are no primary valency forces, such as ionic or covalent bonds, between the layers. The adhesion does rely on the much weaker secondary valency bonds, such as Van der Waals forces. While covalent bonds, which hold together the polymer network in each layer, can have binding energy up to 170 kcal/mole, Van der Waals forces are less than 10 kcal/mole (Hare 1995). Mechanical adhesion, which depends on an uneven surface and good wetting of that surface, can be very strong (Pavlopoulou and Watkinson 2006). To improve “tooth”, grounds are usually formulated very near critical pigment volume concentration (CPVC) (Hagen et al. 2007). The roughness increases the actual surface area of the substrate relative to the apparent surface area, thus improving adhesion. The level of pigmentation also affects the cohesive

strength of the layer, which can be important in maintaining a balance between adhesive and cohesive strength (Hare 1986).

In an earlier research project, performed here at Queen's (Pocobene 1984), the adhesion between different grounds and a mixture of lead carbonate and cobalt blue oil paints were compared by scratch testing. Two of the acrylic grounds showed better adhesion than traditional gessoes (oil ground with lead white and CaCO_3 in rabbit skin glue); however, a third acrylic ground showed very poor adhesion. The acrylic grounds were all based on a EA/MMA copolymer, but there may have been significant differences in the additives. Different additives can significantly alter the grounds' mechanical and physical properties (Chown et al. 2005).

In Pocobene's research, the samples were aged for 300 hours in a dry oven at 53°C ; it is unclear to what extent any artificial aging simulates natural aging. Another difference between Pocobene's research and this research is that Pocobene's samples included etched aluminum plates as a substrate, rather than Mylar[®]. This could influence the surface texture and aluminum is more likely to react with paint components than the Mylar[®]. For instance, if carboxylic acids reach the substrate, aluminum soaps could form.

In research on the mechanical interaction between paint layers and different priming media on canvas substrates, canvases primed with acrylic ground and a layer of oil paint were artificially aged (91 days at 60°C and 30 of those days included exposure to 14,000 lux) (Young et al. 2004). The mechanical characteristics of these composites were examined, but not the adhesion of the layers. No delamination was reported. Young's group did confirm that acrylic grounds are more flexible than alkyd or oil grounds, acrylics also do not become much stiffer when aged and they reduce cracking in subsequent layers.

In Young's further research (Young 2007), oil, alkyd and acrylic grounds on canvas were tested with subsequent paint layers of all three different mediums. All paint media were tested with two pigments: phthalocyanine blue and cadmium red. Samples were subjected to the same artificial aging regime mentioned above. Samples of free films were prepared as well, but those were aged under different conditions. The researchers concluded that there is no obvious incompatibility in any of the combinations tested; however, some interesting differences were noted and are discussed next.

Canvas is quite flexible and can deform significantly, causing cracking in any brittle paint layers. Cracking can promote delamination between layers. Samples of acrylic paint over acrylic ground had the lowest stiffness and did not crack under mandrel and folding tests. Those properties were maintained even after artificial aging. Oil paint over acrylic ground was not tested, but was expected to be stiff and crack more easily. Alkyd over acrylic was much stiffer than acrylic over acrylic, and became even stiffer after aging. Aged acrylic over alkyd combinations failed after mandrel tests at a 4mm diameter, while alkyd over alkyd only failed at a 1mm diameter. A number of adhesion tests were attempted, but none gave satisfactory results. The adhesion tests did indicate that “young” oil paints are more likely to delaminate from an acrylic or alkyd ground than aged ones (Young 2007).

Young’s group has attempted cross-hatch testing, butt testing and peel testing, but at this point each of the tests still presents some problems (Young 2008). A new option that may allow quantification of delamination is pulse thermography or pulsed-phased thermography (PPT) with infra-red light (Gavrilov et al. 2008; Maev et al. 2008). Applying this method in the future could improve the correlations found in this work, where samples were simply defined as delaminating or not.

2.5 Summary of Work

To find the cause of delamination, samples were examined with many analytical techniques in search of correlations with the distribution of delaminating samples. Initial examination was done with light microscopy. The surfaces of all the grounds as well as cross sections of representative samples were examined. The paint media was determined with pyrolysis gas-chromatography mass-spectrometry (PY-GC/MS). This is a well established technique in the art conservation field (Stolow and Rogers 1973; Chiavari et al. 2005) and many reference spectra were available in the literature (Learner 2001; Ploeger 2005). The identification of the media in the grounds would probably be significant in relation to surfactant build-up. The surfactants on the grounds surface were observed visually, by scanning electron microscopy (SEM), since on other acrylic samples surfactant spots were observed by this method (Ploeger 2005). Surfactants were

examined chemically with laser desorption/ionization mass-spectrometry (LDI-MS) and FTIR, following the work done by Chown et al. (2005) and Ormsby (2008).

Pigments and fillers were easily identified by x-ray fluorescence (XRF) and FTIR, using internal references; however, since some quantification was required, ten samples were also examined by inductively coupled plasma (ICP) and used to create calibration curves (Maor et al. 2008). The distribution of elements in cross-section, which is usually related to pigment distribution, was examined with SEM coupled with an energy dispersive X-ray spectrometry (EDS) detector. Since some of the metals could have formed metal soaps and migrated independently of the pigment particles, metal-soap distribution was examined with FTIR. Metal soaps have successfully been mapped in cross sections of paintings that are hundreds of years old (Noble et al. 2003); in this case some technical difficulties were encountered and more work is necessary.

In order to characterize the roughness of the grounds, both a gloss-meter and atomic force microscopy (AFM) were employed. The AFM technique had already proved useful in examining acrylic roughness (Ploeger 2005). The combined results of all these methods give a better understanding of the delamination problem, particularly in the case of oil paints over acrylic grounds.

Chapter 3

Experimental

3.1 Samples

This research made use of samples prepared in 1999 by Marion Mecklenburg at the Smithsonian Institution. The samples were combinations of eight different acrylic grounds and 20 paints, on Mylar® (polyethylene terephthalate). The paints were either oils or alkyds, from several manufacturers, and included the following pigments: verdigris, titanium white, lead white (also called flake white), raw sienna, cobalt blue, ultramarine, light red oxide, yellow ochre, terre verte, Indian red and burnt sienna. Much of the work focused on ten paints (numbers one to ten) where there were samples on all the purpose-made grounds (table 1). Grounds P1-P5 are paints or other media which were not formulated as grounds, but could be used in that capacity by artists. There are only one or two samples with each of these materials. The full list of sample composition and condition is in appendix A. The sample numbers from that list are used to identify samples throughout this paper. The samples were prepared identically and stored together so that variables related to technique or environment may be ruled out.

Table 1: Grounds and paints in the 1999 composite samples.

Paints		Grounds	
1	Custom manufactured verdigris in oil with lead drier (PbO)	A	Aaron Brothers White Gesso
2	W&N*, Titanium White in oil	B	W&N Clear Gesso Base for Acrylics
3	Grumbacher, Flake White in oil	C	W&N Acrylic Gesso Primer
4	W&N, Flake White in oil	D	Utrecht Artists' Acrylic Gesso
5	W&N, Raw Sienna in oil	E	Utrecht Professional Acrylic Gesso
6	Custom manufactured Cobalt blue in oil	F	Liquitex Acrylic Gesso
7	W&N, Titanium White in alkyd	G	Dick Blick Artists' Acrylic Gesso
8	W&N, Flake White in alkyd	H	Grumbacher Artists' Acrylic Gesso
9	Gamblin, Ultramarine blue in oil	P1	Liquitex Basic Titanium White
10	W&N, Raw Sienna in alkyd	P2	Golden Artists Acrylic Titanium white
11	W&N, Cobalt Blue in alkyd	P3	Grumbacher Academy Titanium White
12	W&N, Light Red Oxide in alkyd	P4	Dick Blick Gel Medium
13	W&N, Yellow Ochre in alkyd	P5	Grumbacher Clear Blend Acrylic Medium
14	W&N, Terre Verte in alkyd		
15	Gamblin, Indian Red in oil		
16	Gamblin, Yellow Ochre in oil		
17	Custom manufactured Burnt Sienna in oil		
18	Custom manufactured verdigris in oil		
19	Gamblin alkyd White		
20	W&N, Burnt umber in alkyd		

* W&N = Winsor Newton

The samples were prepared by drawing down parallel strips of acrylic ground on Mylar® (polyethylene terephthalate) and, approximately a month later, strips of the paint were drawn down in the other direction, in a cross-hatch pattern (figure 11a). There are therefore areas of paint alone and areas of uncovered ground, as well as the composite structures. Several layers of vinyl tape were used to create barriers and a metal scraper was used to draw down the paint in an attempt to make the layers as even as possible. Grounds were originally cast at a thickness of 0.021 inches and the paints were originally 0.004 inches thick; however, each material changed with the drying. The large sample sheets were eventually cut into smaller samples to facilitate handling (figure 11b). Final sample size is approximately 5 x 10 cm. Only one sample of each paint and ground combination was examined, so there are approximately 80 samples total. In addition, two samples from severely delaminating paintings were examined by non-destructive methods. The paintings were donated by artists, and are designated by their main colors. Skalka's 'Colorado Lagoon' is 'the blue painting' and the second painting is 'the brown/grey painting'.

Figure 11: (a) Schematic of composite samples. (b) Various samples after aging.

3.2 Methods

Microscopy

Initial observations of all samples were done at Queen's University using a stereomicroscope and a Nikon S-Kt microscope, used with reflected light. Images of cross-sections from samples 4, 12, 24, 35 and 60 were taken at the Canadian Conservation Institute (CCI) with a Leica DMRX microscope. A UV filter and a blue light filter were used in addition to reflected light. Images of cross-sections from the two paintings and of samples 19, 28, 31, 36, 52, 62, 95, 96, 97 and 98 were taken at the Getty Conservation Institute (GCI) with a Leica DM4000M microscope.

For cross-section preparation, the cross-sections were cut from the 1999 samples with a medical scalpel. Relatively large areas (up to several millimeters) were cut in order to get a sample with the paint still attached to the ground in at least some of the area. To get cross-sections of the delaminating paintings, with all the layers intact, samples were cut with the canvas using sharp scissors. Two samples were taken from 'Colorado Lagoon', one from a dark green area and one from a light blue area (sky). Cross-sections were imbedded in Ward's Bioplastic[®], cut with a diamond saw, ground down gradually with different grit papers and finally polished on a rotating wheel covered with cloth and slurry of 0.05 μ alumina in water.

Elemental Analysis

Two methods of elemental analysis were used at Queen's, X-ray fluorescence (XRF) and inductively coupled plasma - optical emission spectroscopy (ICP-OES). XRF data was collected with a handheld, Innov-X systems XT-440L and accompanying Innov-X PC 1.53 software. No sample preparation was needed with this method. The XRF was placed in a stand to hold it steady and maintain the same contact angle with all samples. Samples were placed flat over a piece of Mylar on the the XRF stand, to avoid cross-

contamination, and pressed down with a glass weight. Analysis was done in soil (light element matrix) mode and in most cases the test time was 60 seconds. Results were processed in Microsoft Excel. The non-destructive XRF technique is much faster than ICP and can analyze for more elements simultaneously; however, there are no standards for artists' materials, so it is not quantitative.

For accurate XRF results the samples need to be homogeneous and 'infinitely thick'. To test if the paint was thick enough, the area of paint alone on the 1999 samples was carefully separated from the Mylar and small pieces of gold or silver were placed under the paint, to determine if x-rays of various energy are reduced or not. Silver was used as an extreme example since it absorbs at energy levels much higher than anything likely to be found in a paint sample ($K\alpha = 22.16$ keV). Gold was chosen since it absorbs at energy levels similar to lead, which has the highest energy levels of the metals that are of interest in this study ($Pb\ L\alpha = 10.55$, $L\beta = 12.61$; $Au\ L\alpha = 9.71$, $L\beta = 11.44$). These tests were done in the analytical mode and test time was usually 60 seconds. Since some of the samples were shown not to be thick enough, additional tests were done with a sample of the same paint inserted between the paint and Mylar, creating a double layer. These tests were done in soil mode, in order to allow comparison with the single-layer measurements done on all the samples.

For ICP-OES, samples were taken from paints 1 to 10 since there were enough of those paints to allow for destructive testing. Samples of approximately 100 mg were dissolved in 2 ml nitric acid and 6 ml hydrochloric acid. The samples were heated overnight (18 hours) until almost dry. Double de-ionized water (25 ml) was mixed in and the solutions were filtered. Analysis was done with a Vista AX CCD simultaneous ICP-AES.

Paints 1 to 10 were analyzed by XRF as well; the Zn and Pb peaks were integrated in Microsoft Excel. Linear calibration curves were created with the XRF and ICP-OES results. Separate curves were made for zinc in paints with and without lead, to make the results as accurate as possible. The linear fit equations were then used to calculate an estimated quantity of those elements in the paints analyzed only by XRF. There are too few samples and too many variables to claim these curves allow exact quantification of

XRF results, and therefore the quantities reported for paintings examined only by XRF are approximations.

FTIR

At Queen's University: The paint and ground medium were examined by Fourier transform infrared (FTIR) spectroscopy. Analysis was performed with a Nicolet Avatar 320 FTIR spectrometer equipped with a Nicolet SMART Golden Gate diamond accessory for attenuated total reflectance (ATR). Data was collected with EZ OMNIC 5.2a software and converted into GRAMS/32 AI (6.00) software format for comparison.

Samples at CCI were analyzed using a Bruker Hyperion 2000 microscope interfaced to a Tensor 27 spectrometer. The surfaces of the grounds were analyzed directly in reflectance mode using a Ge-ATR objective (micro ATR-FTIR). The depth penetration of the germanium crystal is approximately 0.66 micrometers. For comparative purposes, fragments of the eight types of ground were analyzed by FTIR in transmission mode using a low pressure diamond anvil micro sample cell. For cross-sections 12 and 24, several areas of the upper part of the paint, the lower part of the paint (near the gesso interface) and the gesso were examined *in situ* using the Ge-ATR objective. A rectangular aperture (approximately 20 micrometers by 100 micrometers) was used to delineate areas of the cross-sections for analysis.

AFM

The surface morphology was examined at Queen's University with atomic force microscopy (AFM) in tapping mode, with a Di Digital Instruments / Veeco Metrology Group Multimode AFM. The probe was VistaProbe T300-10 with tip radius <10nm. Images were collected and analyzed with NanoScope software (version 5). Roughness values were taken as the mathematical mean of deviation from the median line (Ra) and as the root mean squared of the deviation (Rms). For statistical purposes Rms values are deemed more accurate. Samples were cut into squares of approximately 5x5 mm. Scan

size was 20x20 μm . Readings were taken at a minimum of three random locations on each sample and the roughness results were averaged.

Gloss-meter

The samples glossiness was measured with a BYK Gardner micro Tri-gloss instrument (accuracy of ≤ 1 gloss unit) at Queen's University. First measurements of different grounds were recorded at both 60° and 85°. Once it was established that most of the samples were very matte, according to the manufacturer recommendations all the samples were measured at 85°, so that variations will be clearer.

When measuring a ground, the paint and surrounding area were masked off with paper, so that any background included in the reading would be consistent. Each sample was measured in three different locations. Each reading was recorded and the statistics mode on the gloss-meter was used to average the results from all samples with the same type of ground.

PY-GC/MS

Pyrolysis gas-chromatography mass-spectrometry (PY-GC/MS) was performed at Queen's University, with a CDS analytical Inc pyroprobe 5000 connected to an HP5890 Series II Plus gas chromatograph with a HP5972 mass selective detector. The pyroprobe initial temperature was 225° C, it was ramped up at 10 ° C/ms to 600° C and held at that temperature for ten seconds before the pyrolysed samples were flushed with helium into the GC apparatus. The interface was kept at 225° C to prevent condensation. In the GC instrument a BP5 column (30 m X 0.255 mm X 0.25 μm) was used. Temperature was held at 50° C for two minutes then ramped up to 300° C at a rate of 10° C/min. The injection port was at 225 ° C and the detector was held at 280 ° C.

Ground samples were cut from the areas of ground only in the 1999 samples. Samples were approximately the size of the head of a pin. Each sample was placed with quartz wool inside a quartz tube and the tube was inserted into the pyrolyzer coil. Paint samples

were examined both by the above system and with an added methylating agent. Paint samples were slightly larger and cut into several smaller pieces dispersed along the tube with quartz wool in between. This was done in an attempt to make the pyrolysis more homogenous. For methylation, a micro-syringe was used to add one micro-litre of 25% aqueous tetramethylammonium hydroxide (TMAH) solution to the quartz tube, before placing it in the pyrolizer coil.

LDI-MS

A drop of water was placed on the ground surface of each sample. After one minute the drop was collected with a Pasteur pipette. The materials leached from the ground were then analyzed at Queen's University with laser desorption/ionization mass-spectrometry on an Applied Biosystems Voyager DE STR MALDI TOF instrument with mass resolution of 20,000 and mass accuracy of 0.01% Da. Analysis was performed in reflectron TOF (time of flight) mode.

An automatic pipette was used to measure 2 μ of each aqueous sample. The sample solution was mixed at a 1:1 ratio with a matrix of 2, 5-dihydroxybenzoic (DHB) in water (20mg/ml), 0.1 μ of the mixture, was placed on the MALDI plate and allowed to dry before being placed in the MALDI instrument. In addition, 0.1 μ of the original aqueous solutions, without the matrix, were placed on the plate and dried out for analysis.

SEM

At CCI, the surfaces of the ground samples were imaged using a Hitachi S-3500N VP SEM in variable pressure mode. This enabled the samples to be imaged without carbon coating. Various settings were attempted in order to optimise results for each sample, pressure from seven to 50 Pa and a beam voltage between four and 15 kV. Energy dispersive X-ray spectrometry (EDS) was performed on three cross-sections: a cross-section from the 'brown/grey painting' and sections from samples 12 and 24, using the Hitachi S-3500N VP SEM integrated with an Oxford Inca X-act analytical silicon drift x-

ray detector and an Inca Energy+ x-ray microanalysis system. The SEM was operated at an accelerating voltage of 20 kV in all cases. Samples 12 and 24 were carbon coated. The SEM was operated in high vacuum mode using a secondary electron detector for samples 12 and 24, and in variable pressure mode at 15 Pa with the sample from the painting. Using this technique, elemental analysis of volumes down to a few cubic micrometers can be obtained for elements from boron (B) to uranium (U) in the periodic table at a level of approximately 0.1–1% or greater (for EDS).

At the Getty, cross sections of samples 12, 24, 96 and 98 were analyzed using a Philips XL30 ESEM-FED with Oxford INCA EDS system run in ESEM (H₂O) mode. The beam accelerating voltage was 20kV for all samples.

Chapter 4

Results and Discussion

The 1999 samples had been kept in storage, so it is not known when they began to delaminate. Only samples with four oil paints are delaminating from the purpose-made grounds: verdigris (with lead drier), titanium white and two lead-white paints from different manufacturers (figure 12a). The distribution of samples by type of ground are in figure 12b. At least one sample is delaminating of every type of ground and four at the most. There are approximately ten samples with each ground and eight with each paint.

Figure 12: Distribution of delaminating samples: (a) by ground, (b) by paint.

In early 2007, there was just one other sample delaminating, a white alkyd (paint 19) on a gel medium. None of the other alkyd samples delaminated. A year later it was noticed that an additional sample, verdigris oil paint without lead drier (paint 18) cast over an acrylic paint, was delaminating as well. Since these two paints were not cast on the same grounds used in most of the samples, it is not possible to compare them properly; however, with some of the analysis methods described below, some insight into was gained into those samples as well.

4.1 PY-GC/MS

The main results of the ground analysis are summarized in table 2. Acrylic grounds B-H were all copolymers of methyl methacrylate and butyl acrylate (MMA-BA). Ground A was more difficult to identify. The main component seen in the chromatogram was styrene with some acrylic and other molecules. More detail about the identification of Ground A is in the FTIR section below. All the pyrograms included a small peak with a mass distribution that matched methyl butylacrylate (MBA). This could be part of the original polymer used to formulate the grounds, or it could be formed during the pyrolysis. In a number of grounds, the plasticizer dibutyl-phthalate (DBP) was identified. In other grounds there were materials with a mass-distribution and retention time similar to DBP, which might be other phthalate-based plasticizers. Many other minor components were not identified since there were no standards or chromatograms in the literature for all the possible additives.

Table 2: PY-GC/MS of grounds

Ground		Main polymer components	DBP or similar plasticizer
A	Aaron Brothers White Gesso	Possibly styrene	DBP
B	W&N Clear Gesso Base for Acrylics	MMA-BA	DBP
C	W&N Acrylic Gesso Primer	MMA-BA	DBP
D	Utrecht Artists' Acrylic Gesso	MMA-BA	No
E	Utrecht Professional Acrylic Gesso	MMA-BA	DBP and similar
F	Liquitex Acrylic Gesso	MMA-BA	No
G	Dick Blick Artists' Acrylic Gesso	MMA-BA	DBP
H	Grumbacher Artists' Acrylic Gesso	MMA-BA	similar

The polymer used in a latex paint could potentially influence the adhesion of subsequent layers. It could change the roughness of the surface or it could change the amounts of surfactants exuded to the surface. Since most of the samples tested were made from the same co-polymer, and ground A displayed similar properties to the acrylic grounds, it is not possible to draw any conclusions about the influence of the polymer on delamination. In addition, the presence of DBP or similar plasticizers did not correlate with the distribution of delaminating samples. The two grounds without such plasticizers are D and F, one of the worst and one the best in terms of adhesion.

The method used for oil and alkyd paints did not provide reproducible, quantitative results. Qualitatively, it was only possible to confirm that the oil and alkyds had been labeled correctly. One interesting result was a difference between the alkyd paints (all Griffin alkyd paints are from W&N). Paints 7 and 10 have almost identical chromatograms (figure 13), in which phthalic anhydride, benzoic acid and a number of fatty acids are clearly identified. Paint 8 (lead white) does not have any phthalic anhydride and was perhaps made using mostly carboxylic acids as the acid component of the alkyd (figure 14). Paint 8 does include a significant peak (retention time ~14 minutes) which can be attributed to dimethyl phthalate ($m/z = 194$), with the most intense peak,

$m/z = 163$, due to the loss of methanol. Dimethyl phthalate was also present in paints 7 and 10; however, it is not known whether it was original to the paint or formed during the analysis.

Figure 13: Chromatogram of W&N alkyd titanium white (paint 7) with mass spectrum of phthalic anhydride.

Figure 14: Chromatogram of W&N alkyd flake white (paint 8).

4.2 XRF and ICP

The results of the elemental analysis showed that most of the paints with delaminating samples contained zinc. The verdigris paint obviously contained a high percent of copper, but also some lead, since litharge, PbO, was added to the paint as a drier. Since two of the delaminating paints were lead-white paints, the elements reported in table 3 are Pb, Zn and Cu. The quantities reported are the results of ICP-AES. The samples for ICP were digested in acid, for the elements discussed here it is safe to assume that all the material present was fully dissolved; however, that would not be the case for every type of pigment.

Table 3: ICP-AES results for zinc, lead, and copper.

Sample		% delaminating	Zn (ppm)	Pb (ppm)	Cu (ppm)
1	Verdigris in oil	25	<50	2440	272000
2	Titanium White in oil	37.5	63400	312	25
3	Flake White in oil	100	34700	578000	<20
4	Flake White in oil	75	124000	485000	<20
5	Raw Sienna in oil	0	556	61	231
6	Cobalt Blue in oil	0	<50	78	21
7	Titanium White in alkyd	0	593	<50	<20
8	Flake White in alkyd	0	172	636000	<20
9	Ultramarine Blue in oil	0	58	<50	<20
10	Raw Sienna in alkyd	0	121	<50	134

Paints 1-10 were measured with XRF as well as ICP. Figure 15 shows an example of an XRF spectrum of paint 2. The area under the XRF Zn K_{α} and under the Pb L_{α} peaks were integrated and calibration curves were created, comparing the results of the two methods (Figures 16 & 17). Paints with and without lead were separated to improve the accuracy, since lead is a heavy metal and provides a much larger target for x-rays than other elements in the paint. The linear equations were then used to convert XRF results from other samples to approximate quantities. In the future more samples should be tested to check, and perhaps improve, the calibration curves. These curves can then be used to obtain semi-quantitative results for any paint measured in the future.

Figure 15: XRF spectrum of paint, Titanium White in oil.

Figure 16: Calibration curve comparing lead quantities by XRF and ICP.

Figure 17: Calibration curves comparing zinc quantities by XRF and ICP.

Based on the calibration curves, the XRF results obtained from the paintings and from paints 11-20, where there was not enough material to allow for destructive ICP testing, were converted to approximate quantities. The results are summarized in table 4. Results are presented in ppm for easy comparison to the ICP results in the previous table (detection limits are estimates).

Table 4: Elemental analysis of delaminating paintings

Sample		% delaminating	Zn (ppm)	Pb (ppm)	Cu (ppm)
Blue paint from 'blue painting'		Completely	~190000	~43000	<150
Green paint from 'blue painting'		Slightly	~70000	~40000	<150
Ground from 'blue painting'		N/A	~110000	~58000	<150
Paint from 'brown/grey painting'		Severely	~160000	~15000	a little
Ground from 'brown/grey painting'		N/A	~210000	~26000	<150
11	Cobalt Blue in alkyd	0	~150	<1000	<150
12	Light Red Oxide in alkyd	0	<150	<1000	<150
13	Yellow Ochre in alkyd	0	<150	<1000	<150
14	Terre Verte in alkyd	0	<150	<1000	trace
15	Indian Red in oil	0	<150	<1000	<150
16	Yellow Ochre in oil	0	<150	<1000	<150
17	Burnt Sienna in oil	0	~1000	trace	trace
18	Verdigris in oil	1 of 2 samples	<150	<1000	a lot
19	white alkyd (TiO ₂ + ZnO)	1 of 2 samples	~45000	<1000	<150
20	Burnt Umber in alkyd	0	~1000	trace	trace

The thickness required to reduce an x-ray beam can be calculated for specific materials, provided their density and mass attenuation coefficient are known. This information is not known for paint films, which are too variable. To get a general estimate of the thickness required, the thickness required of specific elements was calculated. For example, for a film of pure Ti, a thickness of 0.003 cm or higher could be considered infinitely thick (see more details in Maor et al. 2008). Several paints were measured with pieces of gold or silver placed behind the paint. If the sample is not thick enough, x-rays make it through to the metal placed behind the paint layer. Silver always showed on the spectra, indicating that the paint film is not thick enough to completely reduce 22 keV x-rays. Gold did not show in spectra collected from lead white paints, but did show up when placed behind titanium white paint, raw sienna paint (figure 18), and very faintly behind

verdigris paint. Gold peaks were much larger in the alkyd titanium white than in the oil titanium white.

Figure 18: XRF spectrum of raw sienna oil paint with a piece of gold behind it.

The thickness of the titanium white paint layer was measured with calipers and its average thickness is 0.03 cm; however, since it is not only made of metals, but rather a less dense material, the x-rays are not reduced entirely. This results in an XRF spectrum showing gold in addition to the zinc and titanium present in the paint film.

With the titanium white paint (2) and raw sienna paint (5), it was possible to insert another sample between the paint and Mylar. As expected, there were differences in the spectrum of a single layer of paint and a double layer (figure 19). The zinc peak in the titanium white double layer was 5% larger than in a single layer. In the raw sienna double layer the very small zinc peak was almost 20% larger than in a single layer.

Figure 19: XRF spectra (from 8 to 10 keV) of single and double layers of titanium white oil paint.

The thickness testing indicates that the XRF results were often lower than they would have been in a thicker sample of the same composition. When the sample being measured by XRF is not infinitely thick, any variations in thickness influence the results. The samples were prepared in a method that was meant to produce samples of even thickness; however, there are slight variations. This means that the results aren't uniformly lower, and so cannot be corrected easily; therefore, the integrated value measured from the titanium white paint has an estimated error of $\pm 5\%$. Estimated errors are based on the assumption that the double layers of paint tested were infinitely thick. When only trace amounts of a metal cation were present, as in the raw sienna paint, the error can be much larger and is estimated at $\pm 20\%$ (for zinc); however, that does not change the order of magnitude of the results. When large amounts of lead were present, the paint layer is essentially 'infinitely thick', so the results are quite accurate.

The margin of error for the results in table 4 is fairly large, in particular for the measurements taken from actual paintings, where the paint can be very thin and uneven. For the purposes of this project however, these approximate results are perfectly adequate, since the differences in zinc and lead quantities between delaminating and non-

delaminating samples were very large. For example, in the 'blue painting', the zinc in the severely delaminated blue paint was estimated at 19% and about 7% in the slightly delaminated green paint. Since these are significant quantities and not trace amounts, most of the x-rays are reduced, increasing the accuracy. Even if those results are wrong by 5%, as estimated for the titanium white paint discussed above, the difference would still be significant. Since zinc is a heavier element than titanium and there is lead in the paints as well, the paint is probably closer to an infinitely thick layer, making the results more accurate.

The elemental analysis indicated a strong correlation between the presence of zinc in the paint or ground and the presence of delaminations. If there was lead in addition to zinc in the paint, the problem could be exacerbated. In both the severely delaminating paintings, there were high levels of zinc and some lead in both the paint and the ground. In the 1999 samples, more samples with lead white paints (3 & 4) are delaminating than samples with titanium white paint (2), which contains almost twice the zinc as paint 3.

The grounds of the 1999 samples were tested only by XRF. The qualitative results are sufficient since they are all very similar and none of the grounds contained any of the problematic elements. The results are summarized in table 5. Most of the grounds contain a lot of titanium, some calcium and a very small amount of iron (probably a contaminant). Ground B is the clear acrylic gesso; therefore it does not contain any titanium.

Table 5: XRF of grounds

Ground	Elements detected
A	Ti (l), Ca (s), Fe (vs)
B	Ca (l), Fe (vs)
C	Ti (l), Ca (s), Fe (vs)
D	Ti (l), Ca (m), Fe (vs)
E	Ti (l), Ca (m)
F	Ti (l), Ca (m), Fe (s)
G	Ti (l), Ca (l), Fe (vs)
H	Ti (m), Ca (l), Fe (vs)
P1	Ti (l), Ca (m)
P2	Ti (l)

Peak size: (l) = large, (m) = medium, (s) = small, (vs) = very small

The presence of Ca indicates the use of a filler, probably CaCO_3 . The filler can be important since the larger particles can make the ground rougher. Ground P2, which was meant to be used as an acrylic paint does not contain Ca and therefore may not contain filler. The modern titanium white pigment particles are small (Laver, 1986) and probably do not give the ground much ‘tooth’. This could explain why paint 18 (verdigris in oil) is delaminating from ground P2 and not from P1 which does contain calcium.

The grounds of the two severely delaminating paintings contained large titanium peaks, but only low levels of calcium (small or very small peaks). These grounds may also be too smooth because only small quantities of filler were used. The last delaminating sample which should be discussed is paint 19 (white alkyd) over ground P4. This ground is actually a gel medium containing no pigment or filler. This was confirmed in the SEM analysis below, and again could explain why paint 19 was adhered to one ground (P5) but not to P4.

4.3 Microscopy

In every case where grounds were examined in this paper, most of the work is done on samples 34-41, which are the samples with paint five, raw sienna in oil. These samples were chosen since there was a full set on all eight grounds, the paint is not sticky (as some oil paints are) and the samples are well adhered, making them easy to handle. Other, randomly selected samples were examined and it was confirmed that samples 34-41 are representative of the norm.

The results of the microscopical examination of the grounds at x40, in reflected light, are summarized in table 6. These results do not correlate very well with the distribution of delaminating samples. While the high number of samples delaminating from grounds D and E could be explained by their smoothness, grounds B and F appeared fairly smooth and yet they provided the best adhesion. Grounds that appeared rough on this scale, C and H, did not provide good adhesion.

Table 6: Appearance of grounds at x40

Sample	Ground	Description
34	A	Fairly rough. Small holes, mostly not visible without the microscope.
35	B	Fairly smooth. Fewer holes than in A. Bright spots which may be large particles of a filler material.
36	C	Rough surface. Small particles dispersed throughout.
37	D	Very smooth and glossy with large holes (1-3 mm).
38	E	Very smooth and glossy with large holes (1-3 mm).
39	F	Smooth. Small holes (<1 mm) and small bright spots (smaller than in ground B).
40	G	Less rough than ground C. Small holes (<1 mm).
41	H	Rough surface. Appears like many different levels or slight cracking and not visible particles or holes.

The paint surfaces of paints 1-10 were examined as well, and the observations made are summarized in table 7. The paints may be ranked by their roughness:

Smoothest – 7 < 4 < 2, 3 < 8 < 9, 10 < 5, 6, 1 – Roughest. This does not necessarily reflect in any way on the lower surface of the paint and its ability to interlock with the ground layer.

Table 7: Appearance of paints at x40

Sample	Paint	Description
1, 2	1	Rough. Oil was leached out, leaving dark areas and cracks.
9	2	Fairly smooth. Small particles and a few very small holes. Brush marks.
17	3	Fairly smooth. Holes (<1 mm). Brush marks.
26	4	Smooth. Some holes. Brush marks.
34-41	5	Rough.
42	6	Rough. Paint is still sticky. Air bubbles are rounder than in other samples and holes go down to the ground layer.
50	7	Very smooth. Some holes (<1 mm).
59	8	Slightly rough. Homogeneous appearance.
67	9	Fairly rough. Sticky (not as bad as 6). Many holes (~1 mm). Brush marks.
75	10	Fairly rough. Homogeneous appearance.

Examination of cross-sections elucidates many aspects. The cross-sections were particularly valuable in the case of the paintings, since less was known of their composition. In the ‘blue painting’ the sample taken from a dark green area (figure 20 left) showed the presence of a very thin light green layer underneath the dark green paint. The sample taken from the light blue area (figure 20 right) showed a single layer of paint delaminating from the ground. High levels of zinc were found in the XRF analysis

(above) of the light blue paint and some zinc was found in the green paint. This is probably due to the fact that the zinc was in the lower layer of the green paint. The artist recalls using a zinc-white paint the summer this painting was created (Skalka 2007). These findings are consistent with the theory that a zinc white paint used to create the lighter shades is the cause of delamination.

Figure 20: Cross-sections of ‘blue painting’. Left: Dark green area at x20 magnification. Right: Light blue area at x10 magnification.

In the ‘brown/grey painting’ the cross-section (figure 21) was particularly surprising, since it showed a very large number of layers (over 20) in a painting which has an almost uniform paint on the surface. The delamination is taking place between a white layer and a grey layer above it. Since the white layer extends over the whole section examined it was originally mistaken for a ground layer, but it is actually one of the middle paint layers. To maintain consistency with the rest of the samples and avoid confusion, the problematic white layer is still referred to as ‘ground’. There is also some lack of adhesion lower in the cross-section, between a white layer and a brown layer above it. This delamination is not as severe, and has not caused the paint to flake off at that level yet.

Figure 21: Cross-section of 'brown/grey painting' at x10 magnification.

In the cross-sections taken from the 1999 samples several phenomena were observed. Many samples showed some pigment settling, leaving a thin oil-rich layer at the top. The UV light and blue light filters often give clearer images since many of the samples of interest were white, making it difficult to focus on them. The fluorescence was often stronger at the top of the ground layer, suggesting that oil has sunk into the grounds.

Figure 22 shows two samples of different lead white paints over the same acrylic ground. The fluorescence at the top of the ground seems more extensive in the sample with paint 3. Cross-sections were only prepared from certain samples, so it is not possible to say whether the extent of the presumable oil penetration into the ground depends more on the type of ground or type of oil. The fact that paint 3 shows more fluorescence at the interface of the layers could be significant, because every sample with that paint is delaminating. Figure 23 shows a second cross-section with paint 3, over a different ground. The fluorescence seems almost as extensive as in the first sample. It is not known why ground H fluoresces slightly orange. An image in blue light (420-490 nm) is provided as well, as the delamination is clearer there; though obviously the delamination is not as extreme as in the paintings.

Figure 22: Cross-sections in UV light at x20 magnification. Left: Sample 28 (lead white paint 4 and ground C). Right: Sample 19 (lead white paint 3 and ground C).

Figure 23: Cross-sections of sample 24 (lead white paint 3 and ground H) at x20 magnification. Left: UV light. Right: Blue light.

Samples with verdigris paint showed extensive crystallization, a lot of white material and many voids in the paint layer (figure 24). The white material could be crystallized copper soaps. The image shows that while the delamination, seen on the right of the sample, began at the interface with the ground, the crack extended slightly into the paint layer. This explains the fact that when paint was separated from the ground in the verdigris samples, there were some spots of what appeared to be green staining left behind on the ground. Interestingly, the fluorescence in this case is not right at the top of the ground layer, but a little further in. This could suggest that oil, or perhaps metal soaps, migrated into the ground, then the paint layer crystallized so no more material went into the

ground, while the fluorescent material already in the ground, continued to sink down. This same phenomenon is apparent in samples with paint 18, the verdigris without lead drier.

Figure 24: Cross section of sample 4 (verdigris paint with lead drier over ground D) at 20x magnification. Left: Incident light. Right: UV light.

Other photo-micrographs of cross-sections were quite useful in understanding results obtained by other means and are presented in the appropriate sections below.

4.4 Gloss-meter

The gloss readings of each ground were fairly consistent, not only in different areas of the same sample, but even in samples with different paints on top. This indicates that the method of preparing the samples was similar enough, so that the materials are the only issue influencing the gloss or roughness. For this reason, the gloss readings from each sample are not reported. The 85° gloss readings from all the samples with the same type ground were averaged and are summarized in table 8 with the standard deviation and number of readings taken. The results do not all agree with the observations made at x40 magnification.

Table 8: Gloss of grounds

Ground	mean gloss	SD	n
A	12.7	2.6	30
B	0.9	0.1	29
C	2.3	0.2	29
D	52	7.2	30
E	55.7	6.2	30
F	8.3	1.8	30
G	5	0.8	30
H	1.1	0.2	29
P1	13.2	0.2	4
P2	59.2	2.4	4
P4	61.0	3.4	2
P5	3.6	0.4	4

Grounds D and E (both by the same manufacturer), had a smooth and glossy appearance, with large holes probably caused by air bubbles. The gloss-meter gave these grounds ratings > 50 , which is quite glossy. The large holes in the surface of those grounds apparently did not disperse light significantly. All the other grounds showed very low gloss levels. The slight differences between these grounds do not match the microscopical examination. For example, ground F which appeared smooth in the microscopical examination, with small holes and bright spots, which could be either a filler material or crystallized surfactants, had a gloss-rating of 8.3. Perhaps the smaller features caused more light-scattering. Ground B, which had appeared fairly smooth, but had the same bright spots, got the lowest gloss rating of all. Ground A, which appeared fairly rough got the highest gloss level after grounds D and E.

Clearly, features which may not be interpreted as roughness by a human eye do scatter light and vice versa. Perhaps this technique can register very smooth surfaces, but it does not differentiate well between variations in roughness of non-glossy surfaces, even though it was used with 85° light as recommended for matte surfaces.

As with the microscopical observations, roughness, as indicated by gloss levels, does not correlate as well as expected with the distribution of delaminating samples, although some do correlate. Grounds D and E are glossy and have a relatively high level of delamination, grounds B and F, which have the least number of samples delaminating from them, are quite matte. Of the additional grounds (paint or medium) measured, P2 and P4 are glossy while the other two are matte. This could explain why there is a sample with paint 18 delaminating from P2 and not from P1 and a sample of paint 19 delaminating from P4, but not from P5. The smoothness of P2 is explained by the XRF results showing no Ca, indicating no filler was used in this paint. P4 is a gel medium and does not contain any pigment or filler.

The rest of the samples do not correlate so well. Ground G has over 30% of the samples delaminating, yet it is less glossy than F. Grounds A and C are about average in terms of adhesion, but A is very matte and C is only a little less matte. Ground H is the most extreme, having a very low gloss-rating (1.1), yet more than 30% delamination; however, since ground H had a significantly different appearance than the other grounds, this behavior might be explained by other means. A more accurate method for measuring roughness was required, and AFM proved very successful for that purpose.

4.5 AFM

The results of the roughness analysis from the AFM data indicated that the roughness of the ground can be significant. The mean roughness results are displayed in figure 25. Ground B was too rough to measure with the equipment used in this study (rougher than the others). It is included in the graph for the purpose of illustrating the results as fully as possible, with a value slightly higher than any of the other grounds. As with the gloss-meter, grounds D and E were the smoothest and grounds B and H were the roughest; however, with AFM more differentiation was obtained for the rest of the samples.

Figure 25: Mean roughness of grounds in 1999 samples

If the distribution of delaminating samples by ground layer (figure 12a) is compared to the roughness, seen in figure 25, there is a certain degree of correlation. Rough grounds, like F and B provide good ‘tooth’, so most of the paints remained adhered, even if they contained some zinc. Smooth grounds, like D and E, do not have enough crevices that allow the paint to interlock, so more samples are delaminating. Unlike the gloss-meter results, in this case grounds A and C have similar roughness, about half-way between the smooth and very rough grounds. This correlates well with the numbers of samples

delaminating. The exception is ground H, which has a mean roughness (Rms) of 695 nm, yet has a relatively high percent of samples delaminating from it.

Measured roughness can be due to different features in the samples. It is important to look at the three-dimensional AFM images to gain a better understanding of the results. The AFM images (figure 26), show that ground H actually has very smooth areas and very large lumps, and not the more homogeneous texture of the other grounds. Figure 27 includes several images of grounds with a normal texture. Please note the differences in scale on the z axes. The large lumps in ground H were also seen when the cross-section with that ground was viewed in blue light (figure 23 above), and are probably CaCO_3 that was not milled down enough. When compared to other cross-sections (examples in figure 28), it is seen that ground C has some large particles, but fewer, and ground D has much smaller filler particles. The calcium carbonate identification is strengthened by the XRF results which showed ground H had a Ca peak even larger than the Ti peak.

Figure 26: AFM images of different areas of ground H

Figure 27: AFM images: (a) – ground G, (b) – ground D, (c) – ground A, (d) – ground E.

Figure 28: Cross-sections at 20x in blue light. Left: Sample 60 (lead white paint 8 and ground C). Right: Sample 12 (titanium white paint 2 and ground D).

The correlation between the roughness of the other grounds (A-G) and the percent of samples delaminating is shown in figure 29. The square of the correlation coefficient (R^2) is 0.7, indicating a good correlation from a statistical point of view. It is then possible to claim that a rough ground will provide a better surface for adhesion, provided it is not too uneven.

Figure 29: Comparison of the roughness (Rms) of grounds and the percent of samples delaminating from that ground. Based on grounds A-G only.

4.6 LDI-MS

As expected, the LDI-MS analysis showed surfactants on the surface of the acrylic grounds. An example is provided in figure 30. The spacing of 44 amu is characteristic of surfactants in the polyethylene oxide (PEO) family. Many different surfactants can be

used in acrylic paints. A number of surfactants had been analyzed previously (Chown *et al.* 2005) and those results were used as references. Grounds B and G contain a surfactant that matches the mass distribution of Triton X-405 (figures 31 & 32) and ground F contains a very similar surfactant (perhaps Triton with a different number of ethylene glycol molecules).

Figure 30: Mass spectrum of material leached from ground C.

Figure 31: Mass spectrum of Triton X-405 (with matrix).

Figure 32: Mass spectrum of material leached from ground B (with matrix).

Each of the grounds contains a number of PEO type surfactants; however, besides the Triton X-405, none of the other surfactants matched a known reference. Most surfactants gave clear spectra without the DHB matrix, but Triton X-405 appeared strongly only with the matrix. The grounds were compared, to see if certain surfactants could be related to the delamination problem. As the results in table 9 show, there is no correlation between the type of surfactant and the distribution of delaminating samples. In addition to the surfactants, all the grounds contained three unidentified peaks at 353, 381 and 647 amu. These peaks seem to have been slightly suppressed by the matrix.

Table 9: Surfactants leached from the grounds

Surfactant	Range (amu)	Spacing (amu)	Peaks (amu)	Grounds
Triton X-405	1100-2200	44	1814	B, G
a	200-1000	44	305, 349, 393	All grounds
b	200-700	44	297, 341	B, C, D, E
c	400-800	44	493, 537	G
d (maybe Triton)	1100-2000	44	1462 (includes 1814)	F

This method showed the surfactants very clearly; however, it does not allow quantification. It is possible that larger quantities of certain surfactants on the ground surface influence adhesion, even if the type of surfactant is not a determining factor. Theoretically, since the samples were collected by placing a drop of water on the surface, the water could be leaching surfactants from the bulk material. Despite this, there are two main reasons to assume that the above results represent surfactants that had already migrated to the surface. First, the water was on the surface for only a minute, so a significant amount of material would not have been leached from the bulk. Second, it has already been well established that surfactants do migrate to the surface of acrylic films during aging. Even if some surfactants were leached from the bulk, the leaching would likely reflect the rate at which surfactants had migrated during aging, so the comparison would still be valid.

4.7 FTIR

Zinc, lead and copper, found in the delaminating paints, can all form metal soaps with fatty acids in oil. The metal soaps have major absorbance peaks in IR in the 1530-1600 cm^{-1} range. All the delaminating samples contain metal soaps (figure 33). For the sake of clarity, spectra of only copper stearate and zinc stearate are provided as references. It should be noted that overlap between the peaks for various metal soaps is expected. For instance, lead stearate absorbs at 1541cm^{-1} , practically identical to zinc stearate. Zinc oleate, on the other hand, has a medium absorption peak at 1589cm^{-1} , quite close to that of copper stearate at 1586cm^{-1} (Robinet and Corbeil 2003).

Figure 33: FTIR-ATR spectra of oil paints from delaminating samples.

The non-delaminating samples were examined by FTIR-ATR as well and none of them showed signs of metal soaps (figure 34). Flakes of paint from the delaminated paintings were examined and so were the exposed grounds. All showed absorption in the 1530-1600 cm^{-1} range (figure 35). In the spectra of the brown/grey paint there is a succession of three small peaks around 1600 cm^{-1} , characteristic of alkyd paints and not indicative of additional metal soaps; however, the peak at 1539 cm^{-1} matches the zinc stearate reference perfectly.

Figure 34: FTIR-ATR spectra of oil paints from non-delaminating samples.

Figure 35: FTIR-ATR spectra of paints and grounds from delaminating paintings.

The blue paint and the ground of the ‘brown/grey painting’ match reference spectra for oil paints. The blue paint contains CaCO_3 in addition to the pigments. The ground of the ‘blue painting’ has some significant differences and did not match any reference spectra. The artist recalls it was painted on an old pre-primed canvas, which he thought was oil, but had a greasy feel which he could not explain (Skalka 2007).

Paints 1 and 18 are both custom manufactured verdigris in linseed oil. The only difference was paint 1 had 1.6% litharge (PbO) added. The comparison of the spectra of these two paints (figure 36) shows no significant difference, indicating that the metal soap peaks in the $1530 - 1590 \text{ cm}^{-1}$ region are not due to lead soaps. The SEM-EDX analysis provided below also found aluminum in the verdigris paint and this too could form metal soaps. Aluminum soaps and copper soaps can have very similar FTIR spectra as shown

for the metal stearates. The shoulders near 980 cm^{-1} in both paint spectra may correspond to the peak at 983 cm^{-1} in the spectrum of Al stearate, indicating that there are aluminum soaps present, probably in addition to copper soaps.

Figure 36: FTIR spectra of verdigris oil paints. Paint 1 has a lead drier, paint 18 does not.

The FTIR spectra of the grounds in the 1999 samples mostly confirm information obtained from other tests. Ground A has a different spectrum because it is not a simple acrylic co-polymer, but all the other grounds are very similar. There are some differences between the fillers used. The standard filler was CaCO_3 in the calcite form; however, ground F included kaolin in addition to calcite. The Utrecht grounds (D and E) apparently contain a slightly different type of filler, as seen by the presence of two peaks at 872 and 853 cm^{-1} instead of the single peak of CaCO_3 .

The spectra of ground A looks like a mixture of polyvinyl acetate (PVA) and acrylic. This is surprising because in the PY-GC/MS analysis, the main component was identified

as styrene. In the PY-GC/MS method used, PVA shows up as acetic acid and benzene eluting together in the first minute (Learner 2001) and could easily be missed. The fact that no styrene showed on the FTIR is harder to explain. A more quantitative PY-GC/MS analysis, with appropriate reference materials would be necessary to elucidate this issue. This was not done at this point, because the media of ground A provides similar adhesion properties to the other acrylic grounds, meaning it is not a factor in explaining the delamination problem.

The two white paints used as grounds under paint 18 were tested as well. Ground P1 is very similar to the purpose-made grounds. Ground P2 is significantly different since it doesn't contain any filler, while all the others contain CaCO_3 or a similar material (figure 37). This confirms the XRF result showing there was no calcium in P2 and the theory that a lack of filler made this paint glossy.

Figure 37: FTIR-ATR spectra of acrylic grounds and acrylic paints used as grounds.

The micro-FTIR analysis done at CCI allowed for more localized testing of the 1999 samples. The surfaces of the grounds were examined for surfactants. The use of a germanium crystal instead of the diamond used at Queen's means a smaller depth penetration, more suited for looking at surfactant build-up on the ground surface.

Ground F, showed a series of extra peaks (2891, 2877, 1363, 1343, 1278, 1241, 1115, 1061, 964, 843 cm^{-1}) in the ATR-FTIR spectra (figure 38) that are attributable to an alkyl phenol ethoxylate type surfactant, such as the Triton X series. Ground E, showed two of these bands, 1343 and 1116 cm^{-1} , which correspond to the most intense surfactant peaks in ground F, indicating that it also may contain an alkyl phenol ethoxylate surfactant on its surface. Transmission spectra were collected from fragments of the grounds and showed the same peaks, but weaker, confirming that there were more surfactants on the surface than in the bulk material.

Figure 38: FTIR-ATR spectra of different spots on ground F, showing surfactants.

The comparison of spectra from different spots on the ground surface shows variations in the intensity of the surfactant peaks. This is seen both in ground F and in ground E (figure 39). Note particularly that the absorption at $\sim 1115\text{ cm}^{-1}$ can appear as a strong peak or a weak shoulder or anything in between. The variation in intensity indicates an uneven distribution of surfactants over the surface. Surfactants were seen, at least to some extent, in almost all areas measured on ground F, but on only a few spots in ground E. Figure 40 compares spectrum E1 (the strongest of the E spectra) and spectra F4, both normalized to the same carbonyl peak intensity. The absorbance around 1115 cm^{-1} is stronger in the ground F spectrum. No such surfactants were observed on the other grounds; however, since only selected, very small areas were examined, this does not prove there are no surfactants on the surface of those grounds.

Figure 39: FTIR-ATR spectra of different spots on ground E, showing surfactants.

Figure 40: FTIR-ATR spectra normalized to the same carbonyl peak intensity.

These results are surprising, since other studies (Ormsby 2008) have found surfactant build-up to be more extensive. This could be because previously acrylic paints were studied and not acrylic grounds. A possible method that could provide more accurate analysis of surfactants and their location in the sample is confocal Raman micro-spectroscopy. This method has been used to measure the concentration of surfactants at different depths throughout a paint film (Chiantore & Scalarone, in MPU, 2006). If it becomes possible to use this method on the 1999 samples, it may shed new light on the influence of surfactants on adhesion.

The micro-FTIR was also used to check the location of metal-soaps in two cross-sections. Figure 41 shows the results of sample 12 (paint 2 over ground D). Spot-tests were repeated in other locations along the cross-sections and produced nearly identical results. Several points of interest are seen in these spectra. First, the lower part of the paint contains more metal-soaps than the top. In sample 12, paint 2 is titanium white oil

paint which also contains zinc oxide, so the peak at $\sim 1540\text{ cm}^{-1}$ can be attributed to zinc soaps. It was thought that metal soaps could be leached into the acrylic layer. The peaks in the ground layer are at 1595 cm^{-1} which is a large shift, so if that is metal soap, it is probably not the same zinc soap seen in the paint layer. Another fact that puts that interpretation in doubt is the fact that the peak is larger in the lower part of the ground.

**Figure 41: FTIR-ATR spectra of a cross-section of sample 12
(paint 2 over ground D).**

The wide absorption peak at $3200\text{--}3300\text{ cm}^{-1}$ is due to water. It is apparent that there is a lot of water in the paint layer, but not in the ground. More specifically, the absorbance is strongest in the lower part of the paint, indicating that the water is collecting on top of the ground. Water could interfere with the adhesion by its own mechanical action. It could also be the cause of increased hydrolysis, which would explain the greater concentration of metal-soaps in the lower part of the paint. Another significant difference is the sharp peak at 1377 cm^{-1} with shoulders at 1397 and 1355 cm^{-1} which appears only in the lower

part of the paint layer. These could be related to metal-soaps. Zinc stearate has a strong peak at 1398 cm^{-1} which might be the 1397 cm^{-1} shoulder; however, there is no definite identification for any of those three peaks.

Figure 42 shows spectra from sample 24 (paint 3 over ground H). Sample 24 exhibits similar phenomena to those discussed in sample 12; however, the differences are slighter as the spectra are overwhelmed by the lead white peaks (1390 , 836 and 677 cm^{-1}). It can still be seen that the absorbance at 1538 cm^{-1} , is significantly stronger in the lower part of the paint (just a shoulder in the upper part). This peak could be either lead stearate, zinc stearate or a mixture of the two, as the lead white oil paint contains zinc oxide as well. The soaps could of course be the cause of the delamination, as their accumulation as the paint ages would disrupt adhesion.

Figure 42: FTIR spectra of a cross-section of sample 24 (paint 3 over ground H).

Following these results, which strongly indicate more metal soaps were present at the delaminating interface, it was hoped that it would be possible to map certain IR wavelengths throughout a cross-section. This was attempted at the GCI; however, due to technical difficulties the mapping has not produced results yet. More spot tests were done and initial results were similar to those obtained at CCI. The presence of more metal soaps does not explain how they got there. Hydrolysis is one option, but the soaps could also migrate. With SEM mapping, described below, it was hoped to answer that question.

4.8 SEM

The surface of the eight grounds was observed in SEM, with back-scattered electron detector (BSE) and secondary electron detector (ESED) to see if surfactants were visible. In most of the samples the surfaces were homogenous. The only variations were small holes, probably caused by air bubbles, or larger particles of media or filler protruding from the surface. Surfactants are composed of lighter elements than the heavily pigmented grounds, and so should appear as darker areas in the back scatter images. In only two samples, ground E and F, darker areas were observed with the BSE detector.

On the surface of ground F (figure 43), most of the area was darker and there were only small light spots. Since it is unlikely that any heavy elements are forming those lighter spots on the surface, it may be that almost all the surface is covered with surfactants. The lighter areas would then correspond to the acrylic surface, not covered by a surfactant layer. This interpretation is corroborated by the FTIR results, where ground F was the only sample which showed appreciable amounts of surfactants.

Figure 43: Back scatter image of the surface of ground F taken at 7 Pa.

Ground E (figure 44) has only small areas that could be surfactants. In figure 44 the dark oval shape is probably a hole, not a chemical difference in the surface. The surfactants might be the dark streak in the lower section of the image. In the FTIR examination, ground E was the only other ground, besides F, where any peaks corresponding to surfactants were observed; therefore, it makes sense that the few dark areas on this ground could be surfactants.

Figure 44: Back scatter image of the surface of ground E taken at 7 Pa.

The fact that no such darker areas were found on the other grounds does not mean that there are no surfactants accumulated on the surface. Since the LDI analysis did find surfactants in all samples, it is more likely that the surfactants are more evenly dispersed over the surface, and simply not as abundant as in ground F. It may be that the micro-FTIR-ATR spectra of ground E that showed surfactant happened to be taken in an area of surfactants, such as the streak seen in SEM.

Whether there is or is not a surfactant layer on the other grounds, SEM appears to confirm that ground F has the most surfactant build-up. Since this is the ground to which the most samples adhered well, this could disprove the theory that surfactants migrating to the surface interfere with adhesion. The theory cannot be completely disproved by these results, since it is only the one sample and it is very rough, improving adhesion. A method by which surfactants could be identified quantified more accurately is required.

Four of the cross-sections from the 1999 samples and the cross-section of the 'brown/grey painting' were examined by SEM and the elements were mapped by EDS.

Element mapping can indicate whether the metal soaps detected by FTIR formed preferentially at the interface, in which case the metal cation would be fairly evenly dispersed, or migrated to the interface. All cross-sections showed low levels of aluminum, which could not have been detected by XRF. Not only can aluminum form metal soaps with the oil, it is possible that it was added already in the form of aluminum-soap, as a dispersant or plasticizer.

In samples 12 and 24 (titanium white oil paint and lead white oil paint respectively) and the painting's cross-section, the aluminum is evenly dispersed throughout the layers. In sample 96 (verdigris oil paint), the Al is clearly concentrated at the top and bottom of the paint layer (figure 45). The light areas in the BSE image correspond to a sulfur-rich particle and a higher concentration of copper, which are shown in the complete element maps in appendix B. Since this verdigris paint (paint 18) was manufactured together with paint 1, the verdigris paint with the lead drier, paint 1 can be presumed to include aluminum as well. It is likely that the delamination is due to aluminum soap migration and not copper or lead soaps as had been originally assumed.

Figure 45: BSE image and aluminum mapping of sample 96.

Sample 96 is not actively delaminating; however, in the cross-section there is some delamination (figure 46). This could be due to the stress caused during cross-section preparation. It also strengthens the theory that the verdigris paint has a tendency to

delaminate. It delaminated first from sample 95, which was on P2, a smooth substrate, but under stress will delaminate from the rougher substrate as in sample 96.

Figure 46: BSE image of sample 96 taken at x250 magnification.

The dark area at the top of the ground layer (figure 45), is rich in carbon. It is an indication of oil or components of the oil leaching into the ground. This explains how the aluminum migrated to the lower interface. It would probably have migrated up with the evaporation of volatile components. It is not known in what form the aluminum was introduced into the paint or why the aluminum soaps would migrate so extensively.

In sample 98 (alkyd paint with TiO_2 and ZnO), there were many changes since the presumably homogeneous paint was applied. First the BSE image (figure 47) must be explained. The ground in this sample is a gel medium with no pigment or filler and so does not show up in the BSE image. The bottom of the ground can only be identified by the particles that stuck to it during sample preparation. There is cloudiness around the cross-section, which is material that came off the cross-section before the embedding

media had hardened. There is also extensive cracking throughout the paint layer, indicating extreme brittleness.

Figure 47: BSE image of sample 98 taken at x100 magnification.

The elemental mapping shows that the darker area at the top of the paint layer corresponds to an area with less pigment (selected elements in figure 48). The Ti has settled to the lower area, as seen in the left side of the titanium map. Interestingly, there is a clear divide between the pigment-rich area and the depleted area. The line between these sections shows high levels of Al, Si and O (in appendix B), so it is safe to assume it is aluminosilicate. It is not known why this middle layer formed or why it formed at that particular level. The zinc mapping corresponds to the cloudiness around the cross-section. The cloudy areas also include some calcium, probably from the calcium carbonate filler. The zinc also appears to have settled to the lower section of the paint layer, although this is slightly obscured by the zinc spreading into the embedding media.

Figure 48: Mapping of Zn, Ti, Si and Al in sample 98 by SEM-EDS.

It is possible that zinc soaps migrated to the interface with the ground and that this promoted delamination; however, since the zinc has moved into the embedding medium it is not possible to check on this cross-section. In the future, it may be useful to break a piece of sample 98 as cleanly as possible (perhaps by first placing it in liquid nitrogen), and examining the fracture cross-section without embedding the sample.

In the cross-section of sample 12 the following phenomena were observed (figure 49): There was some pigment settling seen in the Ti map, though without the clear demarcation of sample 96. The top of the ground layer is richer in carbon and oxygen, once more indicating oil or oil components leaching into the ground. The zinc (in appendix B), on the other hand, seems evenly dispersed. This means that the higher levels

of zinc soaps seen near the interface in the FTIR analysis are due to preferential formation of zinc soaps at the interface and not migration.

Figure 49: BSE image and EDS mapping of Ti, C and O in sample 12.

In the cross-section of sample 24 (figure 50) once more the main pigment, this time lead white, appears to have settled while the zinc remains evenly dispersed. This could be related to the nature of the zinc soaps, acting as dispersants. In this case it was interesting to note the very large Ca areas in ground H, which are the CaCO_3 particles detected by many of the other methods described above. There is no clear migration of organic components into the top of the ground; however, the ground is very rich in Ca and O because of the filler, and this may be making any such migration harder to detect. Based on these results, it is not possible to determine if the higher concentration of soaps near

the interface is due to lead soaps migrating or zinc (and perhaps lead) soaps forming near the ground.

Figure 50: BSE image and EDS mapping of Pb, Ca and Zn in sample 24.

The cross-section of the ‘brown/grey painting’ showed zinc in many of the layers (figure 51). The layers that are delaminating from each other are not the richest in zinc. The zinc, once more, appears evenly dispersed throughout each layer, as is the aluminum. Only one of the layers has lead in it and it is not at the delaminating interface. Since there are many thin layers instead of the single thick layer in the 1999 samples, more precise observations about pigment settling or leaching of media were not possible.

Figure 51: BSE image and EDS map of zinc in cross-section of ‘brown/grey painting’.

Unfortunately, no micro-FTIR analysis was done on this sample, so it is not known whether there is more zinc soaps in the delaminating layers than in others. It is also not known what the medium in each layer is. With the FTIR-ATR done at Queen’s, the white lower layer had been identified as oil and the upper paint as alkyd; however, both surfaces of the paint that had flaked off were analyzed and gave identical spectra. The SEM image and the photo-micrograph show that the flake was actually composed of eight or nine separate materials. The diamond used in the ATR objective may have too much depth penetration, creating a spectrum due to the average of several layers. Based on the observations made on the alkyd paint 19 (in sample 98), zinc white behaves very differently in an alkyd and an oil paint. More work is required to clarify this issue.

Chapter 5

Conclusions

This project's aim was to find the cause of oil-based paint delamination from acrylic grounds. Analysis of the 1999 samples made it possible to narrow down the possible factors and find what the delaminating ones had in common. Relevant factors were then checked in actual delaminating paintings to see if the same conditions were present there as well. The samples showed clearly that even when using high quality acrylic grounds, oil paint may delaminate from them. The determining factor is the metals present in the oil paint and not the type of ground. It was discovered that all delaminating paints, both in the 1999 samples and in the delaminating paintings, contained metal soaps, while paints that remained adhered to all different grounds, did not.

The metal soaps were due to lead, zinc or copper pigments reacting with fatty acids or to aluminum soaps which were probably added as a plasticizer or dispersant. The zinc soaps are one of the main causes of delamination as they were found in almost all the delaminating paints. The only exception was the verdigris paints (1 and 18). The severely delaminating paintings all contained high levels of zinc, indicating that more zinc can make the delamination worse. The presence of lead in addition to zinc may exacerbate the problem, as seen by the fact that all samples with paint 3 are delaminating, even though it contains less zinc than the titanium white paint 2. This may be related to the form the metal-soaps take when there are both zinc and lead soaps present.

All the lead white oil paints contained zinc, so it is not possible to determine the effect of lead alone; however, in alkyd paints, the lead white alkyd (paint 8) is well adhered, while the alkyd paint in the 'grey/brown painting' which contains both lead and zinc, is delaminating. Similarly, the titanium white alkyd without zinc (paint 7) is well adhered, while paint 19, which contains both TiO_2 and ZnO , is delaminating. The drying process of alkyds and oils is quite similar; therefore, it is safe to assume that lead white paints without zinc could adhere better and it is the zinc that caused the delamination. Paint manufacturers are probably aware of the detrimental effects of zinc on alkyd paints; since

alkyds dry quickly and can become quite brittle, adding zinc could make the paint much too brittle. This is why very few alkyd paints include the ZnO pigment.

The results of the micro-FTIR analysis showed higher concentration of metal soaps near the bottom of the paint layer. In the samples with zinc oxide, the SEM-EDS mapping showed the zinc is evenly dispersed. This means the zinc soaps formed preferentially at the interface, rather than migrating there. The micro-FTIR also showed more water near the interface. This could mean that water is absorbed into the paint layer and is collecting on top of the ground. This causes more hydrolysis, making more free fatty acids available for soap formation.

In the verdigris paints, the situation is different. The verdigris pigment does form metal soaps or other degradation products, making the whole paint brittle. The extensive changes were clear in cross-sections, since the colors changed and the paint layer is full of white crystal-like material and many voids in between, and dark green material at the surface. Once the paint has become very stiff and brittle, it is more likely to delaminate. The delamination is apparently due to aluminum soaps and not directly due to the verdigris pigment. This was concluded by the fact that aluminum is present only at the top and bottom of the paint layer. The FTIR spectra confirm that aluminum soaps are present. In this case the aluminum soaps were probably added when the paint was formulated and then they migrated to the interfaces, disrupting the adhesion with the ground.

Other variables could also have some influence on adhesion, for instance surfactant build-up, dirt, or grease accumulation. These issues could be influenced by the medium of the acrylic ground, which is not a significant factor in this study. No correlation was found between surfactant build-up and the distribution of delaminating samples; however, the results were not as conclusive or as qualitative as was required, so more work should be done before eliminating surfactants as an issue. The only factor which had a clear correlation with the distribution of delaminating samples examined was the roughness of the grounds.

AFM proved to be the most informative method of evaluating the roughness of the grounds. As expected, it was found that rougher grounds provide better tooth and so

improve adhesion. The roughness seems to be due mostly to the size and quantity of filler used in the ground. Grounds, or paints serving as grounds, that had little to no filler in them did not provide a surface to which the paint could easily adhere. Any paint with metal soaps painted over such a ground, delaminated. Similar phenomena were observed when the filler was made up of fine particles, as in grounds D and E. Paints with metal soaps over rougher grounds are more likely to remain adhered, though it is possible those will delaminate as well with time if more metal soaps form or migrate to the interface.

To summarize, based on the samples examined here:

- All delaminating samples contain metal soaps and particularly zinc soaps.
- Presence of lead in addition to zinc increases the problem.
- There is a high concentration of soaps at the interface which disrupts the adhesion.
- Rough grounds provide better adhesion than smooth ones. If the ground is rough, paint may adhere despite zinc in the paint.
- No correlation was found between surfactant build up on the surface of the ground and delamination.

Many of the conclusions in this paper are based on a small number of samples. In the future, it would be good to test more samples of the same materials, and perhaps additional samples of different paints and grounds. In particular, samples with lead white paint without zinc in it and an oil paint with only zinc white as the pigment should be prepared and tested to isolate the effects of those metal ions. Also the alkyd paint with zinc white should be painted over the same set of grounds used in the rest of the samples, to allow for more accurate comparisons of the effect of metal soap on alkyd and on oil.

If the future FTIR mapping of cross-sections confirms that zinc soaps form at the interface when more water collects there, it should be possible to control the delamination problem by controlling exposure to relative humidity. It is hoped that a greater understanding of the cause of such delamination will also lead to the development of better consolidation methods or perhaps improvements in paint and ground formulations that will prevent such loss of adhesion from occurring at all.

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Appendix A

1999 Samples

Samples composition and Condition

Sample #	Gesso type	Cast date	Paint type	Cast date	Delaminating
1	A	11-05-99	1	15-06-99	NO
2	B	19-04-99	1	15-06-99	NO
3	C	19-04-99	1	15-06-99	NO
4	D	09-04-99	1	15-06-99	NO
5	E	09-04-99	1	15-06-99	YES
6	F	14-04-99	1	15-06-99	NO
7	G	04-05-99	1	15-06-99	YES
8	H	06-05-99	1	15-06-99	NO
9	A	10-05-99	2	14-06-99	NO
10	B	15-04-99	2	14-06-99	NO
11	C	19-04-99	2	14-06-99	NO
12	D	09-04-99	2	14-06-99	YES
13	E	08-04-99	2	14-06-99	YES
14	F	14-04-99	2	14-06-99	NO
15	G	15-04-99	2	14-06-99	NO
16	H	06-05-99	2	14-06-99	YES
17	A	07-05-99	3	14-06-99	YES
18	B	11-04-99	3	14-06-99	YES
19	C	19-04-99	3	14-06-99	YES
20	D	09-04-99	3	14-06-99	YES
21	E	08-04-99	3	14-06-99	YES
22	F	15-04-99	3	14-06-99	YES
23	G	05-05-99	3	14-06-99	YES
24	H	05-05-99	3	14-06-99	YES

Sample #	Gesso type	Cast date	Paint type	Cast date	Delaminating
26	A	07-05-99	4	14-06-99	YES
27	B	16-04-99	4	14-06-99	NO
28	C	19-04-99	4	14-06-99	YES
29	D	08-01-99	4	14-06-99	YES
30	E	08-04-99	4	14-06-99	YES
31	F	14-04-99	4	14-06-99	NO
32	G	05-05-99	4	14-06-99	YES
33	H	06-05-99	4	14-06-99	YES
34	A	11-05-99	5	14-06-99	NO
35	B	15-04-99	5	14-06-99	NO
36	C	09-04-99	5	14-06-99	NO
37	D	08-04-99	5	14-06-99	NO
38	E	15-04-99	5	14-06-99	NO
39	F	08-04-99	5	14-06-99	NO
40	G	04-05-99	5	14-06-99	NO
41	H	06-05-99	5	14-06-99	NO
42	A	10-05-99	6	15-06-99	NO
43	B	15-04-99	6	15-06-99	NO
44	C	19-04-99	6	15-06-99	NO
45	D	09-04-99	6	15-06-99	NO
46	E	08-04-99	6	15-06-99	NO
47	F	14-04-99	6	15-06-99	NO
48	G	15-04-99	6	15-06-99	NO
49	H	06-05-99	6	15-06-99	NO
50	A	07-05-99	7	11-06-99	NO
51	B	11-04-99	7	11-06-99	NO
52	C	19-04-99	7	11-06-99	NO
53	D	09-04-99	7	11-06-99	NO

Sample #	Gesso type	Cast date	Paint type	Cast date	Delaminating
54	E	08-04-99	7	11-06-99	NO
55	F	15-04-99	7	11-06-99	NO
56	G	05-05-99	7	11-06-99	NO
57	H	05-05-99	7	11-06-99	NO
59	B	16-04-99	8	14-06-99	NO
60	C	19-04-99	8	14-06-99	NO
61	D	08-01-99	8	14-06-99	NO
62	E	08-04-99	8	14-06-99	NO
63	F	14-04-99	8	14-06-99	NO
67	B	16-04-99	9	15-06-99	NO
68	C	19-04-99	9	15-06-99	NO
69	D	08-01-99	9	15-06-99	NO
70	E	08-04-99	9	15-06-99	NO
71	F	14-04-99	9	15-06-99	NO
72	G	05-05-99	9	15-06-99	NO
75	B	16-04-99	10	11-06-99	NO
76	C	19-04-99	10	11-06-99	NO
77	D	08-01-99	10	11-06-99	NO
78	E	08-04-99	10	11-06-99	NO
79	F	14-04-99	10	11-06-99	NO
82	A	07-05-99	11	11-06-99	NO
83	A	11-05-99	12	11-06-99	NO
84	G	05-05-99	13	11-06-99	NO
85	H	06-05-99	13	11-06-99	NO
86	F	14-04-99	14	11-06-99	NO
87	F	14-04-99	14	11-06-99	NO
88	A	10-05-99	15	15-06-99	NO
89	H	06-05-99	16	15-06-99	NO

Sample #	Gesso type	Cast date	Paint type	Cast date	Delaminating
90	P1	26-02-99	10	10-06-99	NO
91	P2	26-02-99	20	10-06-99	NO
92	P3	26-02-99	17	21-04-99	NO
93	P4	02-03-99	17	21-04-99	NO
94	P5	26-02-99	17	21-04-99	NO
95	P2	02-03-99	18	10-06-99	NO
96	P1	02-03-99	18	10-06-99	NO
97	P5	02-03-99	19	26-04-99	NO
98	P4	26-02-99	19	10-06-99	YES

Key to the Samples

All names are listed as on the tubes or jars.

Grounds

Type A. Aaron Brothers White Gesso

Type B. Winsor & Newton Clear Gesso Base for Acrylics

Type C. Winsor & Newton Acrylic Gesso Primer

Type D. Utrecht Artist's Acrylic Gesso

Type E. Utrecht Professional Acrylic Gesso

Type F. Liquitex Acrylic Gesso

Type G. Dick Blick Artists' Acrylic Gesso

Type H. Grumbacher Artist's Acrylic Gesso

Paints

- Type 1. Custom manufactured verdigris in linseed oil with 1.6% litharge (PbO, a drier)
- Type 2. Winsor & Newton Artist's Oil Colours, Titanium White
- Type 3. Grumbacher Artist's Oil Colors, Flake White
- Type 4. Winsor & Newton Artist's Oil Colours, Flake White
- Type 5. Winsor & Newton Artist's Oil Colours, Raw Sienna
- Type 6. Custom manufactured cobalt blue in cold pressed linseed oil
- Type 7. Winsor & Newton Griffin Alkyd, Titanium White
- Type 8. Winsor & Newton Griffin Alkyd, Flake White
- Type 9. Gamblin Artists' Oil Colors, Ultramarine
- Type 10. Winsor & Newton Griffin Alkyd, Raw Sienna
- Type 11. Winsor & Newton Griffin Alkyd, Cobalt Blue
- Type 12. Winsor & Newton Griffin Alkyd, Light Red Oxide
- Type 13. Winsor & Newton Griffin Alkyd, Yellow Ochre
- Type 14. Winsor & Newton Griffin Alkyd, Terre Verte
- Type 15. Gamblin Artists' Oil Colors, Indian Red
- Type 16. Gamblin Artists' Oil Colors, Yellow Ochre
- Type 17. Custom manufactured Burnt Sienna in cold pressed linseed oil
- Type 18. Custom manufactured verdigris in cold pressed linseed oil
- Type 19. Gamblin Alkyd White
- Type 20. Winsor & Newton Griffin Alkyd, Burnt umber

Other Materials used as grounds

- Type P1. Liquitex Basic Titanium White
- Type P2. Golden Artists Acrylic Titanium white
- Type P3. Grumbacher Academy Titanium White
- Type P4. Dick Blick Gel Medium
- Type P5. Grumbacher Clear Blend Acrylic Medium

Appendix B

SEM-EDX element mapping

Sample 12 (paint 2 over ground D)

Electron Image 1

C Ka1_2

O Ka1

Mg Ka1_2

Al Ka1

Si Ka1

P Ka1

S Ka1

Ca Ka1

Ti Ka1

Zn Ka1

W La1

Sample 24 (paint 3 over ground H)

Electron Image 1

C Ka1 2

O Ka1

Al Ka1

Mg Ka1 2

Ca Ka1

Ti Ka1

Zn Ka1

Pb La1

Sample 96 (paint 18 over ground P1)

Electron Image 1

C Ka1_2

O Ka1

Al Ka1

S Ka1

Si Ka1

Ca Ka1

K Ka1

Cl Ka1

Ti Ka1

Cu Ka1

Sample 98 (paint 19 over ground P4)

Electron Image 1

C Ka1_2

O Ka1

Al Ka1

Si Ka1

S Ka1

Ca Ka1

Ti Ka1

Zn Ka1