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## A COLLOIDAL DESCRIPTION OF TEMPERA AND OIL PAINTS, BASED ON A CASE STUDY OF ARNOLD BÖCKLIN'S PAINTING VILLA AM MEER II (1865)

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### Abstract

**To better understand the painting technique of a given period, information from different sources are usually combined: written statements by the artist or his contemporaries, art technological study of paintings, and chemical analysis. However, does the information obtained from different sources fit together and form an integral picture? Based on a case study of a painting by Arnold Böcklin this question was evaluated. It was found that the correlation between binding media and the properties of paints manufactured from them is not clear and straight-forward as is usually believed. To understand these correlations, colloid chemistry is indispensable. This paper presents concepts of a colloidal description of paints consisting of pigment, egg and drying oil. Various methods for the preparation of such paints and their resulting properties are discussed considering aspects of colloid chemistry and rheology, such as stability of emulsions, gel formation, interactions between pigment particles and binders etc. This paper connects a broad variety of information, aspects, models and hypotheses that cannot be discussed in complete detail here. It is intended as a starting point for future discussions and research into various aspects of paints and painting.**

### 1 Introduction

As part of a research project into tempera painting around 1900, paintings by Arnold Böcklin (1827-1901) were studied. First, a review of the written sources was conducted followed by a careful technological study of selected paintings. As a third component, cross-sections and samples for binding media analyses were taken from several paintings. Finally, paints were reconstructed based on the information obtained. Thus, data were collected in four ways: written sources, technological study, binding medium analysis and reconstruction of paints.<sup>1</sup> As will be shown below, results obtained from the first three components appeared to completely contradict each other. It seemed that a part of the data was wrong and a uniform interpretation impossible. However, an unexpected solution for the problems encountered was found after consulting recent literature on colloid chemistry and food technology: Paints are colloidal systems and must be treated as such. As a consequence, their properties sometimes differ quite considerably from what is generally expected if the laws of colloid chemistry are disregarded. For example, whether a paint containing both egg and oil as binders can be diluted with water or oil of turpentine depends less on the relative amounts of egg and oil, and more on other factors, as will be discussed below.

Paints are colloidal systems – this was obvious at the beginning of the 20<sup>th</sup> century, when scientists began to systematically study colloids and their properties,<sup>2,3,4</sup> and books are still being written on this topic today.<sup>5</sup> However, in conservation science the consequences of this concept seem to be mostly forgotten, overlooked or just ignored, although Mayer for example described these aspects very clearly,<sup>6</sup> and important aspects are also mentioned by Gettens and Stout.<sup>7</sup> Fortunately, both colloid chemistry and

food technology have made dramatic progress during the last 20 years, and there is a wealth of information that can easily be obtained from the current literature.

This paper describes some important properties of colloidal systems, which are then compared with the results of the technological study of the painting *Villa am Meer II*, painted by Arnold Böcklin in 1865. Consequently, the properties of mixtures of egg and oil binders are discussed and the parameters relevant for the formation of emulsions and gels evaluated. This concludes with the description of oil and tempera paints based on colloidal principles.<sup>1</sup>

## 2 Properties of colloidal systems relevant for paints

Colloids are bulk materials that are finely subdivided in a characteristic way: it is mainly the particle dimension that governs the properties of colloidal systems.<sup>8,9</sup> Ostwald described in 1914 that objects reveal peculiar properties and remarkable phenomena if they are too small to be seen under a microscope, but too big to be regarded as molecules.<sup>10</sup> These colloidal systems cannot be treated as normal, homogenous systems,<sup>11</sup> they represent a special, “colloidal dimension”, which he called “the intermediate realm of colloids” (*Zwischenreich der Kolloide*) and “the world of neglected dimensions” (*Welt der vernachlässigten Dimensionen*).<sup>10</sup> In a practical sense, any object that has a linear dimension in the range 1 nm to 1 µm can be defined as a colloidal object. These objects include finely subdivided solid particles, but also fine liquid droplets or even macromolecules such as proteins or polysaccharides. Examples of colloidal systems are emulsions, foams, suspensions, aerosols, smoke and fog, as well as gels.

Most pigment particles in traditional paintings have diameters larger than 1 µm. However, it has to be kept in mind that not all three spatial dimensions of the particle need to be shorter than 1 µm to reveal colloidal behaviour. In addition, the size limit of 1 µm is somewhat arbitrary. Berg, for example, sets a size limit of 10 µm and states that emulsions and suspensions with particle diameters up to even several tens of µm act like colloids in many respects.<sup>12</sup> As a consequence, pigments do show colloidal behaviour, although this will certainly be more important for the smaller particles and less so for the larger ones. Binding media containing proteins or polysaccharides (plant gums, starch etc.) will always display colloidal behaviour due to the large size of these macromolecules.

### 2.1 Influence of particle size, inter-particle forces and gel formation

The physical forces that determine the behaviour of macroscopic particles are different compared to very fine particles of colloidal dimensions. For example a macroscopic piece of charcoal will obviously not float in the air but fall to the ground due to gravity. Nevertheless, finely subdivided particles of charcoal can float, as in smoke. Due to the very small mass of small particles, gravitational attraction is not the crucial factor, but collisions with other particles and molecules of the atmosphere, leading to Brownian motion. Similar aspects are relevant for small pigment

particles in paints. If particles are dispersed in binding media, inter-particle forces may become relevant, for example hydrogen bonding between particles or Coulomb repulsion or attraction between electrostatically charged pigment surfaces. For small particles these forces will be much more dominant on short distances than gravity.

For example clay minerals can possess positive and negative surface charges depending on their chemical composition and particle shape.<sup>13</sup> At rest, clay particles in aqueous solutions form gels due to their strong electrostatic interactions, thus the mass does not flow (Figure 1). Gels – the term is derived from gelatine – may be defined as materials that possess a certain degree of stiffness (gel strength).<sup>13</sup> Gels are dimensionally stable but easily deformable disperse systems, which are rich in liquids and consist of at least two components, a solid and water (hydrogels) or another liquid (lyogels).<sup>14,15</sup> In general, small particles may form gels if there are attractive forces between them. Besides clay minerals, fine ground quartz or amorphous silica particles are another example for such behaviour. Depending on pH, the silica surface may possess positive or negative charges, usually leading to repulsive inter-particle forces. Such particles are able to move, slide and roll past each other without coming in actual contact.<sup>13</sup> At a pH with neutral surface charge, the silica particles tend to aggregate and form gels, either by direct hydrogen bonds between Si-OH groups of neighbouring particles or water molecules bridging them.<sup>14</sup> The latter is especially important for quartz suspensions in hydrophobic solvents because small amounts of polar solvents such as water can stabilise network structures in nonpolar solvents.<sup>13,14</sup> Because the stability of the network can be manipulated by surface charges, charged molecules that adsorb to the surface of the particles also have a large influence on gel strength and stability.

At last it is important to note that a gel can be very voluminous, with very large pores between the strands of particles filled with solvent (Figure 1). This means that a gel does not flow although a very high amount of liquid solvent may still be present. Hermansson states that a gel can contain more than 99% water and still behave like a solid that does not flow.<sup>16</sup> Gelatine, for example, can form dimensionally stable gels at 0.6% gelatine and 99.4% water.<sup>15</sup> Egg white, as another example, consists of 90% water and turns into a gel during boiling. The water content does not change during cooking.

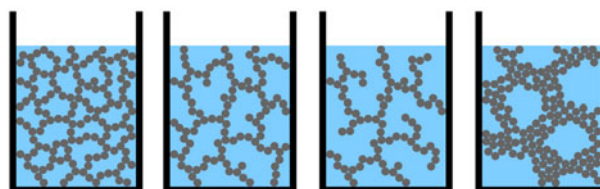


Figure 1: Particles suspended in solvents can form gel networks if there are attractive inter-particle forces. The pores of the network are filled with the solvent. Particles are not necessarily spherical but may be shaped like rods, needles or disks, examples of such gel forming materials are clay minerals or finely ground quartz. However, the “particles” may also consist of protein or polysaccharide macromolecules or their clusters. The structure and properties of the gel do not only depend on the size of the particles, but also on the pore sizes, thickness of strands and connectivity of the strands.

The formation of gel networks may be reversible, a phenomenon that is then called thixotropy: Thixotropy is the property of dispersed systems to become more fluid (lower viscosity) under the influence of mechanical forces (stirring, shaking, shearing) and to regain the higher viscosity at rest. It is caused by fragmentation of the network structure by the mechanical forces. At rest, these fragments are pushed into new contact positions by the Brownian motion of the solvent particles and reaggregate to the volume-filling network.<sup>13,17</sup> Many paints are well known to exhibit thixotropic behaviour. This means that the pigments, the binder or both form internal structures that increase the paint's viscosity. If the paint is applied by a brush, the mechanical force destroys the gel network structures and the paint becomes more fluid. After the application the gel is formed again and thus it is possible to produce impastoed paints that preserve the structure of the brushstroke in the dried paint.

## 2.2 Influence of interfaces

The examples above demonstrate that the viscosity and rheology (flow behaviour) of materials consisting of small solid particles and a liquid can be determined by strong inter-particle forces. In addition, colloidal aspects of macromolecular binding media can also be equally important. This is illustrated using the example of mayonnaise. As is well known, mayonnaise consists basically of oil and raw egg. Although both components are liquid, mayonnaise is not. Thus we observe a peculiar rheological behaviour, even without any solid particles. The reason for this is that the oil phase is dispersed into fine droplets, forming an emulsion (Figure 2). The droplets are so densely packed that they become deformed and cannot move against each other.<sup>17,18</sup> Therefore mayonnaise is stiff, although all its components are liquid. This peculiar property of mayonnaise cannot be explained by the properties of any of its single components, but only by the spatial distribution of the individual phases and the stability of the interfaces which are stabilised by the emulsifiers in the egg yolk. The consideration of phase distribution is a colloidal description of the system. Mayonnaise is an excellent model for paints containing a mixture of egg and oil as a binder, and the phenomena just described have to be considered when discussing the rheological properties of fresh paints, how they can be applied

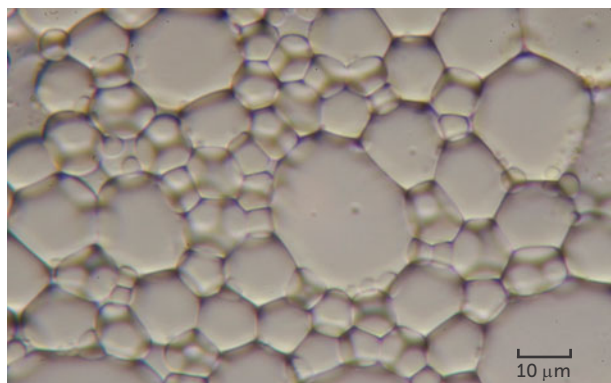


Figure 2: Microscope image of mayonnaise, droplets of sunflower oil in aqueous solution (raw egg and vinegar). Mayonnaise is buttery and does not flow although all its components are liquid. This surprising rheological property cannot be explained by the properties of the individual phases but only by the spatial distribution of the oil phase in the emulsion (droplets) and the stability of the interfaces, which prevents coalescence of the droplets. Picture: Martin Mach, Munich.

with a brush, whether they flow readily after application and to what extent a brushstroke structure is preserved in the dried paint.

From the examples presented it is clear that colloidal systems are not primarily determined by the physical properties of their bulk components as one would intuit. Instead it seems that they are governed by other physical laws than those valid for macroscopic objects. This mainly arises from the fact that systems containing lots of very small objects such as particles, droplets or macromolecules, exhibit a very large area of internal surface, or interfaces – which probably emphasises better that an object is not regarded as isolated but surrounded by a medium, a liquid, a solvent or binder, which may consist of several materials and additives. In colloidal systems, as in mayonnaise, the influence of the surfaces, their properties and their interactions with the medium and its components become so important that these determine the properties of the whole system. Therefore, the word “colloidal” does not denote a material property but a state.<sup>8,19</sup> General important parameters of surfaces and their interactions with the medium include their geometry and structure, surface tension, charge density, and the extent to which these parameters respond to changes in the medium, including salt concentrations, organic additives, and pH, for example.<sup>9</sup>

Now that some principles of colloid chemistry have been introduced, a case study of a painting by Arnold Böcklin will shed more light on how these principles can be used to interpret and correlate information obtained from statements of artists on their paintings and how they are made, technological examination and binding medium analyses. Each part of the information obtained creates its own specific viewpoint which may seem to contradict the others if the colloidal nature of paints is not considered.

## 3 Case study: Arnold Böcklin, *Villa am Meer II* (1865)

### 3.1 Historic written sources

The Swiss painter Arnold Böcklin (1827-1901) painted *Villa am Meer II* (Figure 3) in 1865, during his second stay in Rome. We have unusually precise knowledge of how the painting was executed from the diary of Rudolf Schick (1840-1887), which is why it is used here as a case study. Schick was a young painter who met Böcklin in Rome in 1865 and stayed in close contact with him during 1866, 1868 and 1869. In his diary, he documented various discussions and observations on Böcklin's painting process and painting materials in a very accurate manner.<sup>1</sup> According to Schick, Böcklin prepared all of his paints himself and did not use tube paints at that time. With regard to *Villa am Meer II*, Schick wrote in his diary on February 18, 1869:<sup>20</sup> “*Sky and ocean he painted with Leimfarbe, then continued with oil paint in the other parts, and did not touch again the areas painted first.*” (“*Luft und Meer hätte er mit Leimfarbe gemalt, wäre in den anderen Sachen dann mit Oelfarbe fortgefahren und hätte die erstgemalten Teile nicht wieder berührt.*”) This procedure was confirmed by the German painter Franz von Lenbach, who was in close contact with Böcklin in Rome, even temporarily sharing a studio with him. While Böcklin was working on *Villa am Meer II* in 1864,





Figure 3: Arnold Böcklin, *Villa am Meer II*, 1865, Bayerische Staatsgemäldesammlungen (Inv. No. 11536), 123.4 cm x 173.2 cm. Picture: Bayerische Staatsgemäldesammlungen.

Lenbach reported in a letter to Count Schack,<sup>21</sup> who had commissioned the painting, that it was executed using a “well-established tempera-oil painting technique” (“längst erprobte Tempera-Oel-Malerei”).

The term *Leimfarbe* used by Schick may be somewhat misleading and is difficult to translate. Although *Leim* literally means (animal) glue, *Leimfarbe* in Böcklin's terminology generally denotes an aqueous paint that could be diluted with water.<sup>22</sup> Thus *Leimfarbe* does not necessarily contain animal glue, which is in accordance with the general use of the term *Leimfarbe* during the 19<sup>th</sup> century.<sup>23</sup> Furthermore, Böcklin used the terms *Leimfarbe* and *Tempera* synonymously for aqueous paints.<sup>22</sup> In agreement with this historic use of the term “tempera”, it will be used in this text as an umbrella term for paints that can be diluted with water, but not with oil of turpentine. Accordingly, oil paints can be diluted with oil of turpentine, but not with water.

### 3.2 Technological examination

The technological examination of *Villa am Meer II* correlates well with the information that the sky and ocean were painted with aqueous paints, whereas the landscape was painted in oil. At this point, only a short summary of the painting's art technological examination is given, focusing on paint characteristics that are relevant for this publication. Böcklin's painting technique in Rome will be discussed in more detail elsewhere.<sup>24</sup>

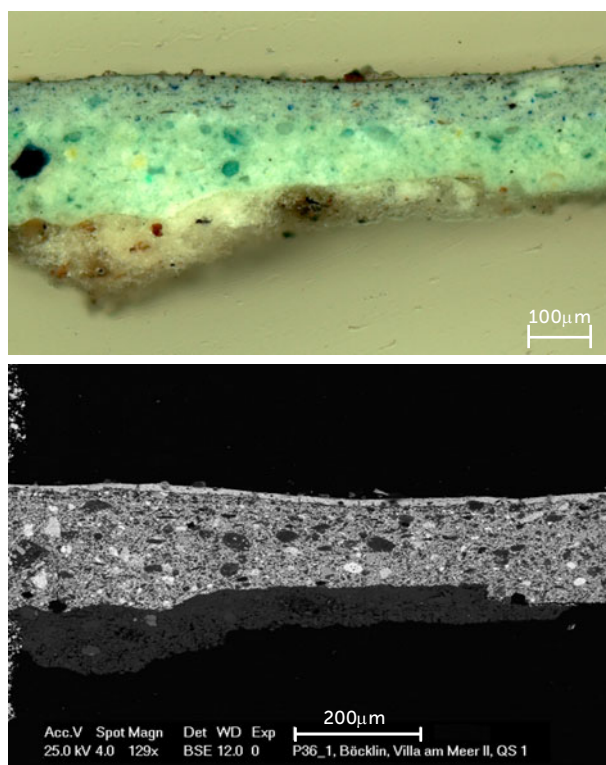


Figure 4: Cross-section of the violet-grey sky, *Villa am Meer II*, visible light (top) and BSE image from SEM-EDX (bottom). Above a white ground, a greenish and a bluish dense paint layer are visible. A third, thin violet-blue layer can best be seen in the BSE image (bright).



The sky was painted with three subsequent opaque paint layers that were uniformly spread over larger areas (Figure 3). These layers are well separated in the cross-section, which indicates that each layer was applied after the previous one had dried (Figure 4). These rather thick and obviously viscous paints were applied horizontally using a broad brush. The brushstrokes are still clearly visible in the dry paint layers. Furthermore, pinholes caused by air bubbles were observed under the stereomicroscope in some areas of the sky (Figure 5). The formation of air bubbles during the preparation and application of paints, which remain stable until the paint is dry, is an empirically well-known phenomenon mainly for aqueous paints. Thus bubbles may be indicative of originally aqueous paints. All the described properties of the sky's paints

can generally be regarded as typical for tempera paints based on aqueous binders that dry quickly and allow rapid painting of large areas.

Details in the sky, such as clouds, are reduced to a minimum, which assists the impression of a relatively uniform and bright blue-grey area of paint. In contrast, the painting of the landscape gives a more naturalistic impression (Figure 6 top). Accurate modelling of details results in differentiated paint structures, as for example the combination of translucent glazes over opaque underpainting. Altogether, the layer build-up is more heterogeneous than in the sky (Figure 6 bottom). The often impastoed underpainting has different functions: On the one hand it served to lay out a first coloured, rough sketch of the composition, on the



Figure 5: Microscope image of the sky: air bubbles are visible in the dried paint.

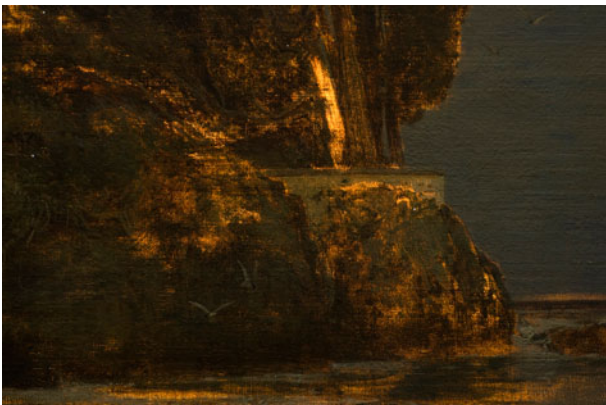


Figure 6: Detail of sky and landscape: The modelling of the landscape is more detailed than that of the sky (top). In transmitted light (bottom), the homogeneous paint layers of the sky contrast with the heterogeneous layer build-up of the landscape. Picture (bottom): Bayerische Staatsgemäldesammlungen.



Figure 7: Detail of the rocks: Thin glazes of red, dark grey, brown and green are applied on top of the bright and structured impasto underpaint layer.



Figure 8: Microscope image of the rocks: In the right upper edge of the picture, air bubbles in the underpaint are visible. Glazes lie in the voids of the rough structure of the underpaint.



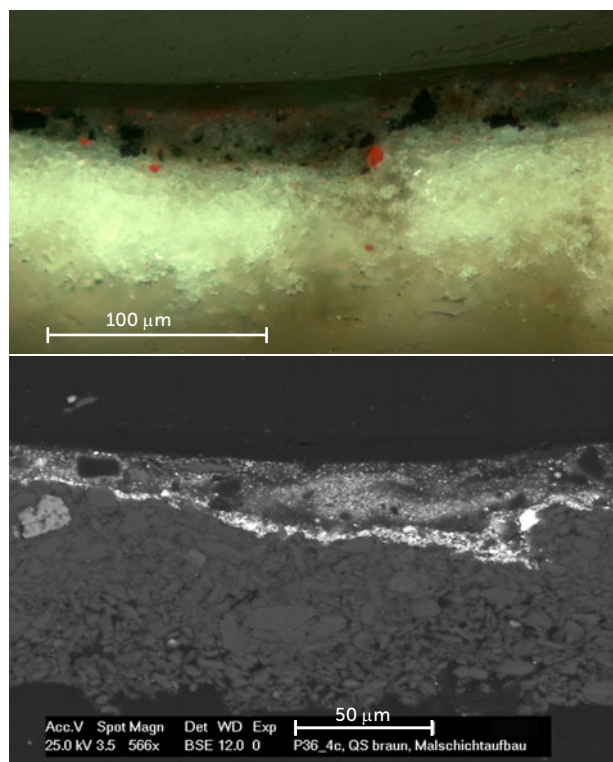


Figure 9: Cross-section of a brown area in the landscape (left edge), *Villa am Meer II*, visible light (top) and BSE image from SEM-EDX (bottom). Above a white ground, several grey-brownish layers painted largely wet-in-wet (cf. BSE image) are visible. The brown translucent glazes on top of the opaque layers (dark in BSE image) reveal an intense fluorescence in UV light (not shown).

other hand it helped to structure the surface of the different paint areas, as can be seen, for example, in the rocks (Figures 7 and 8). The underpaints are lastly covered by generally thin paint layers, often translucent glazes, that do not show any air bubbles and are worked wet-in-wet (Figures 7-9). These are characteristics usually regarded as typical for oil painting.

Despite the fact that the landscape seems to be painted with oil paints, some of the underpaints contained air bubbles (Figure 8), as observed in the sky. Therefore it seems likely that Böcklin first underpainted the landscape at least partially with tempera and continued painting the details in oil. Such a combined technique is also described by Schick<sup>25</sup> and would explain how Böcklin was able to complete the *Villa am Meer II* within only three weeks.<sup>20</sup>

### 3.3 Binding media analyses

Whereas written sources and technological examination both point to the same conclusions, the results of binding media analyses seemed to completely contradict them at first sight. Samples for analysis were taken layer-by-layer from the sky and the landscape at the same locations as the cross-sections (Figures 4 and 9). The identified binding media are reported

in Table 1. Analyses were performed by gas chromatography /mass spectrometry (GC/MS) after a step-wise extraction of the samples with solvents of increasing polarity: isooctane, methanol, methanol/chloroform 3:7, methanol/oxalic acid (anhydrous, 10 wt%) and water. Proteins were analysed after hydrolysis with constant-boiling hydrochloric acid by ion exchange chromatography (amino acid analysis).<sup>26-28</sup>

Surprisingly, the same binders were found in all samples, but in varying ratios: drying oil, copaiba balsam and egg. Because animal fats from the yolk were identified, egg yolk or whole egg was used, however, no further differentiation between these two was possible. The copaiba balsam contained eperuic acid, kauranoic acid, copalic acid, kauranoic acid and pinifolic acid, thus it most likely originates from *Copaifera langsdorffii* L.<sup>29</sup> No polysaccharides were detected in the analysed samples. Some oil and copaiba balsam penetrated into the ground layer, which is bound with animal glue. The varnish consists of dammar with a bit of beeswax, it is clearly non-original because it is also found in areas of paint losses. The synthetic plasticisers originate most likely from the technical-grade solvent of the later varnish, as these substances are easily extracted from plastics in gaskets and storage containers. Table 1 it shows that the varnish materials penetrated deep into the painting during revarnishing.

Böcklin used linseed oil in the paints of the sky and in the upper paint layers in the landscape, whereas he used walnut oil in the lower layers of the landscape. Schick reports that Böcklin used walnut oil in combination with copaiba balsam to mix his oil-resin paints.<sup>30</sup> The fact that this combination was found only in samples of the landscape may support the quotation that Böcklin painted this area with *oil paints*. The abundance of copaiba balsam is not surprising, because this material is mentioned many times as a painting and varnishing medium by Schick.

	Sample	Original binders				Other binders		
		Copaiba balsam	Drying oil & fat	Proteins	Polysaccharides	Beeswax	Dammar	Phthalate plasticisers
Sky, top of painting	Varnish and light violet	+++	++ linseed	++ egg		(+)	+	(+)
	Light blue	++	+++ linseed	+ egg	-	(+)	(+)	
	Light blue and green	+	+++ linseed	+ egg	-	+(+)	+	+
	Ground layer		+	+++ animal glue		+	+	
Landscape, brown foreground (left side)	Varnish		+			+(+)	++	+
	Brown glaze	++	++ linseed	+ egg	-	+(+)	+	(+)
	Grey paints (wet-in-wet)	+++	+++ nut oil	++ egg	-	+(+)	(+)	
	Light grey	+++	+++ nut oil	++ egg			(+)	(+)
	Ground layer	++	+	+++ animal glue			(+)	

Table 1: Binding media identified in Arnold Böcklin's *Villa am Meer II* (1865). Two areas were sampled corresponding to the cross-sections in Figure 4 and 9, layers were mechanically separated to the extent possible. "Other binders" are presumably contaminations from conservation treatments and non-original varnishes.

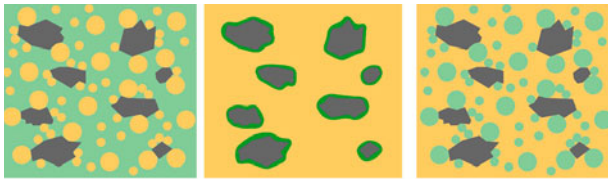


Figure 10: Paints consisting of egg (green phase) and oil (light brown). If the pigment (grey) is directly ground with a mixture of egg and oil, an O/W emulsion is formed (left, cf. Figure 12). If the pigment is ground with egg first, then dried and mixed with oil, a dispersion of protein-coated pigments results (middle). The formation of W/O emulsions (right) has been proposed, but must be seriously questioned because it would need a suitable emulsifier, which does not seem to be present in egg (see discussion in text). The egg is depicted light green when diluted with water, and dark green when dried. The differences between the paints – the spatial distribution of the phases or the amount of water – lead to completely different paint properties.

The ratio of resin to oil is variable in different paints (Table 1) and could be related to the method of application. Böcklin might have added the copaiba balsam directly to the oil in varying ratios. However, Schick also describes its direct use as part of Böcklin's working process: before he overpainted areas of paint that had already dried, he rubbed the surface with copaiba balsam (with or without oil). Copaiba softens the upper and lower paint and therefore results in a better adhesion and interconnection of the layers.<sup>31</sup> It is difficult to determine whether this use of copaiba results in unpigmented intermediate layers or not. It should be noted that Böcklin used to overpaint the freshly applied copaiba with sufficient oil paint without resin to "consume" ("aufzehren") the balsam.<sup>31</sup> In other words, the copaiba would probably be mixed with the upper paint by the action of the brush without necessarily leaving an intermediate layer.

#### 4 Discussion of paint systems containing both aqueous and oleaginous binders

##### 4.1 Possible interpretations of Böcklin's paints

Because oil, resin and egg were detected as binders for the sky, Böcklin's *Leimfarbe* can be identified here as "egg tempera with added oil and resin", and is thus an emulsion of an oil/resin mixture in egg and water (Figure 10 left). Although a part of the copaiba – or even all of it – might be explained by overworking the dried tempera paints with resin, as described above, it seems extremely unlikely that the same is true for all of the oil. First, the amount of oil and resin in the paints of the sky seems far too large and the amount of egg too small for egg being the sole initial binder (Table 1). Second, the impregnation of extremely lean egg tempera paints with oil results in a massive change in

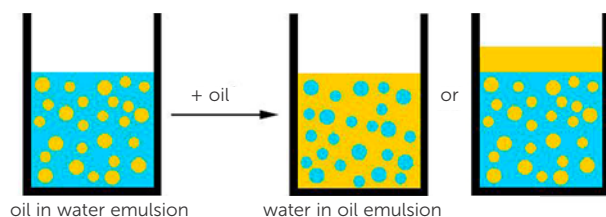


Figure 11: Emulsions can only be diluted with their continuous phase. If oil is added to an O/W emulsion (left) without being dispersed, a separate phase is formed (right). Only if the emulsifier is able to stabilise both O/W and W/O emulsions, a phase inversion takes place at some point (middle). Otherwise, the non-homogeneous system is formed (right).

colour hue and opacity of the paints, which severely complicates painting. Therefore it makes much more sense to add oil (and possibly resin) to the egg tempera right from the beginning.

Surprisingly, all the paints of the landscape contain significant amounts of egg besides the oil and resin, including the glazes and the paints blended wet-in-wet that are all considered to be oil paints (Table 1). However, this is not so uncommon: egg in addition to oils is found in oil paints of painters from many countries and centuries such as Stefan Lochner, Albrecht Dürer, Leonardo da Vinci, or Rembrandt van Rijn to only mention a few.<sup>26-28,32</sup> This was explained by Koller *et al.* as egg being added during washing, cleaning and other preparation steps of the pigments:<sup>26,33</sup> the egg proteins remain on the surface of the pigment particles in a solid state after the evaporation of the water. If these pigments are ground with oil immediately before painting, the protein-coated particles are dispersed in oil, and the result is an oil paint containing protein (Figure 10 middle). Whereas such a pigment and paint preparation seems likely in a workshop of the 15<sup>th</sup> to 17<sup>th</sup> centuries,<sup>33</sup> it is rather improbable that artists in the 19<sup>th</sup> century prepared their pigments the same way. In addition, Schick does not describe such a systematic procedure for Böcklin. Clearly there must be other explanations for protein binders in oil paints. For Rembrandt, for example, the addition of rather small amounts of aqueous binders to the oil has been proposed, either during grinding of the pigment or directly on the palette during the actual painting. This was correlated with the rheological properties of Rembrandt's paints and it was suggested that a two-phase system is formed, possibly the water being emulsified in oil.<sup>32</sup> This suggestion is in agreement with the emulsion theory that was used in German 20<sup>th</sup> century art technological discussions.<sup>34</sup> However, it must be stated that this theory, which will be called "symmetric" emulsion theory here below, is in conflict with basic principles of colloid chemistry. This will be discussed in the subsequent sections.

##### 4.2 The "symmetric" emulsion theory

In 20<sup>th</sup> century German literature on painting, "tempera" was defined as an *emulsion* of aqueous and oleaginous binders.<sup>34</sup> As is well known, oil and water form a system consisting of two phases. If an emulsifier is added, an emulsion is formed with a continuous and a dispersed phase (droplets). Generally two types of emulsions may be produced, oil-in-water (O/W) and water-in-oil (W/O) emulsions (Figure 10 left and right). It is important to point out that an emulsion can only be diluted with its continuous phase; if the dispersed phase is added (cf. Figure 11), it would need to be dispersed properly to result in a homogenous system again. Therefore, the type of emulsion defines the diluent for the paint. In accordance with the German definition of the 20<sup>th</sup> century, Doerner, for example, uses the terms "*magere, wassermischbare Tempera*" ("lean, water-miscible tempera") for O/W emulsions and "*ölmischbare, fette Tempera*" ("oil-miscible, fatty tempera") for W/O emulsions.<sup>35</sup> It has to be stressed that we do not follow Doerner's definitions here. Instead, we follow the terminology used by Böcklin and his contemporaries in the 19<sup>th</sup> century, which was based on dilutability, as introduced above. With regard to Böcklin's use of these terms, water-miscible O/W

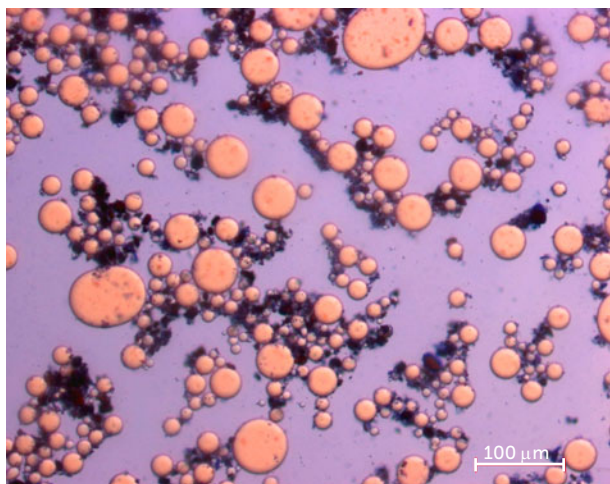


Figure 12: Microscope image of Kassel brown ground with a binder consisting of egg yolk and linseed oil. The aqueous phase was stained blue, the oil was stained red. The paint obviously consists of an O/W emulsion. The pigment is located in the aqueous phase, but shows interactions with the oil droplets, because these are preferentially clustered around the pigment particles. The colour contrast in the image was enhanced using Adobe Photoshop.

emulsions are tempera paints, but oil-miscible W/O emulsions would be oil paints.

It is usually expected that both O/W and W/O emulsions may be produced from mixtures of aqueous and oleaginous binders, and the binders' relative quantities determine which emulsion type is formed.<sup>34,36</sup> Because in this case the mixture is equally able to form either emulsion type depending only on the ratio of phases, it is here called "symmetric". According to this model, both tempera and oil paints can be obtained as emulsions of egg and oil, depending on their relative ratios.<sup>11</sup> If this were true though, the egg/oil ratio must be higher in the tempera than in the oil paint. However, the opposite is true for the analysis of Böcklin's paints in Table 1. In other words, the egg tempera contains less egg and more oil than the oil paint (with respect to their ratios). In addition, the absolute values of egg protein are very low for the paints considered to be egg tempera. If the symmetric emulsion model of tempera and oil paints were valid, the material analyses would point to the interpretation that the landscape was painted with egg tempera, and the sky with oil paints, contrary to Schick's statement and the technological examination. However, application of principles of colloid chemistry leads to the conclusion that many *oil paints* produced with egg and oil are probably not emulsions but suspensions, and therefore the symmetric emulsion model has no relevance. Accordingly, the egg/oil ratio found for *Villa am Meer II* would not be contradictory to Schick's statement and the conclusions of the technological study, as will be discussed in the following sections.

#### 4.3 On the ratio of aqueous and oleaginous phases and the stability of emulsions

When egg yolk or whole egg was mixed with oil and water for the first reconstructions of paints in this study, only O/W emulsions (tempera) were formed. To obtain this information coloured samples were prepared: the oil was stained red with "Wax Red 5B02" (C.I. Solvent Red 27, Kremer Pigmente, Aichstetten, Art. No. 35300), and the water used for the emulsion was

stained blue with normal ink for pens from Pelikan (Hanover). In the microscope, the dispersed and continuous phases can be distinguished (Figure 12). No diluted W/O emulsions could be produced analogous to the image depicted in Figure 12. This is also true for emulsions containing a large amount of oil: the maximum oil content of an O/W emulsion was obtained after adding 1 part of oil to one part of egg yolk, if more oil was added, the emulsion became unstable (see below). However, egg yolk consists of ca. 50 parts water, 33 parts lipids and 17 parts proteins.<sup>37</sup> If 100 parts oil (lipids) are added, the O/W emulsion contains 133 parts lipids and 17 parts protein, thus after evaporation of the water, the mixture consists of 89% lipids and 11% proteins. In other words, a paint consisting of almost 90% oil according to the analysis could still have been a tempera paint (O/W emulsion) when fresh, and a high oil content in a paint is thus clearly not always an indication of an oil paint. This can already be seen in Figure 2: mayonnaise is still an O/W emulsion although it consists predominantly of oil, and there is only a thin film of water between the droplets.

The fact that mixtures of oil and egg seemed to form O/W emulsions exclusively up to a very high amount of oil was surprising at the beginning of the study. Nonetheless, it soon became obvious that this is in accordance with the laws of colloid chemistry. To obtain a stable emulsion, the interface between the phases must be stabilised and protected from flocculation and coalescence. Therefore the emulsifier plays the most important role, which is reflected in *Bancroft's Rule*: The phase in which the emulsifier is more soluble is the continuous phase.<sup>38</sup>

If the emulsifier present in a mixture is equally able to stabilise the interfaces of both O/W and W/O emulsions, a phase inversion will take place when more and more oil is added to an O/W emulsion.<sup>39</sup> However, if the emulsifier is only able to stabilise O/W emulsions, the addition of more oil will not necessarily lead to a phase inversion but to coalescence of droplets, thus breaking of the emulsion at some point, especially if the amount of emulsifier is limited. In that case a continuous oil phase is formed which floats on the remaining O/W emulsion (Figure 11 right). If an emulsifier shows affinity to both phases, many other factors can have an influence on whether a system forms an O/W or W/O emulsion. These are the sequence of the preparation steps (which phase is added to the other or vice versa), temperature, the amount of electrolyte or other additives.<sup>39</sup> With respect to paints, the kind of pigment may also influence the type of emulsion, although the pigment particles would need to be extremely finely dispersed and smaller than the droplets to effect stabilisation.<sup>40</sup> Because of these many parameters, it is not an obvious decision as to which type of emulsion will be formed with linseed oil, egg yolk and a specific pigment. However, experimentally we have not been able to produce paints based on W/O emulsions with any pigment and egg-oil ratio tested. Therefore it seems that the emulsifier in egg yolk can exclusively stabilise O/W emulsions.

#### 4.4 What are the emulsifiers in egg?

Because the emulsifiers play a determining role in the formation and stabilisation of emulsions, the emulsifiers present in egg have to be discussed. Very often,



lecithin is considered to be the emulsifier in egg yolk,<sup>41,42</sup> but literature on food technology shows that the situation is more complex, as will be discussed below.

Lecithin, a phospholipid, is indeed an excellent emulsifier which is frequently used as a food additive for this purpose. Phospholipids are able to stabilise both O/W and W/O emulsions, but a preference for O/W emulsions is reported for systems containing egg yolk phospholipids, triglycerides (soybean oil) and water.<sup>43</sup> However, Doerner pointed out in 1938 that he tested lecithin from soybeans for emulsions and found it to be inferior to egg yolk with regard to emulsification power and working properties for painting. He thus concluded that lecithin is not the only active component in egg yolk.<sup>44</sup> This is confirmed by modern research into food chemistry that reveals a large influence of proteins. Lipids, phospholipids (such as lecithin) and proteins in egg yolk, however, must not be considered independently. We have to keep in mind that the components in egg white and yolk show a high degree of structure and organisation. A fertilised egg develops into a living chick with muscles, feathers, bones and a beak without any components being delivered from outside. This affords an extremely complex system of biochemical processes and a high level of organisation and structure. The processes involved are to a large extent regulated by proteins, and they are also responsible for the transport of molecules in the metabolism.<sup>45</sup> Phenix<sup>37</sup> has pointed out before that egg yolk cannot be regarded as a "natural emulsion" as described in the older literature (cf. Kühn and Gettens and Stout),<sup>41,42</sup> because its degree of organisation is too high. The interactions between lipids and proteins result in the formation of lipoprotein assemblies (of low and high density), which represent the main constituents of yolk. Accordingly the lipids in the yolk are not free but exclusively associated with lipoprotein assemblies.<sup>46</sup> In high-density lipoprotein assemblies (HDLs), the phospholipids are entrapped and protected by the protein structure of the assemblies,<sup>47</sup> but in the low-density lipoprotein assemblies (LDLs), the phospholipids form the outer shell of the spherical particles together with the lipoproteins.<sup>48</sup> In how far these structures survive during the preparation of an egg yolk tempera paint is unclear; however, it seems to be largely proven that the yolk LDLs are responsible for the exceptional emulsifying properties of egg yolk.<sup>48</sup> Because LDLs stabilise lipid droplets in an aqueous environment, it seems logical that egg yolk stabilises O/W emulsions but not W/O emulsions.<sup>IV</sup> This may be true for most proteins that interact with water-lipid interfaces, which is reflected in the statement by Mollet and Grubenmann that the use of water-soluble macromolecular emulsifiers results in formation of O/W emulsions.<sup>38</sup>

It should be noted that the research reported above indicating that the emulsifiers in egg yolk are only able to stabilise O/W emulsions is in agreement with our experimental work. We have not been able to reconstruct paints based on W/O emulsions so far. Nevertheless, there are recipes on how to produce such paints that are supposed to be W/O emulsions with egg and oil. If these emulsions are likely to be unstable, as discussed above, the question arises as to what kinds of paints are then formed instead?

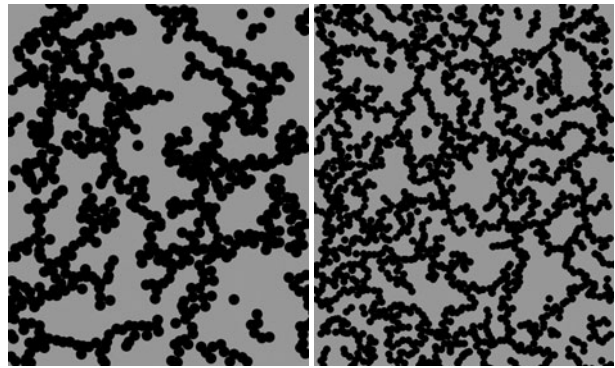


Figure 13: Schematic structures of particulate gels as formed by many proteins. The gel networks may differ by size of the particles, pore sizes, thickness of strands and connectivity of the strands. Such gels often reveal a fractal structure: each spherical particle here would itself consist of a gel structure as depicted, and the same is true for the particles of that gel, and so on, cf. Olsson.<sup>58</sup>

In the following section it will be argued that the water content in such emulsions plays an important role, which suggests that the aqueous binder might form a gel at some point. This hypothesis will be studied experimentally in section 4.6. Although these experiments will not give unambiguous proof of the gel formation hypothesis, the combination of theoretical and practical information will show that many properties of paints containing mixtures of oil and egg binders can be explained rather reasonably by this hypothesis and application of further colloidal principles mentioned above (sections 5 and 6). The consequences will be discussed in section 7.

#### 4.5 Paints produced with mixtures of egg and oil: the role of gel formation

To answer the question what paint systems are formed if recipes for W/O emulsions are followed, it is interesting to compare Doerner's recipes for *wassermischbare Eitempera* (O/W emulsions) and *ölmischbare Tempera* (supposedly "W/O emulsions"), cf. terminology in section 4.2. For O/W emulsions quite a lot of water is added, the composition is 1 part whole egg, 1 part oil (and resin), and 1-2 parts water.<sup>49</sup> For supposed "W/O emulsions", in contrast, Doerner recommends to "strongly restrict the amount of water while the amount of oil is increased, often far beyond the amount for oil paints" ("*starke Einschränkung der Wasserzugabe bei gleichzeitiger Vermehrung der Ölmenge, oft weit über das Maß der Ölfarbe hinaus*").<sup>50</sup> The idea of producing a binding medium for artists' paints by mixing egg yolk with oil with subsequent reduction of water content by careful heating was patented as early as 1906,<sup>51</sup> with a patent of substituting egg white for egg yolk in 1908.<sup>52</sup>

The amount of water in paints is indeed crucial for aqueous binders based on biopolymers, such as proteins or polysaccharides. If the water content is too low, these biopolymers form gels (see section 2.1, Figure 1) through increased intermolecular interactions thus undergoing a phase transition from liquid to viscoelastic (solid).

Gel formation is a typical colloidal phenomenon for macromolecules, especially proteins and polysaccharides, and it is likely to play a very important role for painting in general, which has been underestimated.

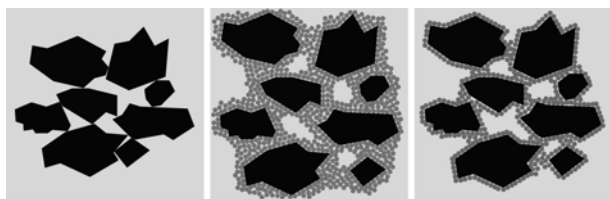


Figure 14: Gel structures in paints can be formed by particles sticking together. These particles may be interacting pigment particles (black particles, left), macromolecules of binders forming particulate gels (grey spheres, middle), or a combination of gel-forming binders bridging pigment particles (right). If the force needed to break the connection between the particles is weaker than gravity, the paint flows. If the force is stronger than gravity but still weaker than the force applied by a brush, the paint shows thixotropy. Once the gel network cannot simply be broken and reformed, but an applied force leads to rupture of the structure, the paint would be denoted “dry”.

The mechanisms are quite well understood for gelatine, which is basically the same as animal glue because both are made from collagen. The strong gel formation power of animal glue can be traced back to the composition and structure of the collagen protein,<sup>53,54</sup> which is a perfect example of the relationship between *form* and *function*. The latter means that proteins have well-defined molecular structures that lead to very well-defined native macrostructures (*form*) resulting in very specific physical-chemical properties that are necessary for their vitally important, life-sustaining biological *functions*. This relationship, which is of paramount importance for proteins and often results in processes of self-organisation and self-assembly<sup>55</sup> (see also section 4.4), is out of the scope of this publication, but should be kept in mind when discussing gel formation.

Gel formation in food is well studied, but usually under conditions that are not relevant for painting. For example, yoghurt or cheese is produced by gel formation of milk proteins by changes in pH, egg protein gels are important in desserts or sauces after heat treatments such as baking or pasteurisation.<sup>16,56,57</sup> Due to their large size, macromolecules usually show strong intermolecular interactions that eventually lead to gel formation. The resulting gel structure depends on various parameters such as concentration of the macromolecules, temperature, pH, salt concentration as well as the presence of other additives such as low-molecular-weight molecules, macromolecules or oil droplets.<sup>16,56</sup>

Examples of gel structures are reviewed in Hermansson,<sup>16</sup> Olsson<sup>58</sup> or Anton *et al.*<sup>56</sup> Biopolymers with a rather linear structure such as gelatine and many polysaccharides seem to preferably form fine strands that build up an entangled network with interactions between strands in the network. In contrast, many proteins form aggregates during precipitation, and the aggregates coagulate to a particulate, fractal network structure (Figure 13). This gel structure is strongly dependent on many parameters, leading to gels ranging from very fine particulate gels consisting of small aggregates to coarse gels with large pores consisting of large aggregates. It has been discussed previously that gels can contain a very high amount of solvents such as water (see section 2.1). In particulate gels, the water can be contained both in the pores and the aggregates that are themselves built up like a gel (Figure 13).<sup>58</sup> This is why such gels are called fractal.<sup>59</sup> The gel structure will certainly play an important role

with regard to behaviour of dried paints and the formation of cracks.

What is the gel structure that is formed if emulsions containing egg yolk are left to dry? It seems not possible to really answer this question at the moment, especially with respect to paints. However, it seems that emulsions of egg yolk with oil rather form particulate gels and not strand-like gels (compare Anton *et al.*,<sup>56</sup> p. 144 with Hermansson<sup>16</sup>), although this information is obtained from gels formed after heating. As repeatedly mentioned above, gel formation is sensitive to very small variations of many parameters. On the one hand, gel formation is often connected with conformational changes of proteins due to denaturation, but on the other hand denaturation is often not necessary for coagulation in the region of the isoelectric point. The occurrence of (heavy metal) ions from pigment surfaces will most certainly have a paramount effect on cross-linking and denaturation of proteins, but this is not studied in literature on foodstuffs. Some proteins also show high affinity for calcium ions in solution leading to coagulation, which might be relevant for paints containing chalk or gypsum as pigments or fillers. In addition to these general considerations, one should note that most gel structures depicted in the food science literature cited derive from heated systems, and it is unclear how this correlates with gel structures formed by evaporation of water. Nonetheless it seems obvious that evaporation of water will eventually lead to gel formation of aqueous binders. It might even be stated that the drying of tempera paints should be described as gel formation of the aqueous binders, even if they still contain lots of water (see section 2.1).

Doerner states:<sup>60</sup> “*Lean tempera dries in a practical sense, although not really, by evaporation of water, despite the oil content. This rapid drying is very advantageous.*” (“*Magere Tempera trocknet praktisch, wenn auch nicht tatsächlich, trotz des Ölgehaltes mit dem Verdunsten des Wassers. Dieses rasche Trocknen ist sehr vorteilhaft.*”) It has been shown in section 4.3 that a “lean tempera” by Doerner (see section 4.2), thus an O/W emulsion in our nomenclature, can consist of almost 90% oil and only 10% protein when dry. Nevertheless it dries quickly by the evaporation of water, although the drying oil certainly needs much longer to dry by autooxidative cross-linking (Doerner probably means this by stating “not really”). This can only be explained with the formation of a gel: The gel of the aqueous binder connects the pigment particles and turns the paint into a “solid”, thus the pigment particles do not move against each other (flow) anymore (Figure 14 middle or right). The gel strength of the binder is presumably improved by the interlocking pigments. The pores of the gel are filled with residual water and the oil (Figure 14 right), which will dry later by autooxidative cross-linking. Accordingly tempera paints do not dry by leaving a solid residue after complete evaporation of the solvent, as for example resin varnishes. Rather the evaporation of water results in precipitation of proteins in the presence of high water content, leading to rapid gel formation bridging the pigment particles, rendering them immobile, despite a high content of liquid oil.

With regard to the high amount of water that can be contained in gels (section 2.1), it is presumably sufficient for gel formation that only a part of the water



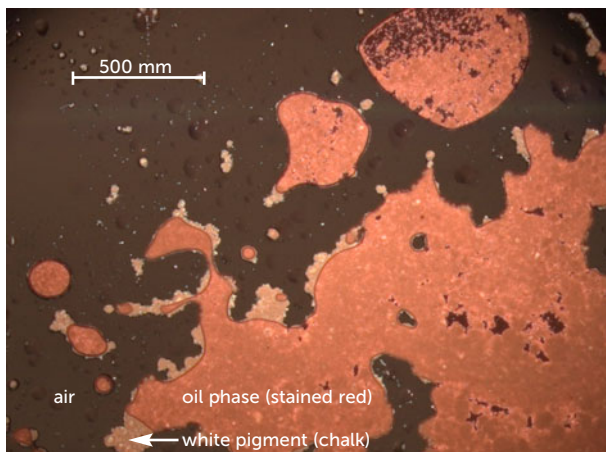


Figure 15: Microscope picture of a mixture of chalk with egg yolk, linseed oil and oil of turpentine. The oil phase is stained red. At this stage with intermediate water content, the pigments form aggregates that are not wetted by the oil (white areas). This grainy material cannot be used as a paint due to its unfavourable working properties.

evaporates. This is also observed if a pigment is ground with egg for several minutes: water has to be added regularly, because otherwise the paint paste becomes too tough to grind due to constant evaporation of water during the grinding process. In contrast, if too much water is added, the paint becomes very liquid, and spreads like water colour. As a consequence, if a paint bound with egg reveals a body and consistency that allows precise application of the paint with single brushstrokes, this paint is already close to the gel formation point of the binder. In other words, the paint dries very quickly by evaporation of a relatively small quantity of water.

With respect to gel formation and water content of aqueous binders, Doerner's statement to "*strongly restrict the amount of water*" for obtaining "W/O emulsions" based on egg and oil receives a new meaning. It can be expected that such paints will quickly lose enough water during grinding for the egg protein to form a gel. Therefore the aqueous phase will become solid and the oleaginous phase becomes the continuous phase. This paint would be an oil paint according to the solubility-based nomenclature defined in section 3.1. However, it would not be a W/O emulsion (which affords two liquid phases) but a *suspension* of solid protein particulates and pigment particles in oil. Because such a paint is no longer an emulsion, *Bandcroft's rule* is not applicable. If this were true, the "symmetric" emulsion theory would clearly not be symmetric anymore, which would greatly diminish the relevance of the term "emulsion" in the context of mixtures of aqueous and oleaginous binders. One should be mindful that the definition of the term "tempera" in German is based on the term "emulsion".<sup>34,60</sup>

With regard to proteins forming solid particles during the manufacture of supposed "W/O emulsions", it is also interesting to note Doerner's remark that the amount of oil is often increased "*far beyond the amount for oil paints*" (see top of this section), with the negative consequences connected to higher amounts of oil.<sup>61</sup> It might be concluded that gelled protein particles could act the same way as fillers do, thus increasing the amount of oil binder needed to produce a workable paint.<sup>V</sup> This might be interpreted as an indication of such "W/O emulsions" indeed being suspensions with only one liquid (oleaginous) phase. This

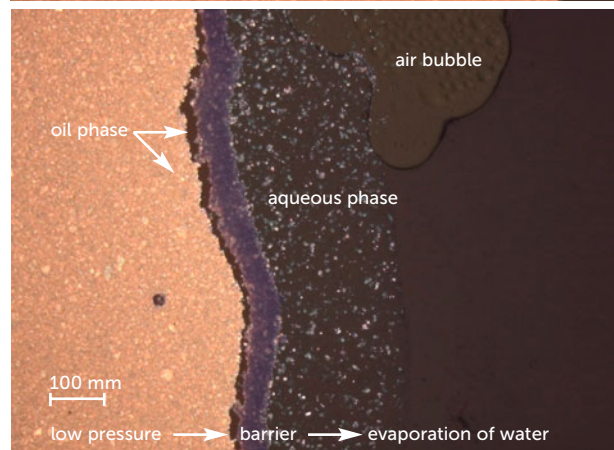
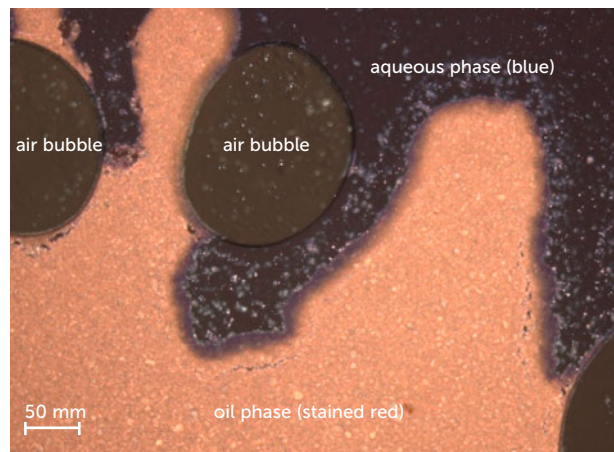


Figure 16: Microscope image of the paint in Figure 15 after evaporation of more water. The paint with an oleaginous continuous phase (oil paint) was brought in contact with water stained blue. As can be seen, the stained water was able to penetrate into the oil paint to some extent (top). After applying low pressure due to evaporation of water, the blue-stained paint layer was pushed away by the oil of turpentine in the oil paint (bottom).

hypothesis was tested with a few experiments described in the next section. These experiments were not performed to reconstruct actual recipes for paints but were intended to test a system containing a pigment, egg and oil for its general behaviour under varying conditions.

#### 4.6 Some experiments with paints containing egg and oil binders

Our study of reconstructed W/O emulsion paints is in good agreement with the gel formation hypothesis in these systems. To investigate the tempera-oil paint transition, chalk was ground with an emulsion of egg yolk and linseed oil. Because enough water was added, it was obvious that the paint initially consisted of an O/W emulsion. At that point, the grinding of the pigment was continued without adding water. Accordingly, the paint paste became very tough and viscous quite quickly due to the evaporation of water. When grinding became too exhausting, the paint paste was diluted with oil of turpentine stained with Nile red, as reported above. At that point, the paint system broke down completely: A paint paste was obtained that is difficult to describe – the material showed good coherence in itself, it was ductile and tough, but not sticky at all. Because it showed no adhesion to anything it was basically impossible to continue grinding

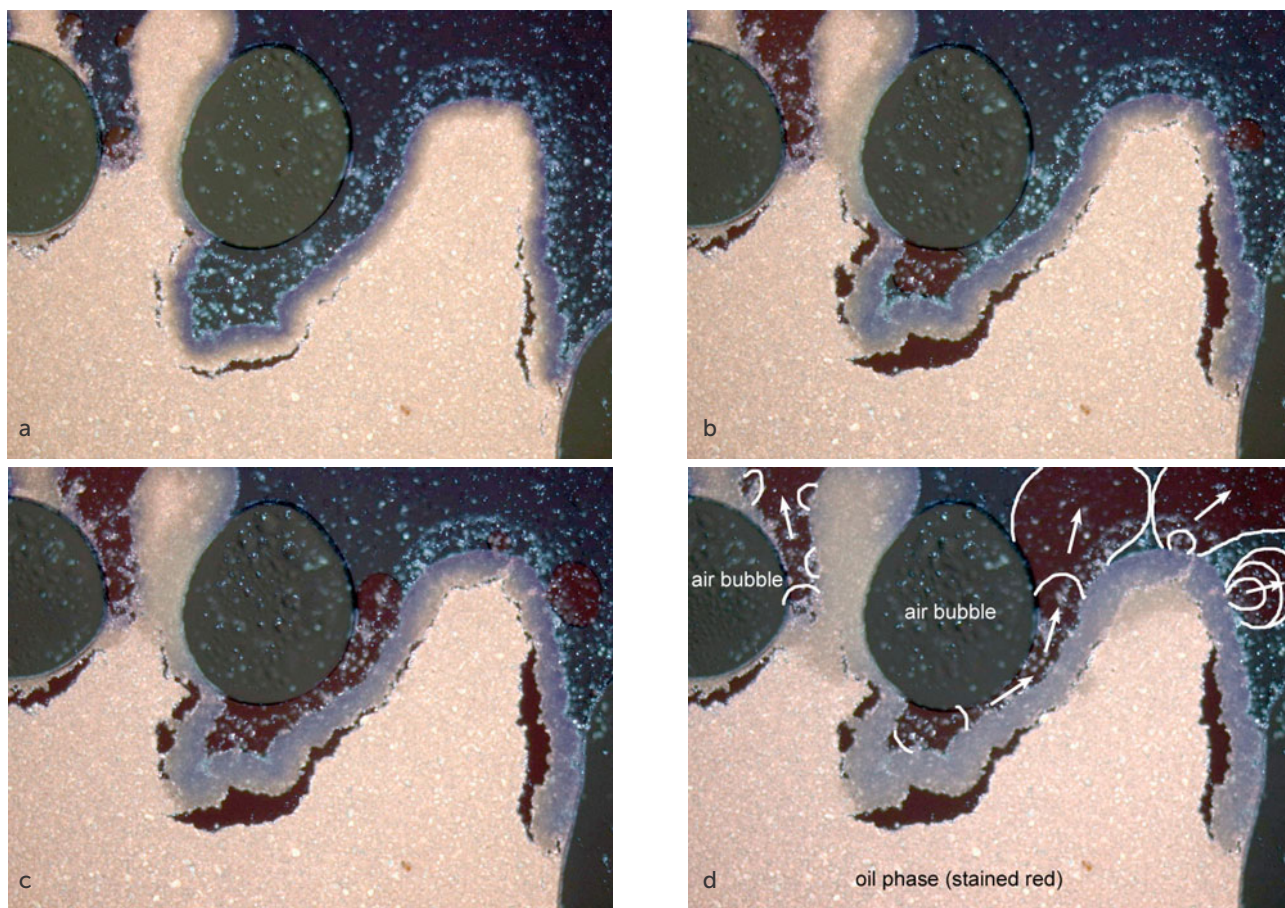


Figure 17: Paint in Figure 16 (top), succession of images (a-d) depicting the events following evaporation of water and consequent low pressure on the red-stained oil paint. The oil of turpentine is sucked into the blue-stained aqueous phase, pushing away the blue-stained paint layer. The phase interfaces and progression of the oil phase visible in the pictures are marked with white lines and arrows in the last picture. It becomes clear that the oleaginous phase is not able to penetrate the blue-stained paint evenly, thus quite obviously a phase inversion took place due to the presence of water. The colour contrast in the microscope was much better than in the pictures, thus the contrast has been increased using Adobe Photoshop for better visibility (original colours cf. Figure 16).

this lump, the muller would just slip. Therefore the mass was patted flat with a spatula to increase surface area and water was allowed to evaporate. After a few minutes, it became possible to grind the paint paste, although it was very grainy and revealed lots of clumps of pigment aggregates. It would have been impossible to use this material as a paint due to its grittiness. For examination under the microscope, a small sample was placed between a microscope slide and a cover slip. In Figure 15, some pigment aggregates can be seen in the upper left area. The oil phase was now obviously the continuous phase, but the pigments were not wetted by the oil, as could be seen by the meniscus of the oil between the glass slides being independent of the paint surface.

After waiting a bit longer for more water evaporation, the properties of the material changed again. It became easier to grind the paint properly, and therefore the pigment aggregates could be re-dispersed. Finally a nice oil paint was obtained that could have been used for painting. To study this material further, an additional experiment was performed: a droplet of red-stained oil of turpentine and a droplet of blue-stained water, respectively, were simultaneously placed on the right and left side of the cover slide. Both solutions were sucked into the void between glass and cover slide by capillary forces, exposing the sample in the middle to each solvent on one side. Accordingly the reaction of the paint to both media could be

observed in the microscope. It appeared that the blue aqueous solution was able to penetrate ca. 20-50  $\mu\text{m}$  into the oil paint (blue paint layer in Figure 16). If the excess liquid outside the cover slide was removed with a paper tissue, the solvents between the glass slides began evaporating at the edges of the cover slide, thus inducing suction and low pressure at the sample. Finally this led to excess oil of turpentine in the paint being sucked into the void. Astonishingly this resulted in the blue paint layer being pushed away from the residual oil paint (Figure 17). The gap between the blue- and red-stained paints was filled with red oil of turpentine.

The described behaviour of the paint system can be explained by the breakdown of the initial O/W emulsion and gel formation within the aqueous phase during progressive evaporation of water. After the addition of excess oil of turpentine in combination with low water content, the emulsion could not be stabilised anymore. Instead of a phase transition into a W/O emulsion, which is not possible due to insufficient stabilisation of the W/O interface, presumably an inhomogeneous, maybe bi-continuous system developed (cf. Mollet and Grubenmann<sup>62</sup>). The paint paste at that stage was tough and showed no adhesion to anything. After more water had evaporated, it seems likely that pigment aggregates were formed within large droplets of residual aqueous solution, which formed the clumps of the grainy paint depicted in Figure 15. Due to the



stability and hardness of these aggregates at this stage, it seems rather unlikely that the aqueous phase was still liquid. We conclude that the proteins probably have formed a gel, which coated and interconnected the particles within a clump. Presumably, the gel was still aqueous at that time, which would explain why these large clumps were not actually wetted by the oil phase, as seen in Figure 15. This would represent a suspension of pigment-egg yolk-gel aggregates in oil without stabilisation of the interfaces. The lack of stabilisation would explain the instability and inhomogeneity of the system, which made it useless for painting. Re-dispersion of the durable aggregates was only possible after more water had evaporated. Presumably at that stage the pores of the egg yolk gel were insufficiently filled with water, and thus the oil was able to penetrate into the gel particles and the voids in between them.

The behaviour of the oil paint towards re-addition of water is highly interesting. According to the staining, water was able to penetrate ca. 20-50  $\mu\text{m}$  into the oil paint (Figure 16). Because this blue-stained water layer is pushed away by the oil of turpentine after application of low pressure, it can be concluded that a phase inversion took place in that area. This is why the gap between the aqueous blue and oleaginous red paints is filled with oil of turpentine and the blue-stained paint layer forms the barrier to the oleaginous phase. This can also be seen in Figure 17. The oil of turpentine does not penetrate the blue-stained paint evenly, but only at few spots where the oleaginous phase can pass. Thus if sufficient water gets access to the proteinaceous phase of the oil paint, a phase inversion takes place without any mechanical action of grinding or mixing with a brush, but no W/O emulsion is formed again.

These experiments indicate that a system of chalk, egg yolk and oil preferably forms an aqueous system, thus an O/W emulsion. If water is removed and the amount of the oil phase increased, the system does not simply turn into a W/O emulsion. Instead it collapses, forming a material that cannot be used for painting. Only by further reduction of the water content, is an oil paint finally obtained. This oil paint, however, is quickly converted back to an aqueous paint (tempera) as soon as water is added. This demonstrates that the system does not act symmetrically to its composition, and the "symmetric" emulsion model is not correct in this case, which is in accordance with *Bancroft's rule*. Because this rule as well as the mechanisms of gel formation are of very general relevance, it may be expected that a broad variety of paints consisting of pigments, egg and oil will behave the same way. The situation is only changed if an emulsifier is added that is able to stabilise W/O emulsions. According to the literature, fatty acid soaps from di- or trivalent metal ions (e.g.  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ) are able to stabilise W/O emulsions, whereas monovalent soaps ( $\text{Na}^+$  and  $\text{K}^+$  soaps) are able to stabilise O/W emulsions.<sup>63,64</sup> Whereas the addition of additives such as aluminium stearates is certainly relevant for modern paints, it is unclear to what extent this is the case for historic paints. Indeed divalent soaps, for example lead soaps from oils containing siccatives, can be expected to allow stabilisation of W/O emulsions. However, this would mean that oils containing lots of siccatives would reveal considerably different properties with regard to the addition of aqueous binders than oils that were prepared without

siccatives. If this were true, though, it is unclear why this difference has not been noted before. In addition, it has to be stressed that systems containing several emulsifiers show non-linear behaviour.<sup>65</sup> A mixture of oil with lead soaps and egg contains emulsifiers for the stabilisation of both O/W and W/O emulsions, but this does not mean that both emulsion types can be equally stabilised in a quasi-symmetric way. Ionic emulsifiers, such as metal soaps, are generally rather weak emulsifiers because the electrostatic repulsion between the charged head groups decreases the stability of the interfaces.<sup>63</sup> A system containing both lipoprotein assemblies from egg and lead soaps can therefore be expected to preferably stabilise O/W emulsions. However, no experiments have yet been performed to test this hypothesis.

## 5 Correlation between composition and properties of paints

In the sections above, the properties of mixed egg and oil binders have been discussed. How does this apply to actual paintings, and how can we find out by chemical analysis whether a painting was created with oil or tempera paints? From the discussion so far it has become obvious that these questions cannot be answered by a simple chemical analysis of the bulk materials contained in a paint. As has been demonstrated from various points of view, the properties of paints depend mostly on the distribution of the phases and the state of these phases, whether they are solid or liquid. This is mostly influenced by how the paint was prepared and manufactured. Thus from a bulk analysis of the binders it is not possible to draw conclusions on the properties of the initial paint, such as dilutability, for example.

Paints are colloidal systems in multiple ways: the pigments in a paint usually form a colloidal dispersion; an inhomogeneous distribution of binders in emulsions or gels is colloidal; macromolecules in aqueous binders (proteins and polysaccharides) are colloids. Colloids are largely characterised by their surfaces, which determine the properties of the whole system. Accordingly, a paint's properties are largely influenced by the interactions between pigment particles or emulsion droplets (see the discussion of thixotropy and mayonnaise in section 2.) The interactions between particles depend on the properties of their interfaces, which can be expected to be modulated for example by a protein-coating, as depicted in Figure 10 (middle).

The paint reconstruction above demonstrated that the availability of water plays a decisive role in the properties of a paint. The amount of water during the preparation of the paint decides when a gel is formed by the aqueous binder, among other factors such as pH, temperature, pigment surfaces etc. This influences whether the continuous phase is aqueous or oleaginous, thus whether there is a tempera or an oil paint. It also has a large influence on the pigment-binder ratio and the optical properties of the paints after drying. Gel formation of the aqueous binder can take place both during the preparation of the paint, when it is still liquid, or after application to the painting, during drying of the paint. Therefore it might be expected that the gel structure and the distribution of the protein is different in paints prepared in different ways.

A paint layer containing egg and oil might have been created in at least five different ways:

- 1) egg tempera paint (without oil) was applied first, and the dry paint was later soaked with oil.
- 2) egg tempera paint with oil (O/W emulsion) was directly used for painting with both binders simultaneously present (Figure 10, left).
- 3) the pigments were first ground with egg and then dried. Later the protein-coated pigments were dispersed in oil (this refers to Figure 10, middle).
- 4) the pigments were ground with egg and oil and the amount of water reduced, thus forming a protein gel when the paint was still liquid (this refers to a "W/O emulsion", if it existed).
- 5) a bit of egg was added to oil paints (prepared without egg) on the palette during paint application.<sup>32,67</sup>

One might expect that the egg protein in paint 1) would form a continuous gel network joining and bridging the pigment particles, similar to Figure 14 (middle or right). The oil would later penetrate into the voids of the dry gel. In paint 2) a similar, continuous gel network could be expected, if the proteins located in the interfaces of the oil droplets (cf. Figure 2) and the surfaces of the pigment particles formed a gel. In contrast, the protein in paint 3) would not necessarily form a continuous network. If the oil paint depicted in Figure 10 (middle) would solidify by autoxidative drying of the oil, the proteins coating the pigments would be embedded in oil without touching each other. In a real paint the pigments would of course be much more densely packed than in the picture, thus many protein coatings would probably be in contact with each other, therefore forming a somewhat larger, branched system. Nevertheless this system might be less extensively interconnected than the networks of paint types 1) and 2). The protein gel in paint 4) could be different from the other three because during the formation of the gel a mechanical force is applied by the grinding of the paint. This can be expected to influence the shape, size and interconnectivity of the gel particles and aggregates that constitute the gel network (cf. Figure 13). It is easy to imagine that small lumps of protein gel become dispersed in the oil that act like pigment particles. However, if the pigments were initially dispersed in the aqueous phase, it also seems possible that a large part of the protein is deposited on the pigment surface during contraction of the aqueous phase due to loss of water. In other words, depending on the initial system, the protein distribution of paint 4) might be quite similar to paint 3).

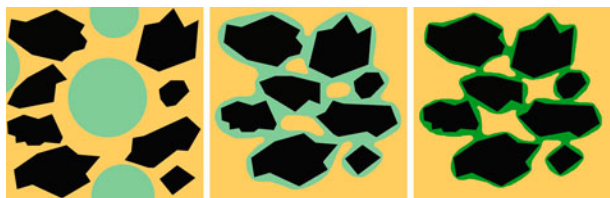


Figure 18: If egg (light green) is added to a pure oil paint (light brown) with a brush on the palette, water droplets might initially form in the oil (left). However, if the W/O interface is not sufficiently stabilised, the water droplets might easily fuse with pigment particles (middle), if they show affinity to the aqueous phase, as is probably the case for many mineral pigments. In that case the aqueous phase interconnects the particle, leading to pronounced thixotropy. After drying the protein might form a network between the particles (right). NOTE: The relative dimensions in the picture, such as size of pigments, thickness of aqueous surface film, or distances between particles are not true to scale.

The protein gel distribution in a paint of type 5) is unclear. It has been suggested that the small amount of egg might form a W/O emulsion,<sup>32</sup> but as mentioned above, this seems rather unlikely from the point of view of colloid chemistry. If a suitable emulsifier is present, for example lead soaps from a siccative, such an emulsion might be stabilised, but this appears rather unlikely in the simultaneous presence of the emulsifiers from egg (see discussion in section 4.6 bottom). However, even if a W/O emulsion was formed, it is unclear why this would greatly enhance the stiffness and thixotropy of such paints,<sup>67</sup> as it was observed during our practical experiments, when small amounts of egg or water were added to pure oil paints. The stiffness of an emulsion can be increased by liquid droplets, as observed in mayonnaise (cf. Figure 2, section 2.2), but in that case it would be expected that a rather large volume of droplets with very stable interfaces must be present. In paints of type 5) neither large volumes of water nor stable interfaces can be expected. In contrast, application of the colloidal principles discussed above offers a straight-forward explanation of why the addition of a little egg or even water might result in pronounced thixotropy of an oil paint: In the case of insufficient and ineffective stabilisation of W/O interfaces, the aqueous phase is forced into the oil phase by the brush, forming droplets but no stable W/O emulsion. Due to the close packing of the pigments in a typical paint, the water droplets will quickly encounter pigment particles (Figure 18, left). Due to the lack of stability of the W/O interface, the droplets might fuse with the pigment particles, especially if the pigments show affinity for the aqueous phase, as reported for quartz or clay particles (section 2.1), and presumably many other minerals. The aqueous phase might then bridge and interconnect the particles (Figure 18, middle). This results in strong interactions by hydrogen bonds, and the particles are kept together by the surface tension of the aqueous phase. This is an excellent explanation for the pronounced thixotropy effect of small amounts of water or egg in oil paints. If egg was added, the egg protein distribution (Figure 18, right) might look similar to paints of type 1) or 2) after drying. Of course the thickness of the pigments' protein coating, the thickness and density of the protein bridges between particles will depend on the amount of protein and water and the internal surface area of the pigment particles in the paint (cf. Mollet & Grubenmann, p. 198).<sup>68</sup>

All five paint types above can contain egg and oil in varying ratios, and they cannot be distinguished by bulk analysis of their binders. However, if it were possible to map the protein distribution within a paint layer or even the protein gel structures in a cross-section, it might be possible to distinguish the five paint types and therefore draw conclusions about the method of production of a given paint. However, this might not be as straight-forward as described above.

Firstly, it has to be considered that the structure of protein gels is very sensitive to a broad variety of parameters, as discussed repeatedly above. Therefore it is probably rather naïve to think that the gel structures in paints 1) – 5) would always be the same for each paint type, while being simultaneously clearly distinguishable from each other. Secondly, the drying process of the applied paint clearly needs to be considered in more detail, because it seems possible that the protein distribution might change during drying.



Groen, for example, observed small round and oval cavities in a red paint layer by Rembrandt in a cross-section.<sup>32</sup> It was suggested that an aqueous component was added to the oil binding medium that was presumably emulsified in oil. From the current perspective this is possible, but rather unlikely, as discussed above: This structure might also be explained by either the aqueous binder having congealed before or during mixing of the paint (see above), or maybe even after the application of the paint, although the latter seems unlikely. For example, if a paint is applied as an O/W emulsion, the continuous phase will collapse at some point during drying. If at that point, the pigment particles are still mobile, the aqueous phase might contract, pushing the pigment particles away. More likely, however, the pigment particles might already be immobile, either due to preceding gel formation of the protein or simply by mechanical interlocking of the pigment particles. In that case, the remaining aqueous phase might contract steadily in the pigment matrix, forming an inhomogeneous system of water droplets in oil. During further drying, the water droplets might continue shrinking until no liquid water is left.<sup>VI</sup> A liquid phase in between particles will be ruled mainly by capillary interactions, and parameters such as surface tension or wetting properties of pigment surfaces will play an important role (see Mollet & Grubenmann,<sup>68</sup> and Berg,<sup>69</sup> for more information). With regard to the distribution of the protein gel in the paint, the crucial question is at which point the gel is formed. If the gel is formed before the collapse of the aqueous phase, a network structure as described above (paint type 2) is probably obtained. However, if the proteins are able to move with the aqueous phase during the collapse, an inhomogeneous protein-distribution in the dried paint might be formed. In that case, the distribution might look like a W/O emulsion of (pigmented) droplets of aqueous binder in oil, for example. However, this would be misleading because it is possible that this structure only develops after the drying of the paint. Whether this applies to cross-sections such as reported by Groen<sup>32</sup>, is unclear. Structures of lumps of pure protein or inhomogeneous distributions of egg and oil within a single paint layer have been identified by infrared imaging in cross-sections of paintings by Arnold Böcklin and Franz von Lenbach (1836-1904) within the research project into tempera painting around 1900 described in the introduction. This will be discussed in a subsequent publication. Clearly more work is needed, however, for a systematic study of such paint systems and the development of analytical methods with sufficient spatial resolution.

## 6 Correlation between written sources, technological examination and chemical analysis

For Böcklin's painting *Villa am Meer II* it cannot be determined by current scientific analysis techniques whether the artist considered his paints to be oil or tempera paints, and thus whether they could be mixed with water or oil of turpentine. The identification of egg, drying oil and copaiba balsam is clearly insufficient for differentiation between paint types 1) – 5). Although, a study of the protein distribution in paint cross-sections by infrared imaging and selective staining of proteins was undertaken, and will be discussed

in a subsequent publication, the results were ambiguous.

The written sources concerning *Villa am Meer II* are informative and very helpful, but also incomplete and partially ambiguous. The use of copaiba balsam could have been expected but not ascertained without analysis. The precise binding media of Böcklin's *Leimfarbe* would not be known from the sources: it might be animal glue, casein or even plant gums or starch. Here it was shown to be egg tempera. Information from written sources is often very general, thus it is unclear for example, to what extent *Leimfarbe* was used for rapid underpainting of the landscape, which was then continued in oil paints. In many cases the written sources put their emphasis more on practical aspects of painting. *Leimfarbe*, representing an aqueous binding medium, has short drying times and allows a fast working process.

The technological study of paintings is very informative. The visual appearance of paints, the way they were applied and their morphology on the painting, allow extensive conclusions about the viscosity, rheology and applicability of the initial, fresh paint. However, these characteristics are often ambiguous. Whether a paint is viscous or not depends on the pigment-binder ratio, the viscosity of the binder, the interactions between the pigment particles, and the interactions between the binder and pigment surfaces. Often internal structures (gels) are formed in a paint, sometimes temporarily (cf. thixotropy), sometimes rather permanent (protein or polysaccharide gels). These interrelations are extremely complex and accordingly no unambiguous classification of tempera or oil paints by stereomicroscopic study is possible. The same is true for visual examination of the optical properties of paints. An opaque, dense paint can be produced from both egg tempera and oil paint. Translucent glazes can not only be produced with oil paints but also with tempera paints that contain enough oil right from the beginning or are later soaked with oil. A matte appearance of a paint, usually typical for tempera paints, can also be achieved by oil paints with a high pigment-binder ratio (cf. Dietemann *et al.*).<sup>70</sup> Whether two paints can be mixed wet-in-wet or not depends on their drying speed and rheological properties. Tempera paints are usually not mixed wet-in-wet because of their quick drying due to evaporation of water. However, in the course of the 19<sup>th</sup> century, diverse additives, such as glycerol, were added to tempera paints. Glycerol is polar and acts somewhat like water, but it evaporates extremely slowly. This might increase the drying time of tempera paints and allow them to be blended similar to oil paints. Schick describes Böcklin's use of glycerol in his tempera paints for this very purpose in 1866:<sup>71</sup> "To keep the [tempera] paint flexible for a longer time and for better shaping and blending, Böcklin admixed glycerol." ("Um die [Tempera-]Farbe länger biegsam zu halten und besser modellieren zu können, nahm Böcklin Glycerin darunter.") This means that attribution of tempera or oil paints based on their visual appearance is ambiguous, at least since the 19<sup>th</sup> century. Also here, more work is needed to elucidate the correlation between composition, additives and rheological properties of paints.

From the discussion above it becomes obvious that information from written sources, technological

examination of paintings and binding media analyses each provide their own perspective, and that none of them is conclusive.<sup>1</sup> Written sources represent the writers' viewpoints and interests that may be quite different from today's art historians, conservators or scientists. Visual examination by a technological study of a painting results in a wealth of information about the initial properties of the paint. Unfortunately it is – at least towards the end of the 19<sup>th</sup> century – neither possible to link these observations with the materials nor with the manufacture of the paint in an unambiguous way. The same is true for chemical analysis of the binders. The reason lies in the vast complexity of the colloidal nature of the paints' components, including pigments, binders and solvents such as water. To draw reliable conclusions, information should be collected and combined from all three kinds of sources whenever possible. Reconstructions, as a fourth source of information, can be used to correlate the collected information and test hypotheses and assumed relationships.

## 7 Final conclusions and outlook

It has been shown that the correlation of information from different types of sources<sup>1</sup> is not straight-forward, mainly because they refer to different aspects of paints and painting. With regard to Böcklin's painting *Villa am Meer II*, this means that information that seems contradictory at first, can nonetheless be consistent. In other words, there is no reason to doubt Schick's statements in section 3.1 that the paints of the sky probably were water-dilutable tempera paints, despite the very high amount of linseed oil and copai-ba balsam detected, and that the paints of the landscape probably were oil paints, despite the rather high amount of egg. Why exactly Böcklin's oil paints contain proteins is still unclear because there are several possible explanations.

With regard to binding media analysis, it must be stated that a general distinction between tempera and oil paints does not seem to be currently possible. From a colloidal description of paints it can be demonstrated that the ratio of aqueous and oleaginous binders can vary within a very broad range for both tempera and oil paints, but that even a precise determination of their amounts does not allow a differentiation. Even worse, if the oil binder of a paint is dominant, additional aqueous binders can easily be overlooked because they are more difficult to detect by many analytical techniques. Such paints can easily be mistaken as oil paints, even if they were applied as aqueous tempera paint, which initially might have been the essential aspect for the artist. For Böcklin the paints of the sky were *Leimfarbe*, although they mainly consist of oil.

It is very common for paints to be classified into tempera and oil paints by their visual appearance. However, in this paper the distinction between tempera and oil paints is based on their dilutability. In many cases "tempera" and "oil" are simply taken to be synonymous with materials. This inconsistent use of terms can lead to serious misunderstandings.<sup>1</sup> For a proper correlation of materials, properties of paints (e.g. dilutability), and visual appearance of paints in a painting, colloid chemistry is indispensable. The problem is that the relevant interrelations are extremely complex and often strongly dependent on minor com-

ponents such as emulsifiers. Reconstructions of paints that could not be discussed here revealed that additives such as glycerol, soaps or tallow may have a considerable influence on the rheological properties of paints, even if added in minor quantities (1-2 wt%). From an analytical point of view these minor components are difficult or even impossible to identify. Soaps for example are also formed during the ageing and degradation of a painting.

Paints consisting of pigments, egg and oil are very complex systems and manifold factors influence the colloidal behaviour of its components. Nevertheless the theoretical principles of colloid chemistry, e.g. *Bancroft's Rule*, as well as the experimental data and literature quoted above, should have made clear that the straight-forward model of mixed binders forming simple emulsions does not apply. We have to reconsider how the binders used to prepare a paint correlate with the paint's properties. It appears that the amount of water plays a decisive role in the manufacture of the paint, which is problematic because a paint's water content during its preparation or application on a painting cannot be determined retrospectively by analytical means due to subsequent evaporation.

We emphasise that reconstructions of paints is a valuable tool to better understand the complex interactions between paint fabrication, materials, material distribution in a paint, optical properties of dried paints, and handling properties including drying time and rheology that allow or prevent wet-in-wet blending. The preparation of a paint will influence its properties more than its composition. Clearly more work is needed to understand in more detail the interactions between binders and pigments that determine the rheological properties.

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Picture credits: Figure 2 Martin Mach, Munich, Figures 3 and 6 (bottom) Bayerische Staatsgemäldesammlung, Munich. All other Figures are from the authors.

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## 10 Endnotes

I. W. Neugebauer researched the written sources and performed the technological examination of the paintings as part of her PhD thesis. The binding medium analyses were carried out and interpreted by U. Baumer, C. Beil, I. Fiedler, W. Neugebauer and P. Dietemann, and paint reconstructions were made by W. Neugebauer and L. Lutz. P. Dietemann dealt with the principles of colloid chemistry. Their correlation with and relevance for painting were mainly worked out by W. Neugebauer and P. Dietemann.

II. The detectable amounts of different classes of binders depend not only on their quantity, but also on the analytical method and their detection sensitivity as well as on their degradation state. It is an essential problem that the degree of degradation cannot be determined precisely for organic binders, which is particularly problematic for proteins. The relative quantities reported in the table are therefore estimations based on the semi-quantitative analysis results as well as practical experience taking into account the comparison of a large number of aged reference materials and a wide variety of samples from artworks from different artists and centuries performed at the Doerner Institut during the last 25 years.

III. The difference of such an W/O emulsion oil paint (Figure 10, right) to the paint depicted in Figure 10 (middle) is that the latter is not an emulsion but a dispersion because the water has evaporated and the aqueous phase (the protein) is a solid.

IV. From a biochemical point of view it might be argued that life is based on aqueous systems, and it is therefore crucial for living systems to ensure the biochemical reactions mentioned above take place in an aqueous environment. It would probably be difficult to maintain life functions in a system like egg yolk if the entire system could easily invert into a W/O emulsion.

V. The same effect of increased oil consumption due to formation of particles has been described by Eibner for the addition of wax to oil paints.<sup>66</sup>

VI. A paint intended for painting, as discussed in section 4.6, must form a stable system for use. This is not the case for an applied paint during drying, because no mechanical action and no plastic deformation during brushing must be stabilised.