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Investigating surface treatments and coatings, their history, application and detection on selected pigments: Umber, Vine Black, Ultramarine Blue, Cu-Phthalocyanine Blue, and two Hansa Yellows, PY3 and PY74

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Abstract

Pigment manufacture in the twentieth and twenty-first centuries has largely been intended for industrial application. Consequently, the artist's materials market which is by contrast very small and specialized, relies on pigments produced for the industrial market. Improvements to enhance performance in an industrial context, has led to the introduction of a variety of different surface treatments applied to pigment particles.

Pigment coatings can consist of one or more thin layers of either organic or inorganic material, or a combination of both. Their nature and their presence in very small amounts present a challenge for the detection and identification of these compounds.

Part I of this thesis explores the literature covering pigment coating materials, application methods and the terminology used to identify the range and types of materials in use. Part II explores the analytical strategies that can be employed to detect these treatments on pigment samples.

The pigments selected for this research include: Umber and Vine Black purchased from Kremer Pigmente during the Carlyle MOLART Fellowship for the creation of "historically accurate" paint reconstructions; Ultramarine Blue pigments since the use of coatings on these pigments is reported in the literature (for greater acid resistance); Cu-Phthalocyanine Blue pigments as these are currently amongst the most popular blue pigments; and the Hansa yellows, PY3 and PY74 from the manufacturer Royal Talens to determine the possible presence of a surface treatment or coating which could be responsible for paint instability.

Analytical methods employed for this thesis work to characterize the organic fraction on pigments surfaces included: Evolved Gas Analysis Mass spectrometry (EGA/MS); Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS); Py-GC/MS using thermally assisted hydrolysis and methylation (THM) with gas chromatography-mass spectrometry (GC/MS) in combination with ultrafast thermal desorption (UTD), meaning the samples were investigated through "slow pyrolysis" and not as flash pyrolysis. This method, developed at RCE, involves a temperature program that enables a one-shot analysis with evaporation before pyrolysis. To characterize inorganic materials, the following instruments were used: Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX); (Scanning) Transmission Electron Microscope Energy Dispersive X-ray ((S) TEM-EDX); and Field Emission Gun Scanning Electron Microscope (FEG-SEM).

Surface treatments influence the physical properties of pigments during the manufacture of coatings, including oil paints. By understanding their applications and chemistry and determining methods for identifying them *in situ* on pigment particles, their influence on the long-term stability within modern artist's oil paint can be assessed.

Keywords: Surface Treatment; Coating; Organic surface treatments; Inorganic surface treatments; Modern pigments.

Resumo

A produção de pigmentos nos séculos XX e XXI foi em grande parte destinada à aplicação industrial. Consequentemente, o mercado de materiais para artista representa um pequeno e especializado universo, que inclui nas suas tintas, pigmentos produzidos para o mercado industrial. As melhorias no contexto industrial levaram à introdução de uma grande variedade de tratamentos de superfície aplicados em diferentes partículas de pigmentos.

Estes revestimentos de partículas consistem numa ou mais camadas finas de materiais orgânicos ou inorgânicos ou uma combinação de ambos. A natureza destes materiais e a pequena quantidade presente nos pigmentos faz com que a sua deteção e identificação seja extremamente desafiante.

A Parte I desta tese explora a literatura que abrange os materiais de tratamento de superfície dos pigmentos, métodos de aplicação e terminologia usada para identificar a variedade e os tipos de materiais utilizados. A Parte II explora as técnicas analíticas que podem ser empregues para detetar estes tratamentos em variadas amostras de pigmentos.

Os pigmentos selecionados para este estudo incluem: Umber e Vine Black comprados à Kremer Pigmente durante o Carlyle MOLART *Fellowship* para a criação de reconstruções históricas de tinta para artista; Pigmentos Azuis Ultramarinos foram também selecionados, uma vez que o uso de tratamentos de superfície é reportado na literatura (para maior resistência a ambientes ácidos, por exemplo); Os pigmentos Cu-ftalocianina Azul estão atualmente entre os pigmentos azuis mais populares e na literatura também são reportados tratamentos de superfície; finalmente os Amarelos Hansa, PY3 e PY74 do fabricante Royal Talens foram selecionados de forma a determinar a presença de tratamentos de superfície e perceber se estes poderão contribuir para a instabilidade da tinta, experienciada pela Royal Talens.

Os métodos analíticos utilizados durante este estudo para caracterizar a fração orgânica na superfície dos pigmentos incluem: Análise de Gás Gerado acoplada à Espetrometria de Massa (EGA/MS); Pirólise acoplada à Cromatografia Gasosa/Espetrometria de Massa (Py-GC/MS); Py-GC/MS recorrendo a hidrólise e metilação térmica assistida (THM) com Cromatografia Gasosa acoplada à Espetrometria de Massa (GC/MS) em combinação com adsorção térmica ultrarrápida (UTD), o que significa que as amostras foram investigadas através de pirólise lenta e não através de pirólise *flash*. Este método, desenvolvido no RCE, envolve um programa de temperatura que permite uma análise *one-shot* com evaporação antes de pirolisar. Para caracterizar materiais inorgânicos, foram utilizadas as seguintes técnicas: Espectroscopia de raio X por Dispersão em Energia com Microscopia de Varredura Eletrónica (SEM-EDX); Espectroscopia de Raio X por Dispersão em Energia com Microscopia de Varredura de Transmissão Eletrónica ((S) TEM-EDX); e Microscopia de Varredura Eletrónica com Arma de Emissão de Campo (FEG-SEM).

Os tratamentos de superfície influenciam as propriedades físicas e químicas dos pigmentos. Ao perceber qual o objetivo dos tratamentos, a sua composição e quais os métodos para os identificar, torna-se possível avaliar a sua influência relativamente à estabilidade das tintas de óleo modernas para artista.

Palavras-chave: Tratamento de Superfície; *Coating;* Tratamentos de superfície orgânicos; Tratamentos de superfície inorgânicos; Pigmentos Modernos.

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Symbols and Abbreviations

CMOP	Cleaning Modern Oil Paints
EGA/MS	Evolved Gas Analyses Mass Spectrometry
Py-GC/MS	Pyrolysis Gas Chromatography-Mass Spectrometry
Py-THM-GC/MS	Pyrolysis Gas Chromatography Thermally assisted Thermolysis and Hydrolysys Mass Spectrometry
GC/MS	Gas Chromatography – Mass Spectrometry
UTD	Ultrafast Thermal Adsorption
SEM-EDX	Scanning Electron Microscope – Energy Dispersive X-ray
(S)TEM-EDX	Scanning Trasmittion Electron Microscope – Energy Dispersive Spectroscopy
FEG-SEM	Field Emission Gun – Scanning Electron Microscope
RCE	Cultural Heritage Agency of The Netherlands
LV	Low Vacuum
BF	Bright Field

Preamble

This thesis, which concentrates on inorganic pigment surface treatments was carried out at RCE and funded by the European programme, Erasmus+. It was supervised at RCE by Dr Klaas Jan van den Berg and in The Department of Conservation and Restoration at Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, by Dr Leslie Carlyle. In Amsterdam this thesis work contributed to the ongoing CMOP project. This work was done in conjunction with Carolina Gomes also a student from NOVA University who focussed on the organic components in pigment surface treatments.

Modern artist's oil paints pose a series of degradation phenomena which are poorly understood in the Conservation field [1]. Some examples are the formation of vulnerable surface 'skins' of binder on paint surfaces, efflorescence, and unpredictable water and solvent sensitivity [2]. Within the field of Conservation, it is important to understand the original materials used in an artwork and how they may have changed as well as the impact of any materials to be used during treatment. [3]. Also, as Carlyle notes, certain questions concerning the appearance of paint may only be answered by making paint reconstructions with historically accurate materials [4]. Part of the need to understand original materials, and to be able to make historically accurate reconstructions to model paint behaviour is to understand manufacturing methods used in the production of paint materials. One area which is of particular interest, is pigment treatments and coatings: when were these treatments first introduced and how they can affect the relationship between the pigment and the binder.

The demands of the industrial world have caused profound changes in the production and material properties of pigments [5]. Because pigment suppliers must respond to specific requirements for a variety of industrial applications and still make a profit, pigments began to be altered early in the 20th century with surface treatments to respond to those needs [6]. The patent literature and articles in technical journals reveal numerous efforts to improve the performance of pigments. The oldest patents found thus far during the literature search for this thesis, were between 1920 and 1932 (See appendix 1).

This thesis reports results of a literature search to determine the historical and current use of pigment treatments and coatings in Part I, and in Part II explores analytical methods for identifying the presence of these treatments/coatings on dry pigments.

Characterizing pigment surfaces can be challenging, especially when the pigment manufacturing source is unknown and there is no information provided on the pigment datasheet regarding surface treatment. Research in the patent and technical literature is the key when looking for the type of surface treatments that have been introduced. This literature can provide detailed material characterization; however, it should be noticed that the patent language becomes more complex over time and is thus more difficult to interpret, making the identification of the treatments or coating processes more difficult.

An overall characterization of pigment inorganic surface treatments is achieved by Energy Dispersive X-ray (EDX) which provides a material characterization [7] and Scanning Electron Microscope (SEM) which can show the surface treatment morphology [7]. Transmission Electron Microscopy (TEM) to understand special resolution of pigment particles and morphology [7], followed by the use of a Field Emission Gun (FEG) - SEM which produces an image of the sample by scanning a high energy beam of electrons, enabling to understand the pigment topography [8]. The organic surface treatment characterization is achieved using EGA-MS to characterize the thermally induced decomposition of pigment surface treatments [9], Py-GC/MS to characterize surface involatile macromolecular complexes found on pigment surfaces [10] and Py-GC/MS using thermally assisted hydrolysis and methylation (THM) gas chromatography-mass spectrometry (GC/MS) in combination with ultrafast thermal desorption (UTD) to characterize the organic fraction on pigments surfaces [11].

These techniques were successfully applied to determine the presence and type of treatments or coatings on selected pigments. These included pigments already used for the Carlyle MOLART Fellowship [12], those which were the object of study in other conservation research projects as well as those in use by the current artist's paint manufacturers Royal Talens.

Part I.
Manufacturers, Terminology, Application and Chemistry and the Selection of Pigments for Study

1.1 Pigment Manufacturers and Artist's Oil Paint Manufacturers

The industrial revolution had a major impact on the paint industry [13]. From the eighteenth century until the present day, the industry developed in a way that making paint was worthwhile as a separate industry, meaning that manufacturers start to be more focused on the pigment production itself, improving pigment technology [14].

As Crowl states "the requirements of the paint industry from the colorant producing industries are varied, since a pigment fulfils several functions in addition to that of providing colour" [15]. As a result, pigment suppliers respond according to the customer's specific requirements. As of October 20, 2017, on the BASF website there were more than seven market areas identified which they serve. None of these listed artist's pigments specifically.

To understand the artist's paint market and its importance in terms of the worldwide production of pigments, meetings with pigment and paint manufacturers were arranged. An interview at the artist's supplier, Royal Talens with Coos van Waas (chemical engineer and product specialist R&D) and Daphne van Mansom (laboratory manager) took place on October 11, 2017. As they explained, artist' oil paint manufacturers represent a very small market within the different paint and coatings industries. Because of their small share of the market, they have little to no influence on suppliers and therefore their specific needs are not catered to by industrial suppliers. Consequently, they must use pigments intended for large industries.

This was further confirmed during a meeting with Connie te Walvaart (account manager for pigments and coatings) and Tanja Takman (account manager for coatings) from BASF representatives, on February 6, 2018, where it was explained that artist's materials do not influence their market. However, they did explain that personal contact is made between the artist's paint representatives and their account manager to ensure that the most suitable pigments are selected.

1.2 Pigment Surface Treatments and Coatings

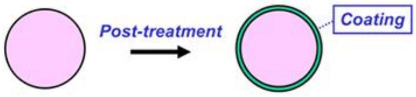

Figure 1. Pigment surface treatment and post treatment, (Illustration taken from Joshum Beetsma, 2017) [16].

In terms of pigments, a surface treatment may be understood as anything applied to improve the performance of the pigment. Surface treatments can include a treatment and/or a coating, which can be applied during pigment synthesis and afterwards (for a coating after the pigment has been synthesized see figure 1).

Many terms can appear in the literature. One of which is *encapsulation*. This consists of a specific polymeric treatment which gives total coverage of each pigment particle [16]. Therefore, and as confirmed in a meeting with BASF representatives, February 6, 2018, an encapsulation treatment is a coating, but a coating is not the only surface treatment possible.

The aim of a surface treatment is to modify the pigment surface, improving the pigment according to its expected performance [17]. The literature provides a list of reasons for pigment surface treatments: to control colour; batch reproducibility, to control the ease of dispersion; to reduce flocculation; improve compatibility with the binder; to adjust paint consistency. As well, surface treatments are intended to increase the chemical stability of the pigment, to reduce its solubility, and for light stability and weather fastness [17, 18].

The concept of coating pigment particles prior to their use on paint has very early origins. In their work von Baum et al. report that proteins such as egg were used to coat pigments and would have many advantages such as becoming less susceptible to yellowing, wrinkling or drying cracks, for example in the use of Ultramarine Blue [19]. Also, in an email to Leslie Carlyle, March 27, 2017, Dr. Mark Clark, provided early recipes from the 14th century Montpellier manuscript Liber diversarum arcium (anonymous) which called for fish glue, for example, which could be ground with the pigment, covering the pigment particles thereby coating them before the addition of the paint binder.

1.3 Moment of surface treatment and coating application

By surface treating pigments at different stages in their production, properties such as chemical constitution, particle size and shape, dispersibility, and others can be controlled with a view to producing pigments suitable for various end-applications [17]. Some issues such as a risk of sintering[1] and shape loss, both of which influence the hue of the pigments possibly causing a shift in hue as well as a decrease in dispersibility, can occur during pigments synthesis. To overcome this problem, surface treatments can be applied during three different stages.

The first stage is during pigment synthesis such as during **crystallization** when surfactants can be added to reduce the solubility of the pigment, or when resins are added to control the particle growth, or during the second stage when **precipitation**[2] and **calcination**[3]**,** also referred to as thermal process**,** occur; during this last stage, compounds such as alumina and also silica, are added to aid for example, the affinity between the pigment surface with another surface treatment such as the coating, to aid phase transformations, or even to coat the pigment [17].

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[1] According to Randall German (2014), “sintering is a thermal process used to bond contacting particles into a solid object” [21].

[2] Precipitation is a method for preparing pigments where two solutions are mixed together and a solid is formed [22].

[3] As mentioned by Kaur and Bhattacharya (2011), “Calcination is a process of heating a substance under controlled temperature and in a controlled environment. This process is known to improve the chroma, tinctorial strength, pigmentary texture, weather stability, light-fastness and thermal stability of the pigment whereas it has adverse effect on the dispersibility of pigments [23].

Finally, *after-treating* the pigments with organic and inorganic materials after the pigment has been synthesized to facilitate wetting and dispersion of pigment particles in the binder when being made into paint is common [17, 18]. The stabilization of the dispersion is achieved through repulsive forces provided by the surface treatments, which prevent the particles from flocculation [20].

1.4 Mechanism of Stabilization

The two main mechanisms for the stabilization of dispersions are **electrostatic stabilization** which reduces flocculation through electrostatic repulsion using an ionic dispersing agent, behaving effectively in water-based systems (with a low dielectric constant[4]) and **steric stabilization** which relies on the adsorption of a layer of resin or polymer chains on the surface of the pigment working most effectively on solvent based systems (with high dielectric constant) [24].

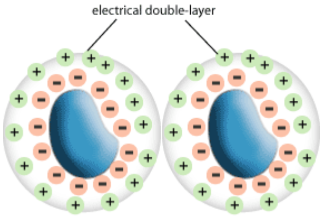

Figure 2. Electrostatic stabilization. Particles covered with charges (cations and anions) repel each other (Illustration tan taken from Inkline 2017) [20].

Waterborne systems are stabilized by electrostatic repulsion. This means that, using anionic or cationic agents, all pigment particles will carry the same charge and dispersion will be stabilized through van der Walls forces (see figure 2) [24]. Also, the thicker the stabilization layer is, the more stable the particles will be [20].

Pigments for oil-based media which are stabilized through steric stabilization (see figure 3) will be explored. As pigment particles approach each other these adsorbed polymeric chains intermingle and in so doing the pigment particles lose a degree of freedom and therefore prevent future attractions. In other words, the anchoring segments (pigment affinic groups) of the dispersing agent are adsorbed on to the pigment surface and the long resin compatible chains are solvated into the binder [24].

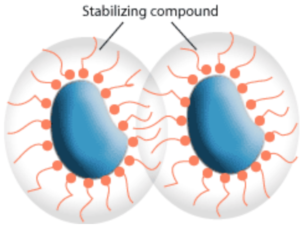

Figure 3. Steric stabilization. Particles covered with soluble tails (anchor groups) repel each other (Illustration taken from Inkline, 2017) [20].

For non-aqueous systems such as oil paint, steric stabilization[5] is most effective [20]. Paint technologists report that even if well ground, a non-stabilized dispersion can easily be destroyed by the letting down[6] [17]. Steric stabilization is only effective if the composition of the coating and method of application are compatible with the pigment surface. The optimum advantages occur when the adsorbed layer is thick enough; at least a molecular layer, and that it gives enough coverage to the pigment surface [6, 18]. The treatments can include the use of colourless compounds such as SiO_2, Al_2O_3, or coloured substances such as pigment derivatives which may be porous or dense in their composition [18]. The literature reports that the coating material makes up less than 10% of the pigment weight [25].

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[4] As of October 19, 2017, Oxford Dictionaries listed on its website that A quantity measuring the ability of a substance to store electrical energy in an electric field.

[5] According to Merriam-Webster, "relating to or involving the arrangement of atoms in space" [26].

[6] The paint production step at which other materials in the paint formulation are added to the pigment paste [27].

1.5 Surface Treatment Materials

The literature reports that there is an enormous array of materials that can be applied to both aqueous and solvent-based systems. Depending on the stage of manufacture, surface treatments follow a sequence of application. For example, surfactants can be added during the crystallization process to control the crystal growth, but they can also be applied to create affinity with further treatments since they can provide an anchoring structure [18].

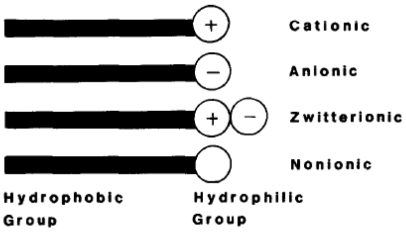

Figure 4. Surfactants according to their nature (Illustration taken from Shanti Swarup and Clifford K. Schoff, p. 2) [29].

Surfactants (see figure 4) are materials that lower the surface tension between two liquids or between a liquid and a solid [28]. They can be either non-ionic, anionic, cationic or amphoteric, depending on their polar head-groups. Non-ionic surfactants have no charge on their polar head-group and are often paired with anionic surfactants for paint, for example; they provide steric stabilization between the pigment particles, thus, preventing settling and flocculation [29]. Anionic surfactants bear a negative charge. These can consist of ammonium salts of long hydrocarbon chain acids or sulfates. These surfactants are commonly used since, upon heating, ammonia is evolved leaving a less water sensitive surfactant [27]. Cationic surfactants bear a positive charge and consist mostly of salts of long-chain amines. These aid dispersion and have germicidal and fungicidal effects. Finally, and as Shanti Swamp and Clifford K. Schoff (1993) explain, amphoteric surfactants “can act as either anionic or cationic surfactants depending upon the pH of the solution” [29] Summing up, the role of surfactants influences the behaviour pigments in the coatings industry regarding solubilization, emulsification, wetting, dispersing, foaming and de-foaming and can also act as antistatic additives.

The constant demand for brighter and more attractive colours has driven pigment manufacturers to improve the performance of organic pigments. Although these pigments possess good colour characteristics, their non-polar surfaces make the adsorption of materials on the surface of the pigment difficult. These dispersants have a much higher molecular weight than the traditional agents which gives a durable adsorption helping to control flooding and floating, a defect that occurs specially in paint systems containing a combination of pigments [6, 20].

Polymeric dispersants consist of functional copolymers that provide effective steric stabilization of pigment particles against flocculation by good steric hindrance[7]. Ideally, the resulting system consists of well solvated and unfurled polymeric chains that should be highly compatible with the binder, allowing a durable and permanent adsorption of the polymeric dispersant onto the pigment surfaces [6]. Some possible arrangements of the anchor groups are shown in figure 5.

A good example of polymeric agents widely used in the industry are resins. Merkle and Schafer (1973) report that treatments with natural polymeric materials started around 1920 with the application of natural rosin, but because of its natural oxidation sensitivity and low melting point, the industry improved this method by adopting rosin derivatives [30].

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[7] As of September 10, 2018 YourDictionary, listed on its website that Steric Hindrance is “the prevention or retardation of a chemical reaction, caused by the arrangement of atoms in a molecule”.

According to Gersont, Melvin and John Grafft. (2000), for rosin to be considered a surface treatment it must be present in at least 5% pigment by weight [31]. Rosin prevents pigment particles from agglomeration and can also facilitate the wetting of the particles, resulting in more transparent and brilliant pigments. Rosin and rosin derivatives such as Barium salts of Abietic Acid are frequently used to coat organic pigments such as the azo pigments and Cu-phthalocyanines [30].

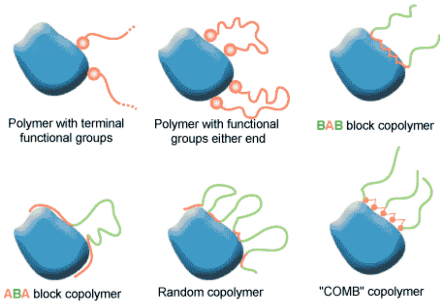

Figure 5. Anchor onto the particle surface either through different anchor groups (Illustration taken from Inkline, 2017) [20].

Another pigment treatment method described in the literature is the use of pigment derivatives. By modifying the chemical structure of the pigment particle, its surface polarity is altered thereby favouring the resin treatment in the binder, stabilizing the dispersion [25, 33].

Pigment derivatives are coloured substances which are closely related to the pigment both in terms of their constitution and hue. Pigment derivatives provide strong adsorption on the pigment surface and facilitate the adhesion or other polymeric treatments which all together improve the compatibility with the binder [31]. Good examples of pigments treated with pigment derivatives are the organic azo pigments with azo compounds such as the ketimines. Cu-Phthalocyanine Blue pigments are also commonly treated with derivatives, for example with phthalimidomethyl [31].

1.6 Coating Materials

After pigment particles have been firstly surface treated, another treatment or treatments can be applied. These are regularly mentioned as coatings, and their nature can be both inorganic and organic. Usually, depending on the pigment and level of coating agent desired, a monolayer of coating material may be enough to cover part of the pigment whereas in other cases, a complete coating of the pigment particles with multimolecular layers is necessary.

Typically, oxides or hydroxides of aluminium, silicium, or zirconium are used. By mixing them with reagents such as $NaAlO_2$, $Al_2(SO_4)_3$, $ZrOSO_4$ it is possible to precipitate two different inorganic treatments, such as $Al_2(SO_4)_3$ and Na_2SiO_3, to form, for example, aluminium silicate [34]. After the inorganic surface treatment has been applied, further modifications with organic surface treatments may occur. These treatments will aid wetting of the pigment during the milling process [34]. One application found, was for titanium dioxide pigment, where silicone oils are used to aid its dispersion in plastics. Pigments for paint are expected to have universal organic treatments and choosing to use them is usually a compromise [34].

1.7 Pigments

Pigment properties such as chemical constitution, crystal form and modifications, and particle size distribution are key elements when selecting the most appropriate pigments for the art market. Inorganic pigments (some of which have been in use prehistoric times, [18], are still of major interest to the coatings industry as well as the art market due their desirable qualities such as: non-bleeding; lightfastness; heat stability; and UV absorption [18]. Although organic pigments are by comparison, less lightfast and less resistant to chemicals such as solvents, they are desirable for their pure, bright and rich colours. As paint technology evolved, particularly in the 20ieth century, it became possible to tightly control pigment characteristics [35].

The particle size is one of the most important properties of pigments. The particle size will influence properties such as hiding power, light adsorption, shade and dispersibility all of which have a direct influence on how the pigment-binder system will behave [34]. For inorganic pigments particle sizes range between 0.1 – 1 µm, for organic pigments, the range is between 0.001 – 0.1 µm [17]. A given pigment is not all uniform in size but contains a mixture of different particle sizes [22, 35].

The smaller the particle size the greater the tendency for agglomeration, therefore it is more challenging to create an effective dispersion [5], however, a larger surface area[8] of pigment is also achieved with smaller particles sizes.

It is always important to remember that the performance of both inorganic and organic pigments depends on the surface treatment and end application [36]. For example, the acid resistance of an Ultramarine grade from Nubiola©, intended for exterior paints will not have a good performance when incorporated in pigment for plastics [36].

1.8 Pigments selected for study

The pigments selected for study were: Umber and Vine Black used in the Carlyle Molart Fellowship,"Historical Reconstructions of Artist's Oil Paint: an investigation of oil processing methods and the use of medium-modifiers" [12]. Investigating these pigment samples and understanding if they possess a coating or not, enabled to understand if the model paints designed for historical paint studies did or did not have any influence from a surface treatment.

Ultramarine Blue pigments were selected for this investigation since the patent literature reported the coating of ultramarine bue with silica. After meeting with Alessa Gambardella who was carrying out research entitled, "Ultramarine disease - Unravelling the mechanism behind binder-pigment interactions in aging Ultramarine Blue paint ", uncoated and coated samples were selected.

When researching Cu-Phthalocyanine Blue pigments, authors reported surface treatments to improve the pigment's performance. Catherine Defeyt's PhD thesis "Copper-phthalocyanine blue pigments in conservation" and samples that she supplied, were essential during this research. Her pigment samples were well dated which made the characterization of the pigment's surface treatment easier.

Two Hansa® Yellows, PY3 and PY74 were selected due to questions from Royal Talens of instability regarding the pigments when incorporated in paint. During this study these pigments from were studied to determine if the presence of surface treatments could contribute to the observed paint instability.

1.8.1 Umber

Umber belongs to the class of iron oxide pigments, also known as earth pigments which have been in use since prehistoric times; archaeological evidence has shown that these pigments were employed for many purposes for more than three hundred thousand years [37]. The natural pigment, with the C. I.[9] number 77727, has two forms: Raw (dark brown) and Burnt (very deep brown) and the main

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[8] As of September 10, 2018, BASF listed in their website that "generally, the higher the surface area, the poorer the flow (…) in certain cases the pigment producer might have surface-treated the products in order to minimize this potential problem" [36].

[9] Colour Index Number – Consists of an extensive international compilation of the structure and properties of dyes and pigments, as well as a system of numbering these materials [39].

components are brown earth pigments containing manganese compounds in addition to iron oxides [37]. Quartz and clays can also be found in the composition, and the type and amount depend on the source of the earth [37].

The dark red or brown earths or Umbers, containing 45%-70% iron oxide and 5%-20% manganese dioxide, were originally imported to Europe from Turkey (via Venice), but are now mined primarily in Cyprus [39, 40]. Current varieties of Umber contain on the order of 5-20% manganese oxide [37].

The chemical formula for Umber is:

$$Fe_2O_3 + Al_2O_3 + Mn_2O_3 + SiO_4 + CaCO_3$$

The preparation of Umber pigments generally include washing to remove mineral impurities such as the coarse quartz, followed by grinding the pigment into a fine powder. The pigment is then usually left to settle in open basins until a stiff mud has formed. Before the pigment is transformed into powder, it is cut into cakes and put to dry [37].

The resulting pigments can vary in terms of hue, depending on the materials present and the particle sizes. According to Kate Helwig (2007), “particle size should be smaller than 25 µm”, and “the particle size is defined by reference to the percentage of particles that will go through a 325-mesh sieve – that is, a screen with a mess size of 44 µm” [5, 18].

1.8.2 Vine Black

As well as the natural iron oxide pigments, Vine Black (C.I. number 77268), has also been in use since pre-historic times continuing to the present day [41]. As the name suggests, Vine Black pigments are prepared by charring vine stalks or tendrils [42, 43]. Chemically, Vine black is essentially composed of pure carbon (C), insoluble carbon compounds and ashes [41] Other chemical elements present are hydrogen and oxygen, commonly present in functional groups on the crystallite or particle surfaces; nitrogen, sulphur and halogens might also be present, depending on the source of the pigment [42].

Properties such as particle size distribution, and the degree of aggregation can vary within a relatively wide range due to the production process. “When it comes to morphology, they’re always derived from the starting material, though it is always possible to find ashes, formed during carbonization on the surfaces” [42]. During research, pigments with varying particle sizes between 10-700 nm were found [44].

1.8.3 Synthetic Ultramarine Blue

In 1828 a new blue colour was introduced to replace natural Ultramarine Blue[10] which was prohibitively expensive. Jean Baptiste Guimet (1828), was responsible for the discovery of synthetic Ultramarine [44].

Synthetic Ultramarine Blue (C.I. 77007), chemical formula is:

$$Na_6Al_6Si_6O_{24}S_4$$

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[10] For more information on Natural Ultramarine Blue see “Natural Ultramarine Blue, and Artificial.” In *Artist's Pigments – A Handbook of Their History and Characteristics* edited by Ashok Roy, 1993” [45].

The materials to produce Ultramarine Blue are relatively inexpensive, typically they're made from China clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent, then, the materials undergo processes such as clay activation, blending and heating raw materials, oxidation and finally purification and refinement [18]. The purity of the ingredients is of considerable importance, one of the requirements being that they should be iron-free [45]. The preferred particle size with good tinting strength varies from 0.7 – 5 µm [18].

However, the problem with the synthetic Ultramarine is that in contact with acids they can lose their colour completely. For that reason, acid resistant grades made with synthetic Ultramarines became available, in which the particles are coated with silica [45]. Nubiola© developed a new range of Ultramarine Blues by coating the pigment surface with silica encapsulation, in the beginning of 21st century, around 2003-2005 [49].

1.8.4 Cu-Phthalocyanine Blue

Rutherford Gettens and George Stout. (1942), report that this was one of the most important inventions of the 20th century after the discovery of Prussian blue in 1704 and synthetic Ultramarine Blue in 1824. The pigment Phthalocyanine blue was first synthesized in 1934 by chemists at Imperial Chemical Industries, Ltd [40]. It was reported to be superior to the other blue pigments then available [40] due its resistance to chemical attack, good heat and light fastness, combined with its clean bright hue [46].

The pigment entered the market in 1936 under the trade name of *Monastral Blue*, but other names including *Winsor Blue*, *Hortensia Blue* or *Rembrandt Blue* (from Royal Talens) were also used [47]. Currently, this pigment is still one of the most important modern synthetic organic pigments used in artist's paint formulations [47].

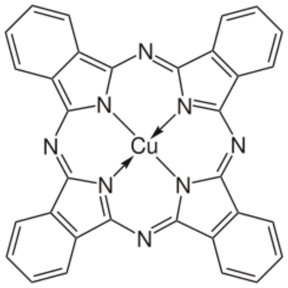

Figure 6. Cu-Phthalocyanine molecular structure (Illustration taken from Willy Herbst and Klaus Hunger, p.422) [49].

The structure consists of a condensed aromatic or heterocyclic ring system which places it in the category of polycyclic pigments (see figure 6). The C.I. number for this pigment is 74160 and the chemical formula is $C_{32}H_{16}N_8Cu$. The molecular structure can be seen on the right. Due to its polymorphism, a variety of crystalline modifications are possible. There are five different polymorphic forms: α, β, γ, δ, and ε. Only two of the forms are commercially important for artist's oil paint [46].

Willy Herbst and Klaus Hunger (2004) report that PB15:0 corresponds to the unstabilized α-CuPc, PB15:1 to the non-crystallizing α-CuPc, PB15:2 to the non-crystallizing and non-flocculating α-form and PB15:3 to the β-CuPc. The PB15:3 type is by far the most used. In terms of hue, the β-modification provides a green and clean shade of blue, while the α-form is distinctly redder than the β-modification [46].

There are two main processes used to produce Cu-phthalocyanine pigments. The **phthalonitrile process** was developed in England and Germany prior to the Second World War and consists of an oxidation reaction. Briefly, the compound is obtained by oxidizing o-xylene with ammonia. The process can occur either in the presence of an oxidation catalyst or with the aid of oxygen and a catalyst, at 330 to 340º C [46]. The **phthalic anhydride** process is mostly adopted in Great Britain and the USA. By oxidizing o-xylene either in the gas phase with vanadium pentoxide as a catalyst or in the liquid phase with dissolved manganese, molybdenum, or cobalt salts as catalysts, phthalic anhydride is obtained [46].

To produce pigments with α-modifications in the crystal structure it is necessary to dissolve crude Copper Phthalocyanine Blue in sulphuric acid, followed by precipitation in water (hydrolysis). As described by Catherine Defeyt (2013) “the β-modification as a rule evolves as a more coarse-grained material than the α-phase. It is prepared by milling the crude Copper Phthalocyanine Blue with salt in the presence of a ‘crystallization stimulating’ solvent. Aromatic hydrocarbons, esters, or ketones are normally used” [48]. The resulting average particle size for both forms is between 0.02 – 0.5 µm [46].

Willy Herbst and Klaus Hunger (2004), report the two most effective techniques to stabilize the pigment against conversion to a different phase or to prevent flocculation during pigment application are:

- minor chemical modifications of the Copper Phthalocyanine Blue molecule, for example by “partial chlorination”;

- admixing other agents such as surfactants to the Copper Phthalocyanine molecule thus stabilizing the surface [46].

Cu-Phthalocyanine Blue particles have the tendency to agglomerate, thus it is common to coat the pigment surface during the final stages of finishing to reduce particle contact. The most common additives include rosins, fatty amines and pigment derivatives [48].

1.7.5 Hansa® Yellows PY3 and PY74

Hansa® Yellows, one of the first classes of synthetic organic pigments produced for the paint industry, are still among the most important yellow pigments in use. They became commercially available in 1910 and the first patent for Hansa® Yellows is No. 257,488 published in 1913 [49]. The first of the Hansa® Yellow pigments to be produced was PY1 in 1909 by Dr. Hermann Wagner. Later, PY3 was developed in 1928 by Hoeschst, and after 1960, the number of these yellow pigments increased to 12, including PY74 [49, 50]. These pigments have been employed in artist’s materials since 1925 [49].

According to Hungerand Herbst (2004), Hansa Yellows belong to the class of monoazo pigments which are formed by azo coupling of aniline (with the diazonium ion chromophore -N≡N) and acetoacetanilide derivatives.

As is reported for other organic pigments, the addition of resins such as rosin is a common aftertreatment to control the particle size of Hansa® yellows. Other treatments including pigment derivatives are also reported to be frequent [35, 50].

Rainer Schunck and Klaus Hunger (1988) report that “with the exception of water and aliphatic hydrocarbons, Hansa® Yellows (…) show a certain solubility in most solvents. This solubility in solvents manifest itself in their bleeding in most solvents, their ease of recrystallization, and their tendency to blooming, bleeding, and crocking in plastics, which severely hampers their application” [50].

<u>Pigment Yellow 3 (PY3)</u>

Pigment Yellow 3 (C.I. number 11710) or PY3, with its main properties being excellent lightfastness and durability, is adopted for various uses, for example textile printing, office articles, artists’ paints, and printing ink [49].

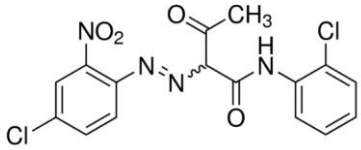

Figure 7. PY3 molecular structure, (Illustration taken from Rainer Schunck and Klaus Hunger, p. 429 [50].

When compared to PY1, PY3 possesses a much greener shade. The pigment is more sensitive to organic solvents and to migration than PY1, however, it is less expensive which can be advantageous for most industries [50].

The chemical formula of PY3 is $C_{16}H_{12}Cl_2N_4O_4$ (see figure 7). Its preparation relies in a reaction product of diazotized 4-chloro-3-nitroaniline with 2-chloroacetaniline [53]. The resulting average particle size ranges between 0.48 – 0.57 µm [50].

Pigment Yellow 74 (PY74)

Similar to PY3, this pigment (C.I. number 11741) is also primarily used in the paint and printing ink industries. Its greenish yellow shade is somewhere between PY1 and PY3 [30].

PY74 exhibits excellent tinctorial strength and can be more advantageous than PY1 due its cost and performance. Its chemical formula is $C_{18}H_{18}N_4O_6$ (see figure 8) and it results from the reaction process of diazotized 4-nitro-2-anisidine with 2-acetonisidide. The mean particle size of PY74 corresponds to 0.18 µm [35, 50].

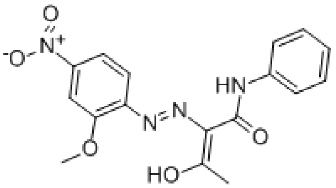

Figure 8. PY74 molecular structure**,** (Illustration taken from Rainer Schunck and Klaus Hunger, p. 429 [50].

2.1 The provenance of the selected pigments

Pigments were selected to enable the exploration of various questions such as what to expect from modern manufacturing, the issue of using commercially available pigments for historically accurate reconstructions [51] and how a surface treatment can be detected in a paint. The following describes the pigments selected for study (see table 1).

Vine Black and Umber pigment were purchased from Kremer Pigmente during the Carlyle MOLART Fellowship, see the report "Historical Reconstructions of Artist's Oil Paint: an investigation of oil processing methods and the use of medium-modifiers" [12]. The specific time when they were purchased is known (1999), which facilitates the investigation in terms of surface treatment, since more direct research can be made on patents and technical literature.

Two Ultramarine Blues, two Cu-Phthalocyanine Blues and two Hansa® Yellows Pigments from the Cultural Heritage Agency of the Netherlands (RCE) Reference Collection were selected and compared to other pigments which had already been studied by three other researchers (see below and Table 1). To search material availability, the RCE has a LOIS database, where materials can be searched by name, type, supplier, C.I. number and any other description the user introduces. When it concerns to the pigment findings, the information available can include name, type of reference, RCE reference number, a brief description of the pigment, supplier, literature and remarks when possible. However, no information was available regarding the selected RCE pigments, except that the day they entered the collection was recorded.

Two samples of Ultramarine Blue and analytical results regarding those samples were shared by Alessa Gambardella, who is using these samples in her ongoing project entitled "Ultramarine disease - Unravelling the mechanism behind binder-pigment interactions in aging Ultramarine Blue paint." She had already established that one was uncoated[11] and the other was coated. The coated Ultramarine Blue pigment is from Kremer Pigmente and their datasheet indicates silica (Si) coating.

Three well characterized and dated Cu-Phthalocyanine Blue pigments were provided by Catherine Defeyt who had been carrying out research on them [46]. These three pigments date from 1956 (PB15:1), 1978 (PB15:0) and 1980 (PB15:2) and were intended for artist's paint.

Also, the artist's paint manufacturer Royal Talens supplied two contemporary Hansa Yellows: pigment Yellow 3 (PY3) and pigment Yellow 74 (PY74). As noted in Part I, these were studied since the company were having stabilization issues with their paints and were interested in whether the presence of pigment surface treatment could be contributing to the instability of their paint systems.

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[11] See results from AKZO NOBEL Chemicals on Alessa Gambardella's on-going project "Ultramarine disease - Unravelling the mechanism behind binder-pigment interactions in aging Ultramarine Blue paint", In: Results and Discussion, 3.1.3.

2.2 The Experimental Design

The detection of possible inorganic and organic surface treatments was attempted on a total of 15 samples which are listed in Table 1 along with the analytical techniques applied. The analytical approach began with SEM-EDX for an initial investigation of the non-characterized pigments and to try to detect the surface treatment and/or coating either by the elemental composition or by visual appearance.

(S)TEM-EDX enables the detection of treatments on the pigment particles, since the particle is sliced before analysis (see sample preparation, appendix 2), while, FEG-SEM enabled the detection of the surface treatment topography on pigment particles.

(S)TEM-EDX was performed on 6 samples. This technique was selected thanks to previous work done by Alessa Gambardella where an inorganic coating had been detected. Her results have not been published yet as they are part of the on-going project noted above [52]. FEG-SEM analyses were performed on 8 pigments and from two samples from Ultramarine Blue paint-outs with triolein[12] from Alessa Gambardella's project [52].

The organic analyses were performed and interpreted by Carolina Gomes[13], using hyphenated mass spectrometry techniques such as EGA-MS and Py-GC/MS. The EGA-MS method enabled the characterization of low mass volatile compounds through slow and controlled heating of the pigment powder and was used to confirm the first findings using Py-GC/MS with a derivatization agent, TMAH (tetramethylammonium hydroxide).

The equipment used is detailed in Appendix 2, and data produced is detailed in Appendices 3 and 4.

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[12] Triolein is a symmetrical triglyceride derived from glycerol and three units of the unsaturated fatty acid oleic acid [53].

[13] Master Project, concurrent with this one [53], also carried out at RCE under the supervision of Klaas Jan van den Berg.

Table 1. The pigments studied, the analytical instruments used and results

	Inorganic analysis			Organic analysis		
	SEM-EDX	(S)TEM-EDX	FEG-SEM	EGA-MS	Py-GC/MS	Py-GC/MS (TMAH)
Umber	☑ No coating.	☑ No coating	☒	☑ No coating	☒	☒
Vine Black	☑ No coating	☑ No coating	☑ No coating	☑ No coating	☒	☒
Uncoated Ultramarine Blue, Kokkie®	☑ No coating	☑ No coating	☑ No coating	☒	☒	☒
Coated Ultramarine Blue, Kremer Pigmente®	☑ SiO coating	☑ SiO coating (Previous results [51)	☑ Coating	☑ No Coating	☑ No Coating	☑ No Coating
Ultramarine Blue 867	☑ No coating	☒	☒	☒	☒	☒
Ultramarine Blue LUKAS	☑ No coating	☒	☒	☒	☒	☒
Cu-Phthalocyanine Blue (IRPA), sample from 1956	☑ No coating	☒	☒	☑ No coating	☑ No coating	☑ No coating
Cu-Phthalocyanine Blue (BRICO), sample from 1978	☑ No coating	☒	☒	☑ No coating	☑ No coating	☑ No coating
Cu-Phthalocyanine Blue (Winsor&Newton), sample from 1980	☑ No coating	☑ SiO coating	☑ Coating	☑ No coating	☑ Alkanes	☑ Alkanes
Cu-Phthalocyanine Blue 2755 – Monastral Blue	☑ No coating	☒	☒	☑ No coating	☑ Alkanes	☑ No coating
Cu-Phthalocyanine Blue 833	☑ No coating	☑ SiO coating	☑ Coating	☑ Rosin Coating	☑ Rosin Coating	☑ Rosin Coating
PY3 – Royal Talens	☑ No coating	☒	☑ Coating	☑ No coating	☑ No coating	☑ No coating
PY3 – 0526	☑ No coating	☒	☒	☑ No coating	☑ No coating	☑ No coating
PY74 – Royal Talens	☑ No coating	☑ SiO coating	☑ Coating	☑ No coating	☑ No coating	☑ No coating
PY74 - 0527	☑ No coating	☒	☒	☑ No coating	☒	☒

3 Results and Discussion

3.1 Umber

Inorganic Surface Treatment:

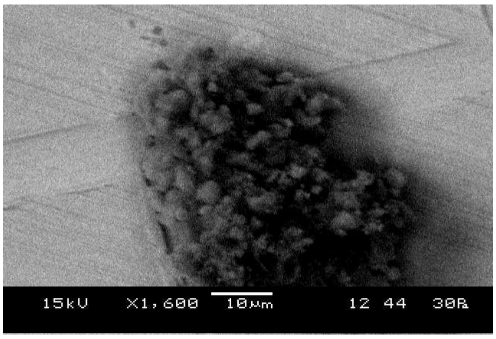

Figure 9. SEM images in LV mode Umber pigment sample. Results acquired by the author.

Umber pigment has a mixture of smaller and larger round particles as seen in figure 9. As shown in table 2, with **SEM-EDX** it was possible to identify a large variety of elements, however, no indication of a surface coating was found using this technique.

Table 2. Elemental characterization (EDX) using SEM, of Umber pigment. Results acquired by the author.
Numbers express Wt. %

C	O	Mg	Al	Si	P	Ca	Mn	Fe
4,1	36,9	6,5	4,0	9,8	0,9	3,1	7,6	27,0

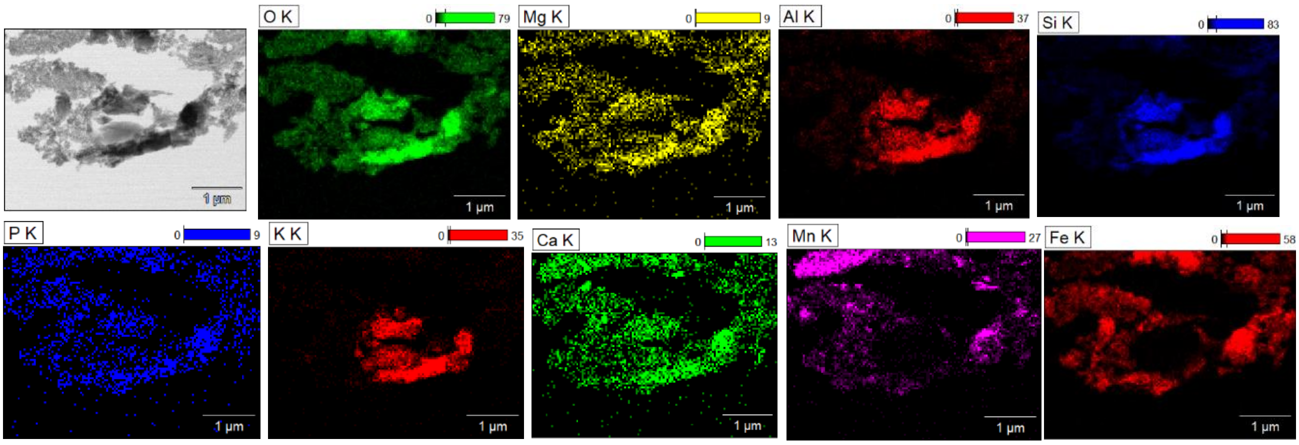

Figure 10. Umber TEM-BF Phase Image and phase-map elemental mapping. Results acquired from Arne Janssen at AKZO NOBEL Chemicals.

(S)TEM-EDX analysis detected the variety of materials present and confirmed that there was no visible coating present in this sample (see figure 10).

Organic Surface treatment:

Regarding possible organic surface treatment identification, the EGA-MS results acquired by Carolina Gomes [54] did not result in any conclusive evidence of organic coatings on the Umber Brown pigment.

3.2 Vine Black

SEM-EDX analysis showed that aside from the expected C and O, also Si and Al were identified (see table 3). However, these compounds may not be related to a surface treatment. As for the SEM images, the pigment particles can be described as rounded and irregular, with no surface coating visible (see figure 11).

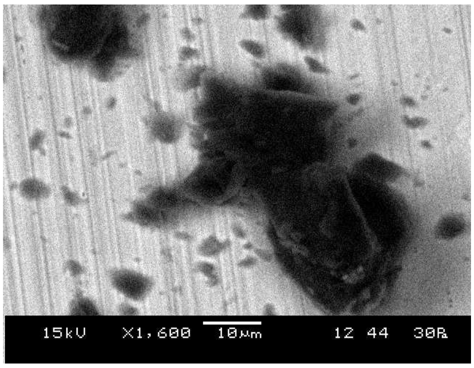

Figure 11. SEM images in LV mode on Vine Black pigment. Results acquired by the author.

Table 3. Elemental characterization (EDX) using SEM, of Vine Black pigment. Results acquired by the author.

Numbers express Wt. %

C	O	Al	Si	S
72,1	20,0	5,4	1,6	0,9

(S)TEM-EDX characterization enabled to understand that no coating is present on the Vine Black pigment surface (see figure 12).

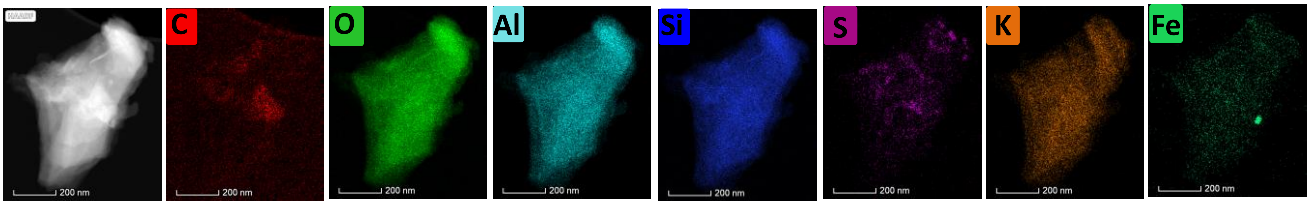

Figure 12. Vine Black TEM-BF Phase Images. Results from Arne Janssen, at AKZO NOBEL Chemicals.

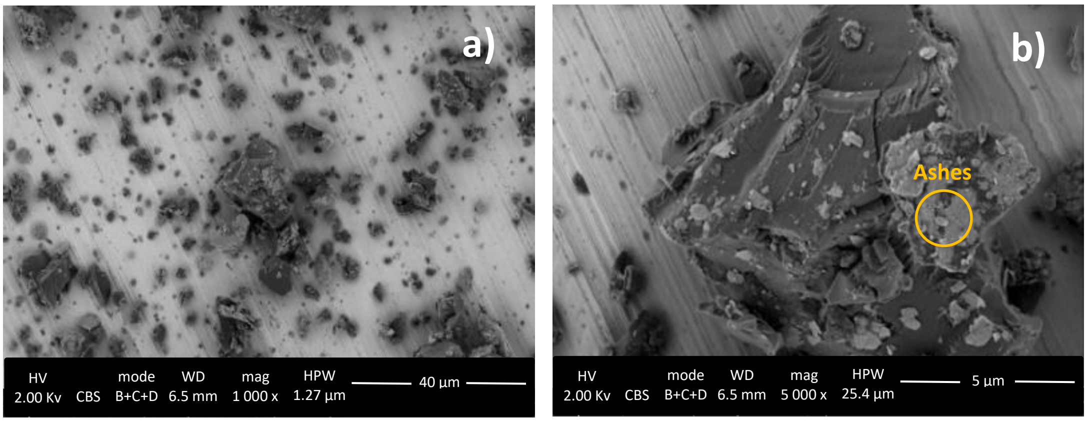

Figure 13. FEG-SEM images in CBS mode showing a) Vine Black agglomerates and b) detailed particle with possible ashes on the surface. Results acquired by Ineke Joosten.

With **FEG-SEM** analysis performed by Ineke Joosten[14], it was possible to determine the appearance of the pigment particles. This technique revealed the presence of two different materials (figure 13): irregular chunks of pigment with lighter greyish irregular material attached. It is thought that the small greyish particles could consist of ashes which resulted from the pigment manufacture during the charring of the pigment [26].

Organic Surface treatment:

Regarding possible organic surface treatment identification, the EGA-MS results acquired by Carolina Gomes [54] did not result in any conclusive evidence of organic coatings on the Vine Black pigment.

3.3 Ultramarine Blue

Inorganic surface treatment/coating:

As noted previously thanks to the work of Alessa Gambardella, the selection of coated and uncoated ultramarine pigments was possible. Having a coated pigment enabled the identification of the appearance of the coating by (S)TEM-EDX making it possible to compare with other pigment samples where it was not known if they had been coated.

(S)TEM-EDX was selected since previous results from Alessa Gambardella demonstrated the appearance of SiO_2 coating on Ultramarine Blue pigments (see figure 14 and table 4) which can be observed as a transparent coating around the pigment particles.

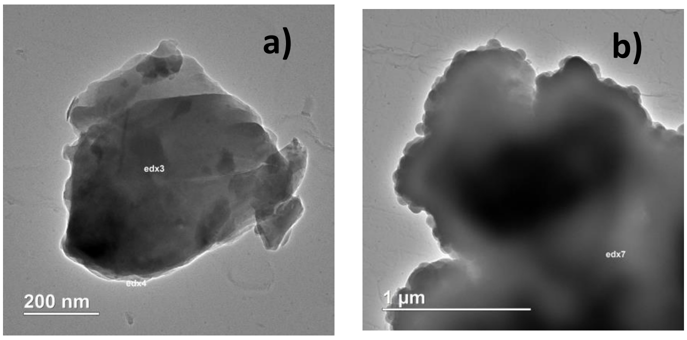

Figure 14. TEM-BF images of an a) uncoated Kokkie Ultramarine sample and b) coated Kremer Pigmente Ultramarine, results from AKZO NOBEL Chemicals. Illustrations are from Allessa's Gambardella's on-going project at the Rijksmuseum [52].

Table 4. Elemental characterization (EDX) using (S)TEM, of an a) uncoated and b) coated of Ultramarine Blues. Results from AKZO NOBEL Chemicals who are supporting Allessa's Gambardella's project [52].

Numbers express Wt. %

		C	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
a)	**Uncoated Ultramarine**	37,9	21,4	0,4	0,3	3,7	10,9	2,1	0,2	0,4	1,7	21,3
b)	**Coated Ultramarine**	2,3	28,5	10,9		12,0	33,6	11,3	0,2	0,5	0,7	

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[14] Scientist at the Cultural Heritage Agency of the Netherlands (RCE). In her PhD research, she specialized in the technology of early historical iron production in the Netherlands. She is responsible for the Electron Microscope Techniques.

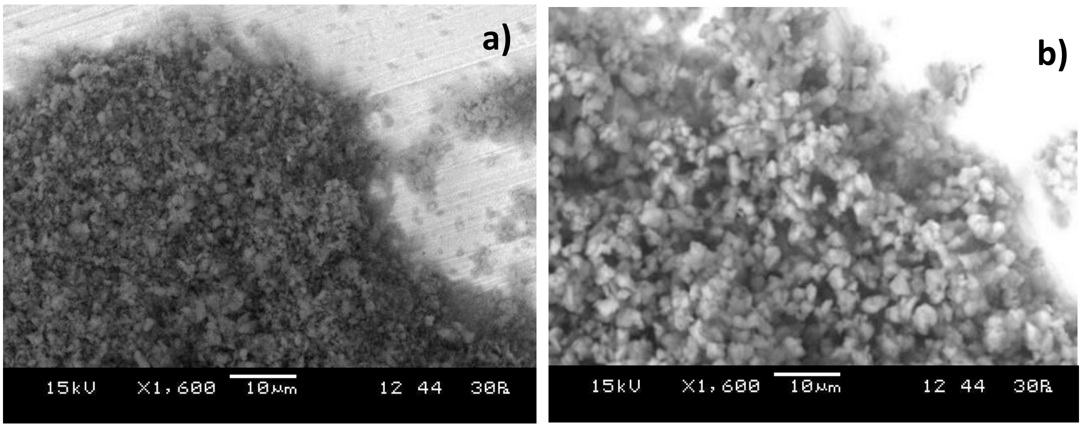

Figure 15. SEM images in LV mode of a) uncoated Ultramarine Blue and b) coated Ultramarine Blue, analysis done by the author of this study. Results acquired by the author.

SEM-EDX was performed by this author. The same uncoated and coated samples were analysed with inconclusive results. As seen in figure 15, it was not possible to detect the surface coating visually using SEM. Both pigment particles have a round, regular shape, however, it is important to note that the coated particles are larger in size.

Table 5. Elemental characterization (EDX) using SEM, of an a) uncoated and b) coated Ultramarine Blues. Results acquired by the author.

Numbers express Wt. %

		C	O	Na	Al	Si	S	K	Ca
a)	**Uncoated Ultramarine Kokkie**	2,9	39,1	2,2	15,6	21,6	15,8	1,4	1,2
b)	**Coated Ultramarine Kremer Pigmente**	2,1	48,9	6,1	10,4	24,1	8,2	0,3	

As for the elemental characterization of the coating (table 5), with SEM-EDX it was not possible to detect the silica coating. The fact that the pigment composition has some of the same materials of the coating makes the identification more difficult. Also, because we are dealing with small amounts of material, discerning if the coating is present is not possible using this analytical technique. Finally, it was not possible to see the surface coating using SEM since the resolution is not high enough with this technique. When compared to TEM resolution the coating is easily detected [55].

FEG-SEM analyses were performed by Ineke Joosten in order to acquire higher resolution images. This technique showed a very clear difference between the uncoated and the coated pigment. As seen in figure 16-b), the coated particles of Ultramarine Blue appear to have a structure similar to the folds we see in images of the brain.

The coated ultramarine particles in figure 16b) are fully covered by a dense silica film [55]. In the **(S)TEM-EDX** imaging small amounts of silica spheres deposited on the surface of the particles can be seen (figure 14-b). The resulting increased particle size of the coated ultramarine occurs due to the addition of the coating material on the particles [55].

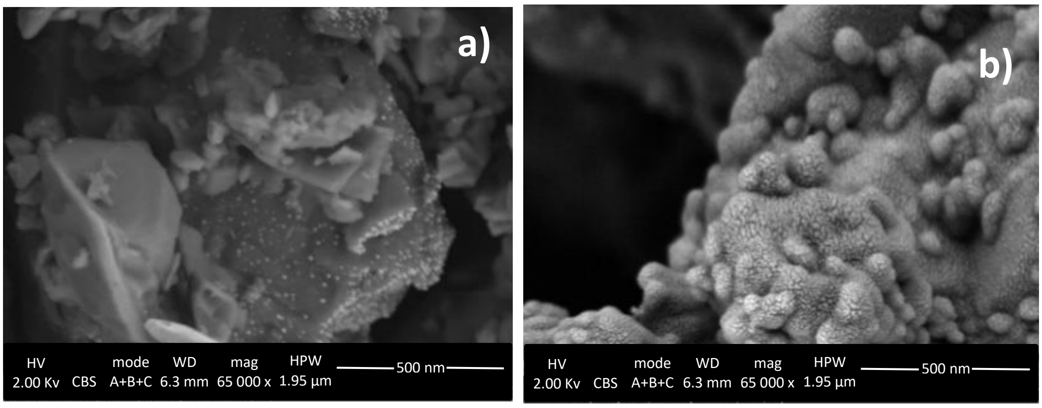

Figure 16. FEG-SEM images in CBS mode showing an a) uncoated Ultramarine surface and an b) coated Ultramarine surface. Results from Ineke Joosten at RCE.

When the RCE reference collection pigments 867 and LUKAS are compared with the uncoated (kokkie) and the coated (Kremer Pigmente) pigments, an elemental pattern can be distinguished. Even though EDX characterization is not quantitative, as seen in table 4, pigment 867 has its values of more approximate to the coated Ultramarine Blue, while the LUKAS sample has values more approximate to the uncoated Ultramarine Blue. This could be an indication that pigment 867 is coated and the LUKAS is uncoated. Nevertheless, these results need to be further confirmed using other techniques such as (S)TEM-EDX or/ and FEG-SEM.

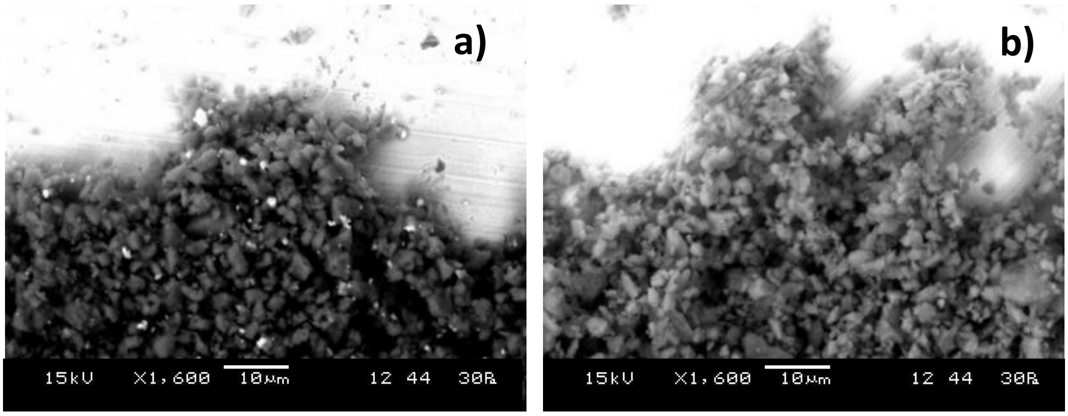

Figure 17. SEM images in LV mode of a) 867 Ultramarine pigment and b) LUKAS Ultramarine pigment. Results acquired by the author.

Table 6. Elemental characterization (EDX) and comparison using SEM of figure 15a) uncoated Ultramarine, Kokkie® with figure 17b) LUKAS pigment from RCE Reference Collection and figure 15b) coated Ultramarine, Kremer Pigmente® with figure 17a) 867 pigment from RCE Reference Collection. Results acquired by the author.

Numbers express Wt. %

	C	O	Na	Al	Si	S	K	Ca
15a) Uncoated ultramarine, Kokkie®	2,9	39,1	2,2	15,6	21,6	15,8	1,4	1,2
15b) Coated Ultramarine, Kremer Pigmente®	2,1	48,9	6,1	10,4	24,1	8,2	0,3	
17a) 867 – RCE Reference Collection	2,2	42,1	4,7	11,9	25,9	13,0		
17b) LUKAS – RCE Reference Collection	2,6	53,1	0,7	15,4	20,3	6,5	1,4	

Regarding the SEM back-scatter imaging, no assumptions can be made regarding the surface treatment. Both pigments have a mixture of round and irregular particles as shown in image 17.

Organic Surface treatment:

Regarding possible organic surface treatment identification, the EGA-MS and Py-TMAH-GC/MS were performed by Carolina Gomes [54] in the coated Ultramarine Blue pigment from Kremer Pigmente®.

The EGA-MS analysis did not provide results that can attributed to any surface treatment. However, the Py-TMAH-GC/MS showed the presence of methyl esters of fatty acids which suggests the presence of an organic coating. In appendix 4, the corresponding peak identification can be found.

3.4 Cu-Phthalocyanine Blue

As noted in the introduction, organic pigments are more difficult to analyse, because there are many forms possible (for example in the case of Phthalocyanine pigments) and because the smaller particle sizes make the analyses process more difficult, since a higher resolution is needed for the same results when compared with inorganic pigments.

The three dated Cu-Phthalocyanine Blue pigments, from 1956, 1978 and 1980, are α-form. Two of them (from 1956 and from 1980) were stabilized during manufacturing against crystallization and flocculation [27]. While the literature describes the use of surface treatments for organic pigments using rosins, fatty amines or pigment derivatives [27], the specifics of the treatment for the different forms of Cu-Phthalocyanine was not found in the literature.

Inorganic surface treatment/coating:

SEM-EDX analysis was performed by this author, for an initial characterization of the Cu-Phthalocyanine Blue pigment particles. The pigment from 1956 presents small pigment particles with a rounded shape (figure 18a) while the sample from 1978 presents larger rounded particles (figure 18b). In contrast the pigment sample from 1980 (figure 18c) exhibits two different types of particles: one type contains copper (Cu) and are therefore presumably Cu-Phthalocyanine pigments and the other type contains Ba and S, which is assumed to be barium sulphate, as exhibited in table 7. In both cases particles are smaller than those from the 1956 and 1978 pigments (compare figures 17 a, b and c). No surface treatment was detected using this technique (see table 7).

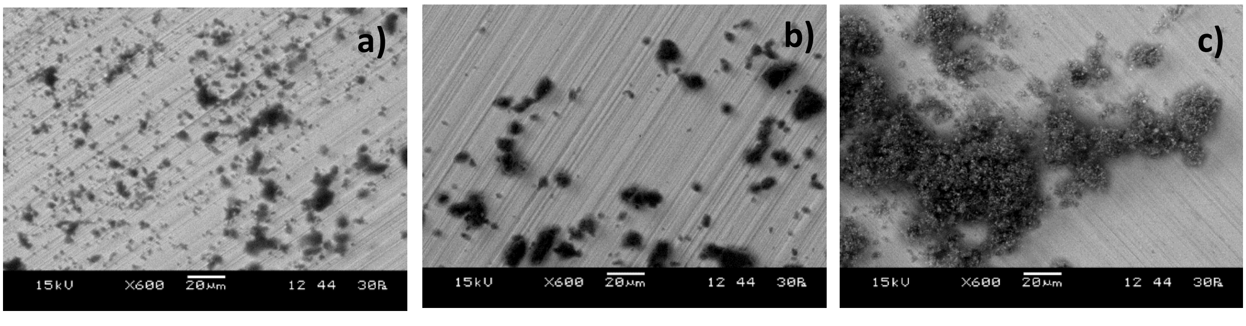

Figure 18. SEM images in LV mode of a) pigment from 1956, b) pigment from 1978 and c) pigment from 1980. Results acquired by the author.

Table 7. Elemental characterization (EDX) and comparison using SEM of figure 18a) pigment from 1956, figure 18b) pigment from 1978 and figure 18c) pigment from 1980 and two pigments from the RCE Reference Collection, figure 19a) and figure 19b). Results acquired by the author.

Numbers express Wt. %

	C	N	O	Al	S	Cl	Cu	Ba
18a) Pigment from 1956	37,2		3,1	1,0	0,2		58,4	
18b) Pigment from 1978	31,6	6,5	2,6	0,3	1,1		57,9	
18c) Pigment from 1980	14,1	3,0	8,5	4,5	4,9		44,9	19,9
19a) 833 – RCE Reference Collection	48,1	16,9	2,0	0,5			32,3	
19b) 2755 – Monastral blue sample – RCE Reference Collection	38,4	10,5	0,8	0,6	0,3	6,0	24,8	

As seen in table 7, the pigment from 1956 has no nitrogen (N), possibly because it was manufactured trough the phthalic anhydride process [28]; the pigment from 1980 is mixed with $BaSO_4$ which was further confirmed using SEM-EDX. “The Ba particles can be observed in figure 18c) as bright dots, and, as shown in table 7, the aluminium (Al) values for this sample are much higher when comparing with the other pigments, which may indicate a possible surface treatment. Two pigments from the RCE reference collection were compared to these three pigments (figure 19 a and b). Both have similar appearance under SEM-EDX analyses. Both pigments present aggregated rounded particles of large dimensions, however, in the 2755-Monastral blue pigment chloride (Cl) was identified.

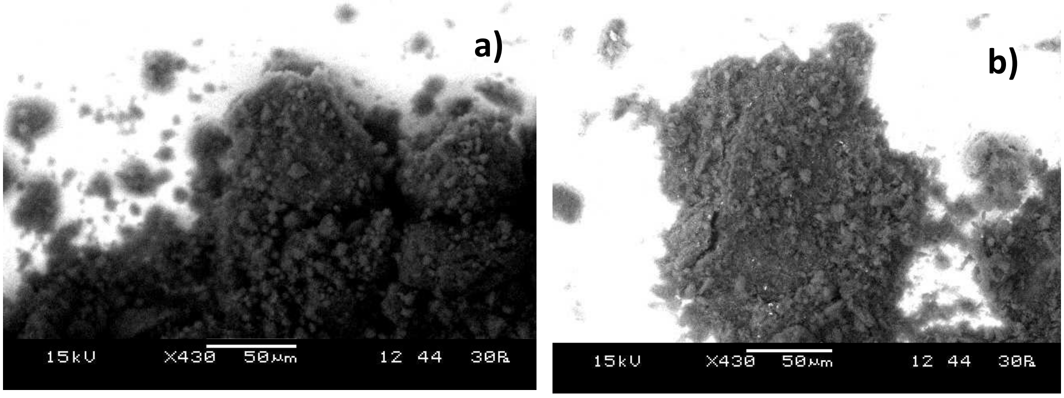

Figure 19. SEM images in LV mode of a) pigment 833 and b) 2755 – Monastral blue pigment. Results acquired by the author.

(S)TEM-EDX results show that combined carbon (C), silica (Si) and oxygen (O) spectrum images could indicate that there is a coating around the pigment on the pigment from 1980 (figure 20a). It can also be pointed out that the surface treatment was homogenously applied around the pigment particle, however, other particles analysed have not showed the same results. This may be an indication that the surface treatment was applied to CuPc particles and not necessarily to the final pigment mixture which includes other materials such as silicates and barium, for example (figure 20b).

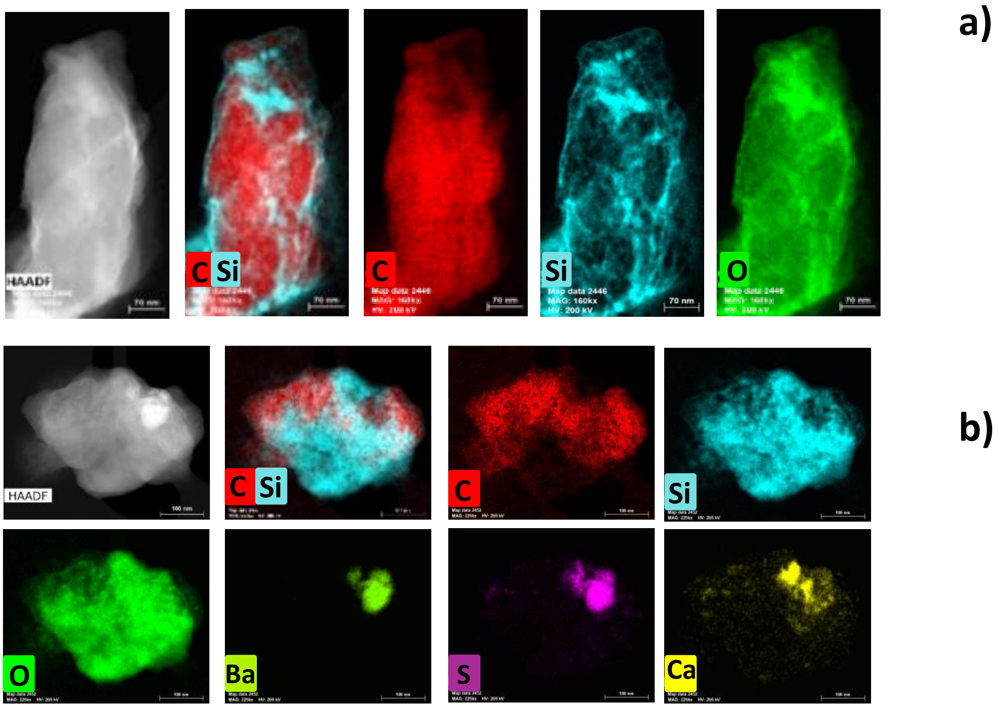

Figure 20. (S)TEM-EDX elemental mapping of Cu-Phthalocyanine pigment from 1980 showing in figure 20a) a possible coated particle with silica and another particle from the same pigment showing a mixture of silicates and Ba particles and no evidence of a Si coating (figure 20b). Results acquired by Arne Janssen at AKZO NOBEL Chemicals.

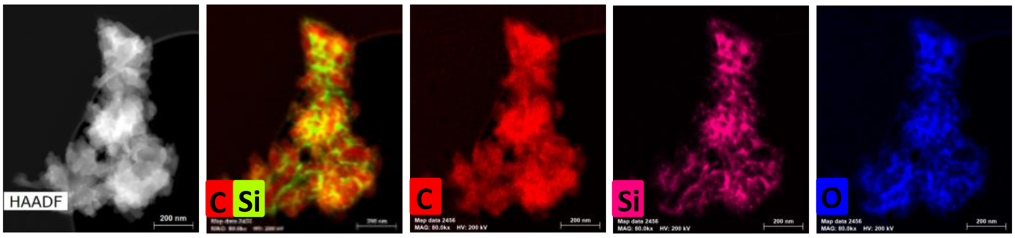

Figure 21. (S)TEM-EDX elemental mapping of Cu-Phthalocyanine from 833 pigment showing a coated particle with silica (Si). Results acquired by Arne Janssen at AKZO NOBEL Chemicals.

Also, (S)TEM-EDX analyses on 833 Blue pigment showed that combined carbon (C), silica (Si) and oxygen (O) could indicate that there is a coating. Contrary to the Blue pigment from 1980, the (S)TEM-EDX results suggest that the coating seems to be within the pigment particle and not around the particle (figure 21).

Two Cu-Phthalocyanine Blues, pigment 833 and the pigment from 1980 were analysed using **FEG-SEM** by Ineke Joosten. This revealed very distinct particles and pigment surfaces. Pigment 833 presents elongated particles with a distinctive surface appearance similar to a “crocodile skin” (see figure 22b), of larger dimensions than the pigment from 1980. The surface of the blue pigment from 1980 is irregular, and a mixture of different particles and materials can be seen in figure 20a).

Regarding the composition, both pigments have silica (Si) in their composition. For pigment 833 this surface appearance may be due to a coating, since (S)TEM-EDX analysis confirmed the presence of silica (Si). The blue pigment from 1980 shows a combination of silica (Si) with pigment particles (see figure 22a) while the 833 pigment show a surface treatment homogeneously applied (see figure 22b).

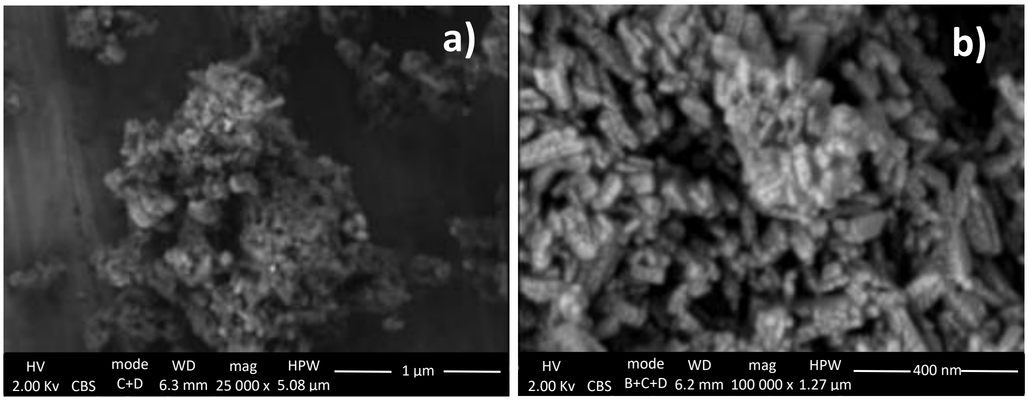

Figure 22. FEG-SEM images in CBS mode showing a) pigment from 1980 and b) 833 pigment, performed by Ineke Joosten.

Organic Surface treatment:

EGA-MS, Py-GC/MS, Py-THM-GC/MS and DTMS analyses were performed by Carolina Gomes [53] on the 5 samples of Cu-Phthalocyanine pigments. The analysis showed did not detect surface treatments with the exception of pigment 833.

Regarding pigment 833, using **EGA-MS,** it was found at low temperature the fragment ions of m/z 239 and 285 which are indicative for dehydroabietic acid (DHA). Findings at this lower temperature also indicates that the material is not crosslinked to the pigment. Further analysis with **Py-GC/MS**, with and without **TMAH**, revealed the presence of diterpenoids (pinacea resin) in different stages of oxidation such as dehydroabietic acid and 7-oxo-dehydroabietic acid (7-oxo-DHA), isopimaric acid and traces of fresh resin methyl abietate. These findings confirmed the presence of rosin and not only dehydroabietic acid [56]. See appendix 4 for the corresponding peak identification.

To see the spectrum, consult Appendix 4, Figure A10 and Table A1.

3.5 Yellow Pigments

As noted in Part I, during a meeting with representatives from Royal Talens, it was explained that they were experiencing paint instability which was thought to result from the yellow pigment used, however the problem with the pigment had not been identified. For that reason, yellow pigments, PY3 and PY74 (see below) from their current suppliers were analysed to determine whether the surface had any treatment which could be influencing the paint stability. These yellow pigments were compared with RCE reference pigments.

Due to the lack of time available, **TEM-EDX** was performed only on the Royal Talens PY74 pigment samples.

Pigment Yellow 3 (PY3)

With **SEM-EDX** it was possible to determine what inorganic compounds were present and to view the pigment size and morphology. The PY3 Royal Talens pigment has small rounded particles (see figure 23a) and as shown in table 8a), only carbon (C), nitrogen (N), oxygen (O) and chloride (Cl) were identified. When compared to the RCE reference collection PY3 pigment, this pigment has smaller particles and alumina (Al) and silica (Si) were identified; also, the chloride (Cl) values are much higher than in pigment PY3 from Royal Talens (see table 8b).

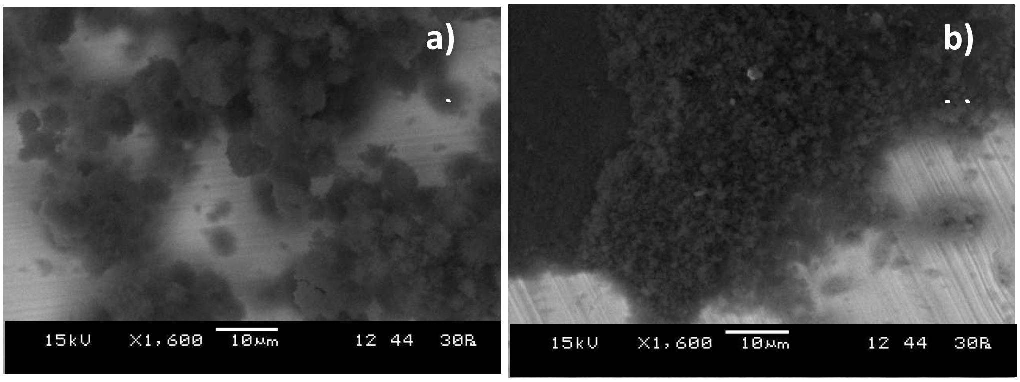

Figure 23. SEM images in LV mode of a) pigment from Royal Talens and b) pigment from the RCE reference collection. Results acquired by the author.

Table 8. Elemental characterization (EDX) and comparison using SEM of a) pigment Yellow 3 from Royal Talens and b) pigment Yellow 3 from RCE reference collection.

Numbers express Wt. %

	C	N	O	Al	Si	Cl
a) PY3 Royal Talens©	35,1	20,4	27,3	-	-	17,2
b) PY3 RCE reference collection	29,3	20,7	24,2	0,6	0,4	25,3

FEG-SEM analysis were performed by Ineke Joosten, on the PY3 provided by Royal Talens only. As can be seen in figure 24, two different materials can be observed. Results acquired by the author.

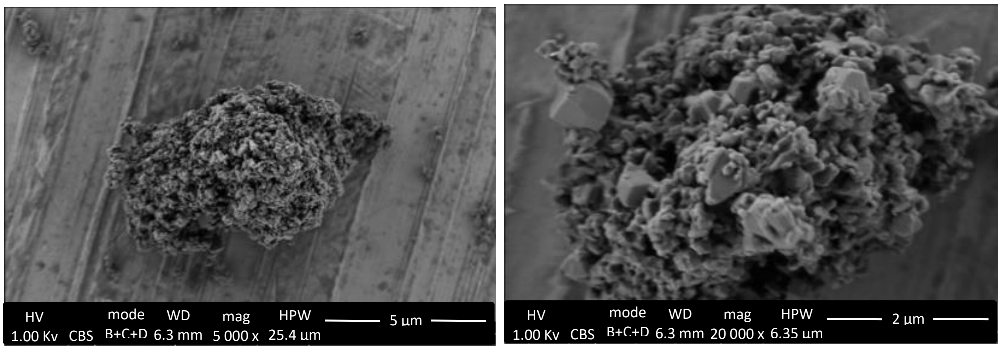

Figure 24. FEG-SEM images in CBS mode showing a) an agglomerate of PY3 and b) a closer look to the agglomerate, showing a combination of PY3 particles. Results acquired by Ineke Joosten at RCE.

Pigment Yellow 74 (PY74)

When the **SEM-EDX** results from PY3 and PY74 pigments are compared, it can easily be seen that chloride (Cl) was found in both PY3 pigments, but not in any PY74 pigments (see tables 8 and 9). Regarding the pigment particles, PY74 from Royal Talens also has very small particles (see figure 25).

Table 9. Elemental charaxterization (EDX) comparison usign SEM between a) pigment Yellow 74 from Royal Talens and b) pigment Yellow 74 from RCE reference collection. Results acquired by the author.

Numbers express Wt. %

	C	N	O
a) PY74 Royal Talens	37,1	23,8	39,1
b) PY74 RCE reference collection	38,4	21,3	40,3

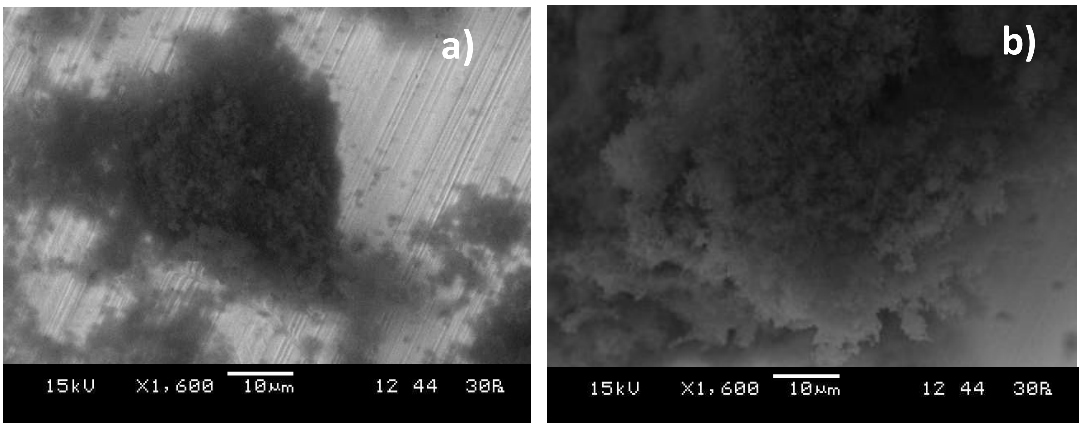

Figure 25. SEM images in LV mode of PY74 a) pigment from Royal Talens and b) pigment from the RCE reference collection. Results acquired by the author.

It is notable that PY74 from Royal Talens and RCE Reference Collection present more irregular shape particles than both PY3 pigment samples (see image 25a). When compared to the PY74 RCE reference sample (figure 25b), a similar morphology to sample PY74 from Royal Talens can be observed.

(S)TEM-EDX was performed by Arne Janssen (AKZO NOBEL Chemicals), only on the Royal Talens PY74 pigment. The results suggest that parts of the pigment particles are coated with a SiO coating (see figure 26). The fact that only part of the pigment is coated raises the question of whether it is an intended partial coating or whether this represents an ineffective application of the treatment of the pigment. If the treatment has been ineffectively applied, then it may be the reason for the unstable paint, however, this needs further study.

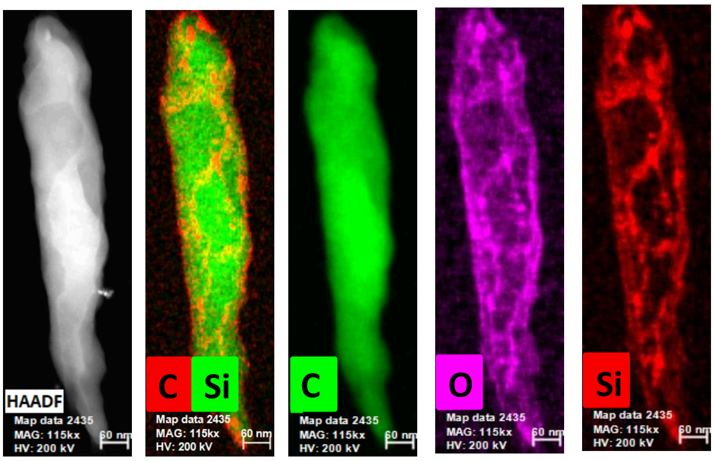

Figure 26. (S)TEM-EDX image mapping on PY74 Royal Talens sample where there seems to be a silica (Si) coating on the particle. Results acquired by Arne Janssen at AKZO NOBEL Chemicals.

FEG-SEM analysis showed that the two PY74 pigments studied vary significantly in terms of their morphology. The sample from Royal Talens presents a flat and irregular shape of larger dimensions (see figure 27a) than the sample from RCE reference collection where the pigment particles are more aggregated, exhibiting a mixture of rounded and elongated particles (see figure 27b). Regarding the presence of a surface treatment: no coating is visible. The small particles size of the PY74 make it particularly difficult to detect surface treatment. However, as noted above TEM-EDX mapping does suggest the presence of a silica coating on the PY74 provided by Royal Talens (figure 25a). Pigment particles show significantly less agglomeration in the pigment from Royal Talens which also suggests surface treatment (compare figures 25a and b).

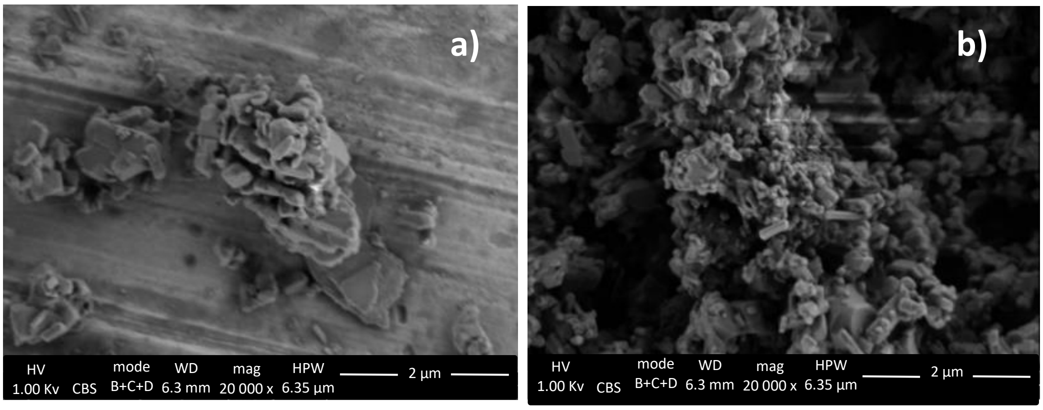

Figure 27. FEG-SEM images in CBS mode showing a) pigment from Royal Talens and b) pigment from RCE reference collection. Results acquired by Ineke Joosten at RCE.

Organic Surface treatment of PY3 and PY74:

EGA-MS and Py-GC/MS, with and without TMAH were performed by Carolina Gomes [53] on the PY3 and PY74 pigments from Royal Talens and one PY3 from the RCE Reference Collection. The other PY74 from the RCE Reference Collection was only analyzed using EGA-MS.

EGA-MS analyses showed different thermal profiles Total Ion thermograms (TIT) (thermograms not shown), and the results suggest that both PY3 decomposes earlier than both PY74. For more information regarding identification, see appendix 4.

4 Conclusions

Studying pigment surface treatments and coatings has provided a unique insight into the pigment and paint industry, and most importantly, it furthered our understanding that artist's paint manufacturers such as Royal Talens are obliged to use industrially prepared materials. Although there is direct contact between raw materials suppliers and the artist's paint makers, and the pigments are generally tested, the total composition of the pigment is not always known. While this may not always represent an issue for the artist's paint manufacturer, in the conservation field, when the materials composition is not fully known it becomes difficult to predict the short and long-term behaviour of materials used by artists.

For this study, a review of the patent and technical literature on pigment and paint technology was fundamental for a first screening of the surface treatment/coating possibilities and what materials could have been applied. As the interview with representatives from the pigment manufacturer BASF revealed, pigment surface treatments are a significant factor in the competition between different manufacturers. Therefore, it is very difficult to obtain this important proprietary information directly from the pigment manufacturer.

When it comes to the detection of inorganic surface treatments or coatings, (S)TEM-EDX and FEG-SEM were the most effective techniques. (S)TEM-EDX enabled the detection of treatments on the pigment particles, since as noted above, the particle is sliced before analysis (see sample preparation, appendix 2), while, FEG-SEM enabled the detection of the surface treatment topography on pigment particles. SEM-EDX provided elemental analysis which in some of the RCE reference pigments enabled a first indication of the possibility of a silica (Si) surface coating (for example in the case of Ultramarine Blue). As for the detection of organic surface treatments, relating compounds to surface treatments can be more challenging since these treatments consist of only approximately 10% of the total pigment weight and therefore represent a very small amount of material. Furthermore, some compounds may be confused with compounds from the pigment synthesis, or from possible contamination. This work demonstrates that the detection of organic treatments/coatings requires a very sensitive analytical technique along with very careful sample preparation and handling.

In case of the two Kremer Pigmente pigments used for the Carlyle MOLART Fellowship, Umber and Vine Black, the pigment surfaces appear not to have been treated with inorganic materials at least, although the results from attempts to detect organic treatments is much less certain. This study also shows that supplier's data-sheets do not always provide information on all pigment treatments. Although the data sheet for Ultramarine from Kremer Pigmente stated that the pigment had a silica coating, the other pigments datasheet did not provide any information even though coatings were detected.

To conclude, it is very important to continue the study of pigment surface treatments and coatings so that researchers are able to study the impact of all materials involved in a given paint system: not only the pigments themselves but also how these alterations to their surfaces affects their interaction with the binder during paint manufacture and over time. It is also important to evaluate the presence and effect of pigment treatments and coatings in actual art works particularly to evaluate whether they play a role in the deterioration of artists' paint.

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[53] Merck. 2018. Triolein. [accessed 20 September 2018]. Available at: <https://www.sigmaaldrich.com/catalog/substance/triolein8854312232711?lang=pt&region=PT>

[54] Gomes, C, Master Thesis, Investigating surface treatments and coatings, their history, application and detection on selected pigments: Lead White, Zinc White and Titanium White. Universidade NOVA de Lisboa, submitted September 2018.

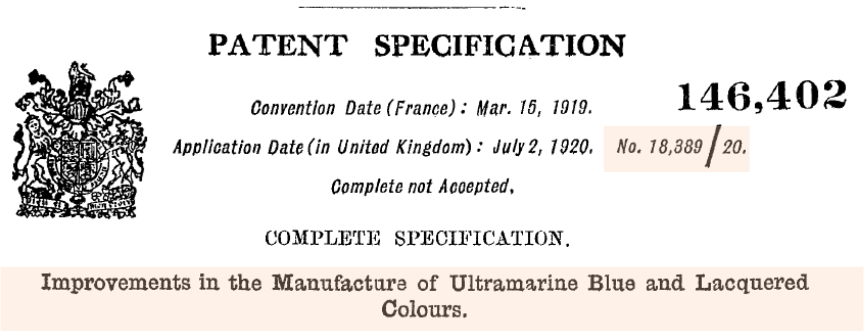
[55] Lia, S & Liub, M. 2011. Preparation of Acid-resistant Ultramarine Pigment by Dense Silica. [accessed 10 September 2018]. Available at: < file:///C:/Users/C%C3%A1tia%20Ferreira/Desktop/10.1.1.1029.3545.pdf>

[56] Challinor, J. M. 1993. Characterization of rosin based commercial resins by pyrolysis and simultaneous pyrolysis methylation gas chromatography/mass spectrometry techniques. Journal of Analytical and Applied Pyrolysis. 25: 349- 360

Appendices

APPENDIX 1. Patent literature showing early coatings

1.1 Early patents, 1920 (figure A1) and 1932 (figure A2).



PATENT SPECIFICATION

Convention Date (France): Mar. 15, 1919. **146,402**

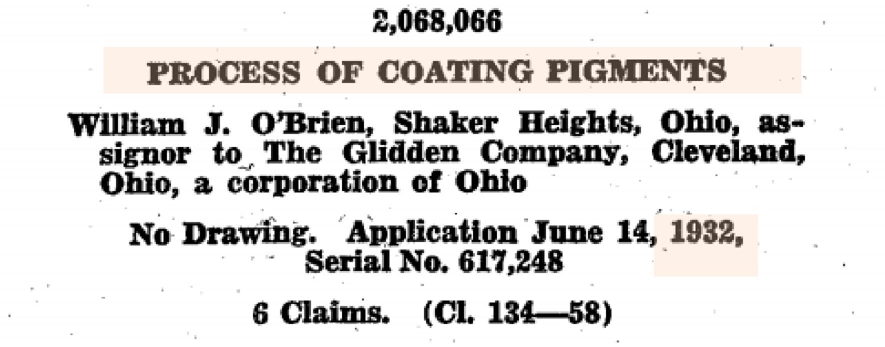
Application Date (in United Kingdom): July 2, 1920. *No. 18,389 / 20.*

Complete not Accepted.

COMPLETE SPECIFICATION.

Improvements in the Manufacture of Ultramarine Blue and Lacquered Colours.

Figure A1. Lance, R. 1920. Improvements in the Manufacture of Ultramarine Blue and Lacquered Colours. GB000000146402A, filed July 2.



2,068,066

PROCESS OF COATING PIGMENTS

William J. O'Brien, Shaker Heights, Ohio, assignor to The Glidden Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application June 14, 1932, Serial No. 617,248

6 Claims. (Cl. 134—58)

Figure A2. Glidden Co. 1932. Process of Coating Pigments.US000002068066A, filed June 14.

APPENDIX 2. Experimental Section

2.1 Materials

All reagents used were of analytical grade. TMAH solvent was used for mass spectrometry techniques including Py-GC/MS. Absolute Ethanol was used to prepare the pigment dispersions. Electron Microscopic studies on pigment powders were carried out on aluminium stubs covered with copper tape. Mass Spectrometry studies were carried out in eco-cups SF®, from Frontier Lab.

The pigment samples were selected from different sources. Eight out of the fifteen samples were collected from the RCE reference collection, including two samples of Ultramarine Blue, two Cu-Phthalocyanine Blues and two Hansa yellows:PY3 and PY74.

Umber and Vine Black pigments were bought in 1999 from Kremer Pigmente and provided by Leslie Carlyle; uncoated Ultramarine Blue pigment was provided by Alessa Gambardella; the sample of coated Ultramarine, purchased in 2017 from Kremer Pigmente was provided by Birgit van Driel; three Cu-Phthalocyanine samples from 1956 (IRPA), 1978 (BRICO) and 1980 (Winsor&Newton) were provided by Catherine Defeyt and finally two samples of Hansa yellows from 2017, PY3 and PY74were provided by Royal Talens.

2.2 Experimental Methods

The inorganic analyses were carried with SEM-EDX at RCE to characterize the pigments and to detect pigment surface treatments or coatings. TEM-EDX analysis were carried within the AKZO NOBEL Chemicals network (supported with funds from Rijksmuseum doctorate Birgit van Driel), by Brenda Rossenar and Arn Janssen. FEG-SEM analysis was performed at the RCE laboratories.

The organic surface treatment detection was carried with EGA-MS, Py-GC/MS, Py-THM-GC/MS and DTMS by Carolina Gomes.

SEM-EDX sample preparation:

In an aluminium stub with copper tape, the smallest amount of sample possible was deposited on the stub surface under a stereomicroscope with the aid of a metallic spatula; excess pigment powder was blown off with air.

TEM-EDX sample preparation:

Electron transparent films for the STEM-EDX investigations were prepared with a Leica UC7 Ultramicrotome. The particles were mixed in purified H_2O and frozen at -80 in the cryochamber of the Ultramicrotome. Afterwards TEM slices were prepared with a cryo 35 diamond knife with a cutting speed of 1 mm/sec and a feed of 70 nm. Sections were collected dry using the charge/discharge function on holycarbon filmed Cu grids.

FEG-SEM sample preparation:

Samples were the same as those used for SEM-EDX.

EGA-MS sample preparation:

Micro-samples of pigment were placed into a stainless-steel cup (Frontier Disposable Eco-Cup LF). Pigment particles were observed under the microscope and agglomerates were broken down. The procedure was repeated with a slight increase in the amount of pigment sample when the results were not significant.

Py-GC/MS sample preparation:

Same procedure as EGA-MS.

Py-THM-GC/MS sample preparation:

With a dissecting needle, 0.05 µL of trimethylammonium hydroxide (25 % in methanol) was applied to a small vial with the smallest amount possible of pigment sample. A dissecting needle was dipped in the solution of pigment/TMAH and a drop was deposited in a stainless-steel cup (Frontier Disposable Eco-Cup LF). The procedure was repeated with the increased amounts of pigment when the results were not significant.

Ultrasonic bath - Pigment dispersions preparation (SEM-EDX):

In a small glass bottle, 3,5ml of absolute ethanol was added and the smallest amount of pigment powder possible added with a metallic spatula. Then the container was put in the ultrasonic bath for 10 minutes. After, a drop of the solution was put oved the copper tape with a Pasteur pipette, let to dry. The process was repeated, and the number of drops was between 4 or 5 drops.

Imbedding Ultramarine Blue Paint Cross-Section Samples in Technovit® Resin (see figure A3):

The paint-outs with triolein of uncoated and coated Ultramarine Blues were prepared in August 2017 by Alessa Gambardella, with 25 µm thickness.

After sampling both samples were imbedded in Technovit® resin with the Alan Phenix technique below (as explained by Alessa Gambardella):

1. A small piece of tape was fixed to a glass slide; then the sample was put on top of the tape and a drop of resin was put over the paint sample, with a Pasteur pipette, to fix it;
2. While the resin was drying, the sample label was prepared using a transparent Avery® label;
3. Then, a plastic Eppendorf was cut and put over the dried resin drop; more Technovit® was pour inside the mould until a uniform layer was formed and put aside to dry for approximately 30 minutes;
4. After the layer of resin dried, more Technovit® was added to the mould, and the label was put in the resin with the aid of tweezers;
5. After the resin cured completely (approx. 1 hour), the plastic Eppendorf was cut with a saw, and then the sample was polished;
6. The polishing process started with a larger grain sandpaper of 1500 followed by gradually smaller grained sandpapers of 2400, 3200, 4000, 6000, 8000 and finally 1200. The sample was polished 10 times on each sandpaper and cleaned in between each sandpaper change with a lens paper to avoid grain contaminations.

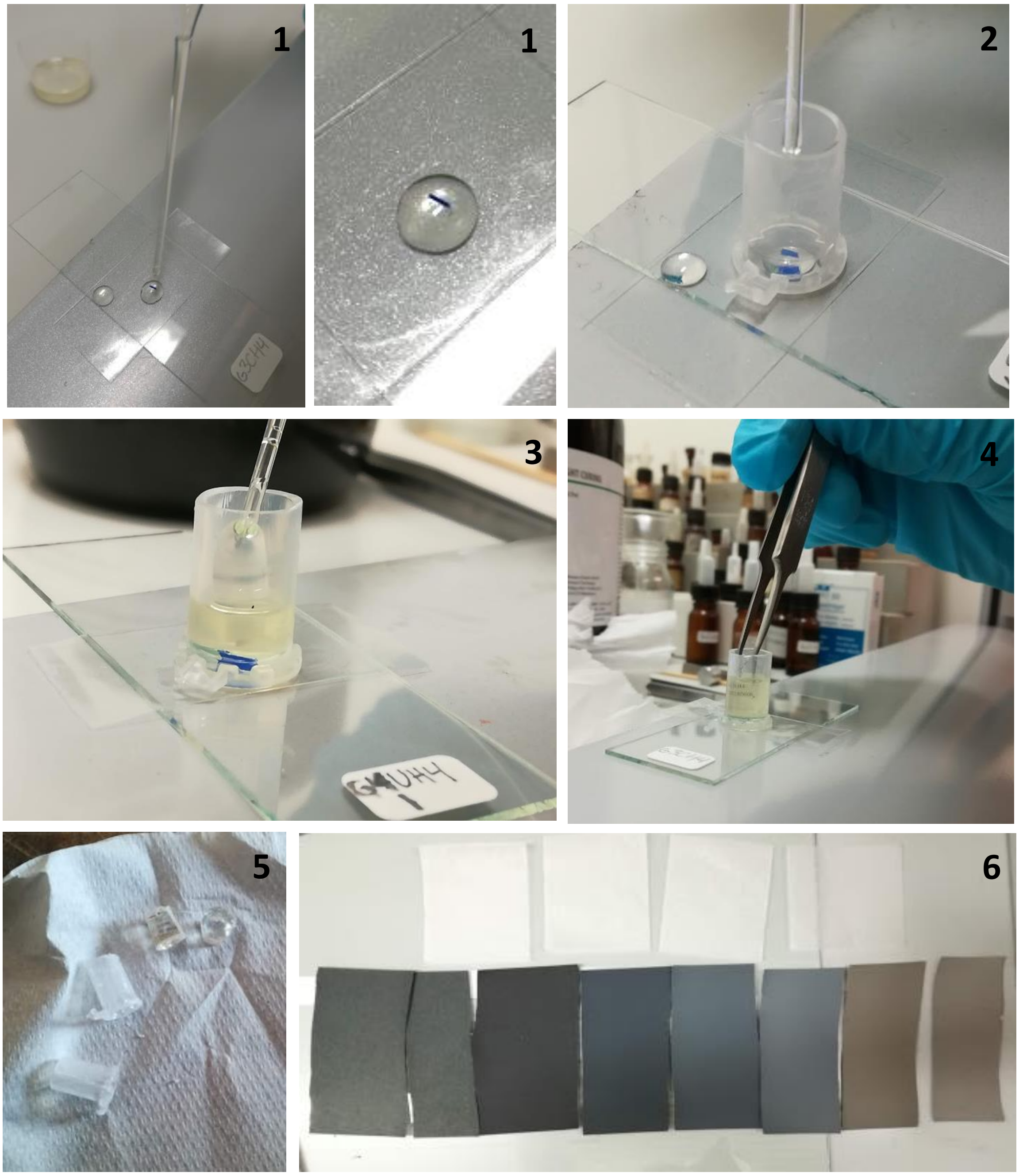


Figure A3. Corresponding images to the major steps of Imbedding Ultramarine Blue Paint Cross-Section Samples in Technovit® Resin.

2.3 Apparatus

The inorganic analyses were carried with SEM-EDX at RCE to characterize the pigments and to detect pigment surface treatments or coatings. TEM-EDX analysis were carried within the AKZO NOBEL Chemicals network (supported with funds from Rijksmuseum doctorate Birgit van Driel), by Brenda Rossenar and Arn Janssen. FEG-SEM analysis was performed at the RCE laboratories.

The organic surface treatment detection was carried with EGA-MS, Py-GC/MS, Py-THM-GC/MS and DTMS by Carolina Gomes.

SEM-EDX

The Scanning electron microscope (SEM) used was a JEOL JSM-5910 with secondary (SE) and backscattering (BSE) detectors coupled to an energy dispersive X-ray spectrometer (EDS). The analyses were carried out under low vacuum conditions where the samples did not have charging effects; The spectra were acquired with a voltage of 15 kV, 10 mm of working distance, spot size 44 and energy of 30Pa. The samples were analysed with Point and Shoot mode.

(S)TEM-EDX

High angle annular dark field (HAADF) scanning transmission electron microscope imaging was performed on a Thermo Scientific Talos F200X S/TEM with a high brightness X-FEG electron source and Super-X energy dispersive silicon drift detector (SDDs). The microscope was operated at an accelerating voltage of 200 kV with beam currents of 500 pA and 750 pA, respectively. EDX spectrum images (SI) were acquired and processed either in the Velox or Bruker Esprit Software with a dwell time of 25 µs and a typical image size of 1024x1024 pixel.

FEG-SEM

Field Emission Gun Scanning Electron Microscope (FEG-SEM) used was Nova Nano SEM450 from FEI, with backscattering (BSE) and concentric (insertable) higher energy electron (CBS) detectors. The analyses were carried out under high vacuum conditions; The spectra were acquired with a voltage of 2 kV and 6,3 mm of working distance.

EGA/MS

The samples were analysed using EGA/MS. The samples were directly introduced into a steel pyrolysis cup. The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. EGA was performed by heating at 70°C/min from 70°C up to 700°C. The analytical column was directly coupled to the pyrolyser via a home-made split device. A short deactivated, uncoated capillary (length- 1m, int. diameter 0.1mm) connects the pyrolyser to the mass spectrometer. Helium was used as carrier with a constant flow of 0.9 ml/min and split ratio of 1:20. The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 270 °C, the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.7 and MassLynx 4.0 software were used for collecting and processing of the data.

Py-GC/MS and Py-THM-GC/MS

All samples were analyzed using thermally assisted hydrolysis and methylation (THM) gas chromatography-mass spectrometry (GC/MS) in combination with ultrafast thermal desorption (UTD).

The method applied was Ultrafast Thermal Desorption (UTD) method, meaning the samples were investigated through “slow pyrolysis” and not as flash pyrolysis. This method, developed at RCE, involves a temperature program that enables a one-shot analysis with evaporation before pyrolysis.

For the THM-UTD-GC/MS analyses sample material was made into a suspension with a few drops of a 5% solution of tetramethylammonium hydroxide (TMAH) in methanol with tridecanoic acid (FA-C13) internal standard and the suspension was transferred to a steel pyrolysis cup. The pyrolysis unit used was a Frontier Lab 3030D pyrolyzer mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. Ultrafast thermal desorption was performed by heating at 500°C/min from 360°C up to 700°C. The analytical column was directly coupled to the pyrolyzer via a home-made split device. A SLB5 ms (Supelco) column was used (length 20 m, int. diameter 0.18 mm, film thickness 0.18 µm). Helium was used as carrier with a constant flow of 0.9 ml/min and split ratio of 1:30. The temperature program was the following: 35 °C (1.5 min), heating at 60 °C /min to 100 °C, heating at 14 °C/min to 250 °C, heating at 6 °C/min to 315 °C (1.5 min). The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 270 °C, the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.7 and MassLynx 4.0 software were used for collecting and processing of the data.

APPENDIX 3. SEM-EDX analysis

3.1 Umber

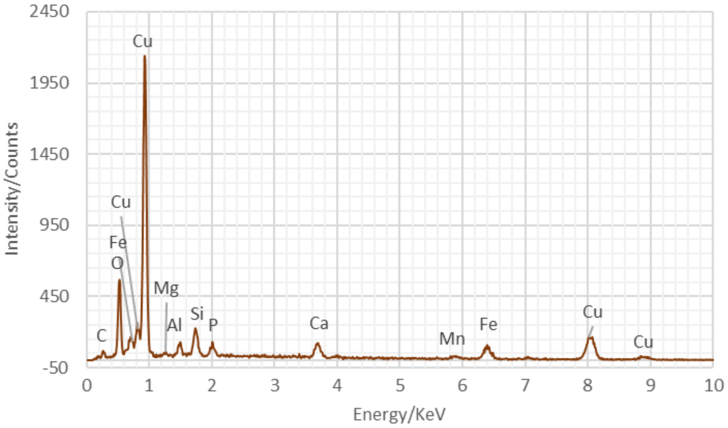


Figure A4. SEM-EDX spectrum of Umber pigment sample, at 15 kV.

3.2 Vine Black

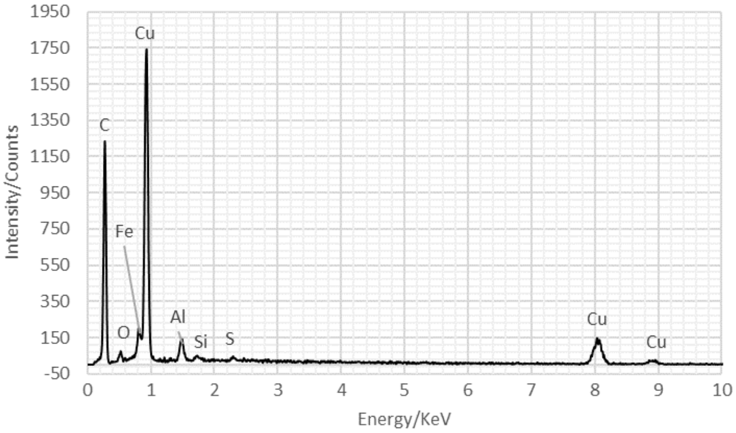


Figure A5. SEM-EDX spectrum of Vine Black pigment sample, at 15 kV.

3.1 Ultramarine Blue pigments

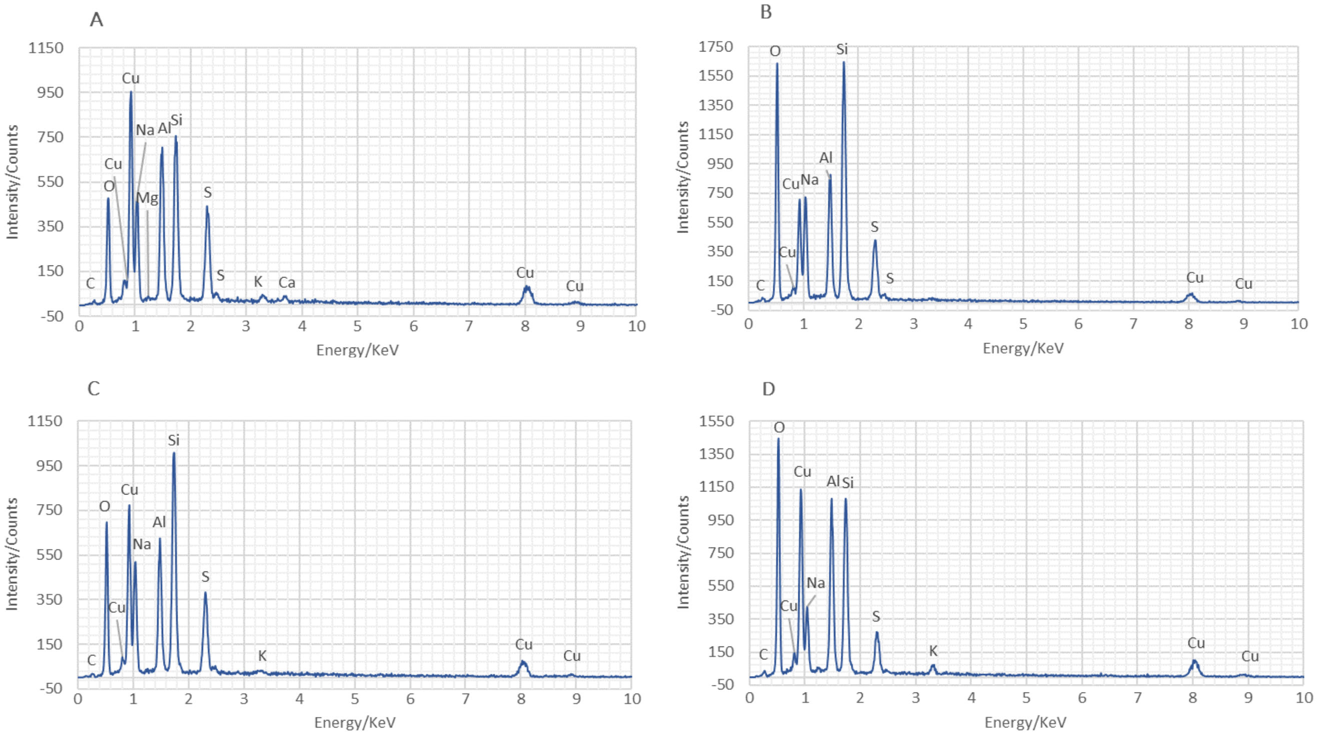
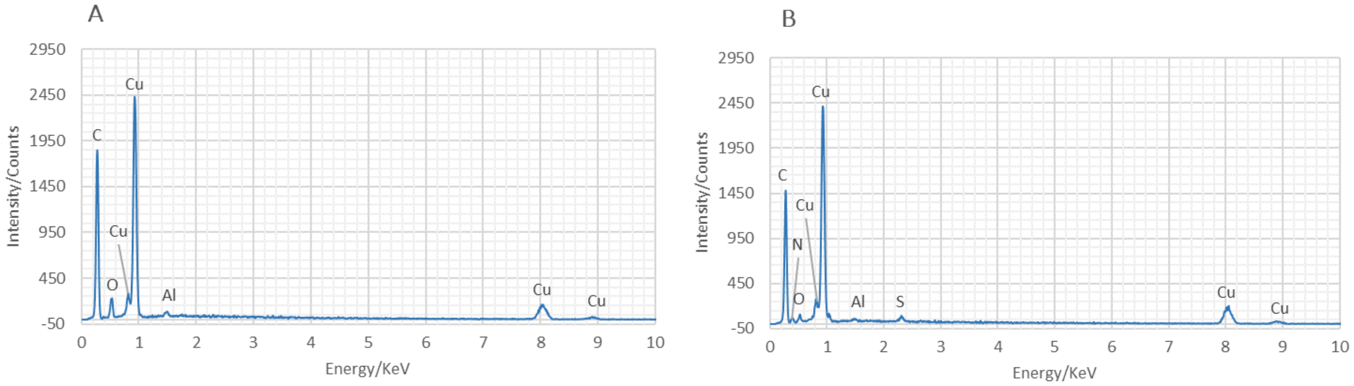


Figure A6. SEM-EDX spectrum of A) uncoated, B) coated, C) sample 867 and D) LUKAS sample Ultramarine Blue pigments, at 15 kV.

3.2 Cu-Phthalocyanine Blue



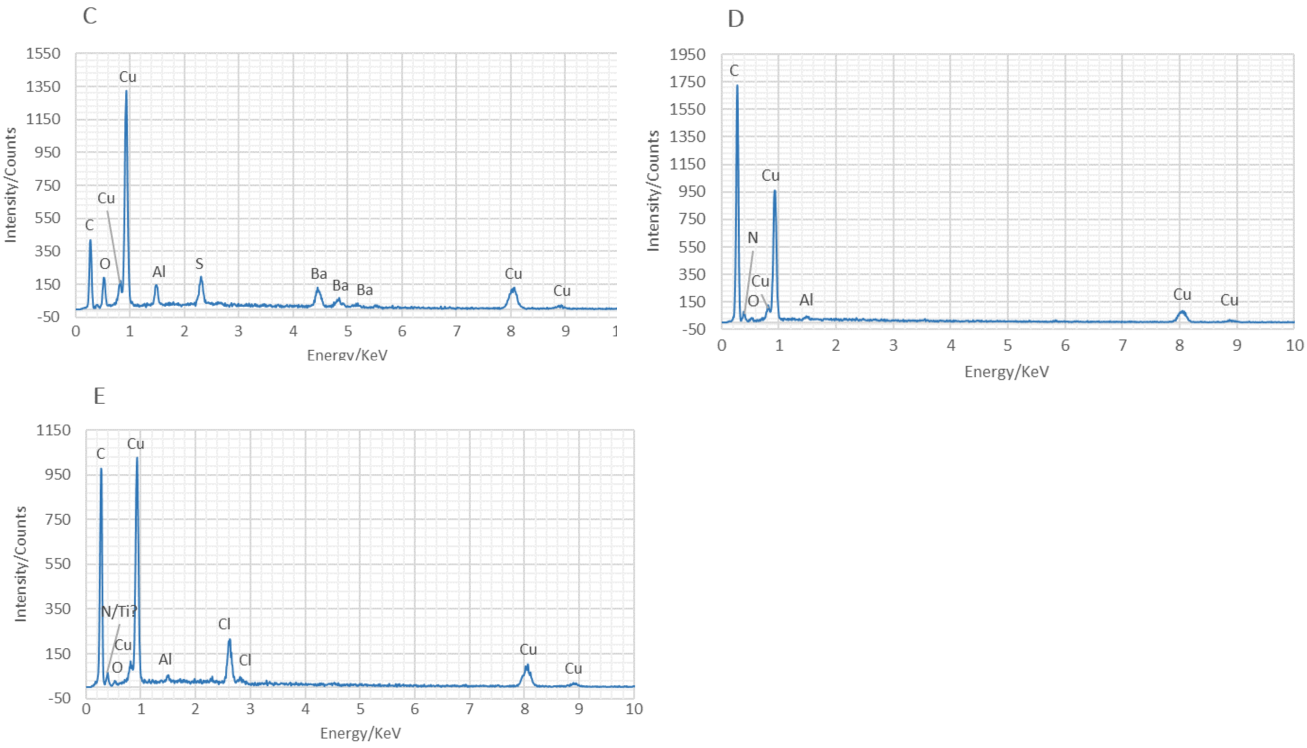


Figure A7. SEM-EDX spectrum of A) 1950 sample, B) 1978 sample, C) 1980 sample, D) 833 sample and E) 2755-Monastral blue pigments, at 15 kV.

3.3 PY3

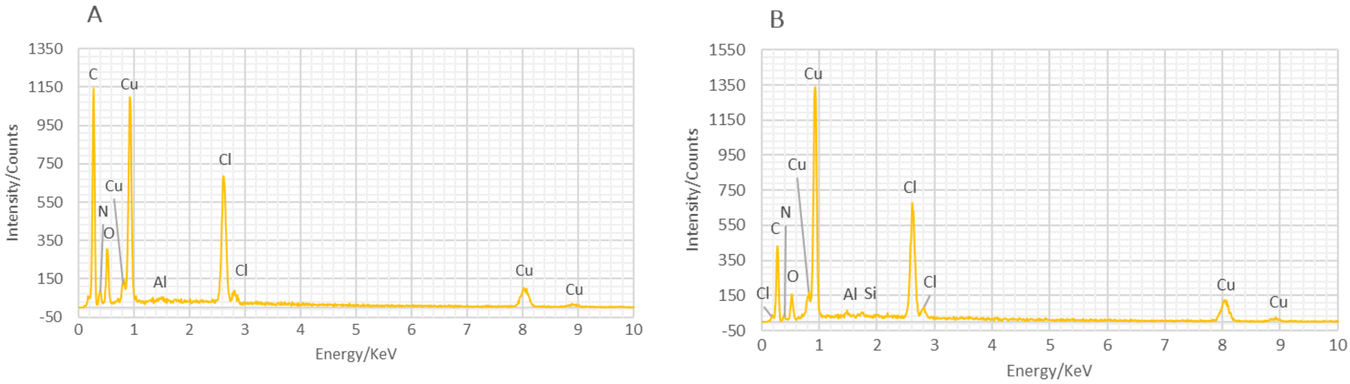


Figure A8. SEM-EDX spectrum of A) Royal Talens pigments and B) RCE reference collection pigments, at 15 kV.

3.4 PY74

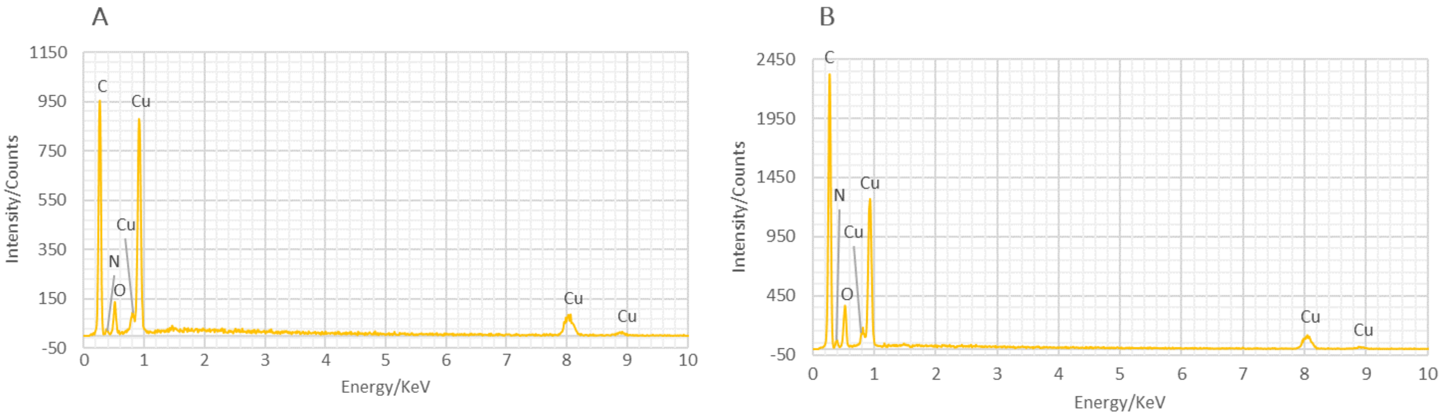


Figure A9. SEM-EDX spectrum of A) Royal Talens pigment and B) RCE reference collection pigments, at 15 kV.

APPENDIX 4. Organic Analysis

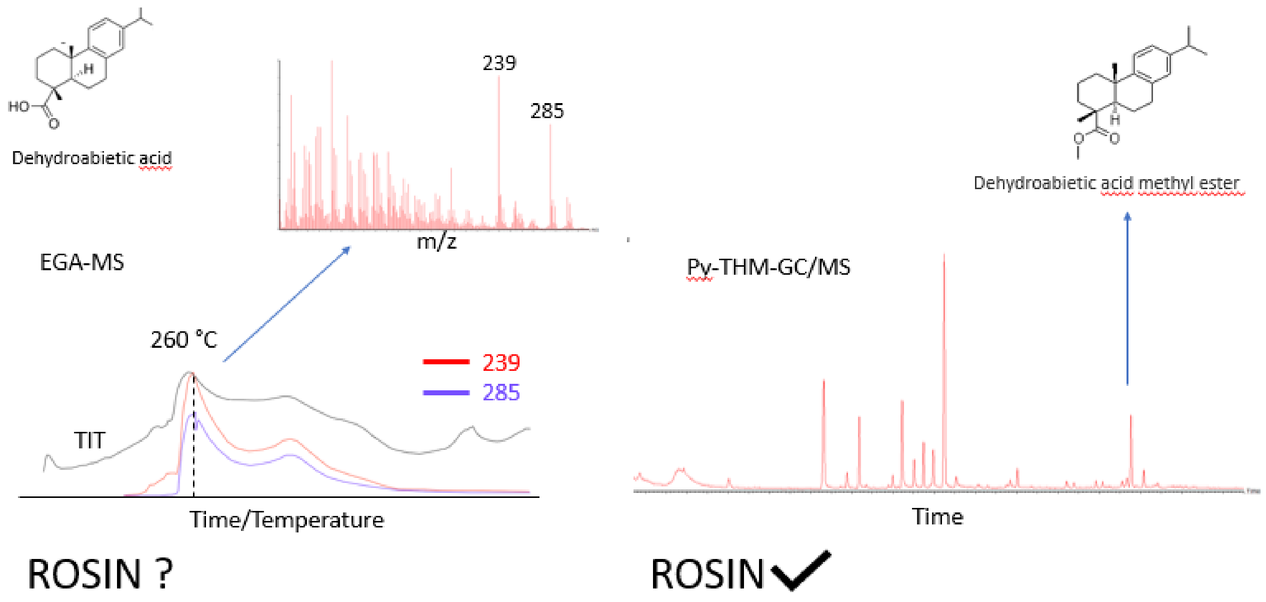


Figure A10. Corresponding peaks of Cu-Phthalocyanine 833 from the RCE Reference Collection.

Table A1. Results of organic analysis, results acquired and processed by Carolina Gomes [53].

Pigment	*Samples*[4]	*EGA-MS*[1,2]	*Py-GC/MS*[2]	*Py-GC/MS (TMAH)*[2]	*Comments/ Conclusions*
Copper Phthalocyanine	Irpa PB15:1 (1953)	**I.** Products from pigment 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104)	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104)	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101)	N
	Brico PB 15:0 (1978)	**I.**.Products from pigment Benzonitrile (**103**, 76) 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104)	**I.** Products from pigment: Benzonitrile (**103**, 76) 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104)	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101)	N

Blue	Winsor & Newton PB15:2 (1980)	**I.** Products from pigment Benzonitrile (**103**, 76, 50) 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104) **II.**SO_2 (64, 48), Tº c. 400-600ºC **III.**Characteristic fragment ions for alkanes: m/z **43**, 57, 71, 85 max at 190ºC[15]	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104) Alkanes: C10, 14 linear and branched	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101)	N Sulphate present Alkanes
	833 w/ ref	**I.** Products from pigment 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104) **III**. Characteristic fragment ions from dehydroabietic acid: m/z **239**, 285 max at 260 ºC (Kokkori 2015)	**I.** Products from pigment: Benzonitrile (**103**, 76, 50) 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104) **III.** Diterpenoids (pinacea resin): Dehydroabietic acid (DHA) (**239**, 240, 299) Methyl abietate (**256**, 342, 227) (Challinor 1993)	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101) **III.** Diterpenoids (pinacea resin): Isopimaric acid methyl ester (**241**, 91, 105) Abietic acid methyl ester (**213**, 131, 273) 15-methoxydehydroabietic acid, methyl ester (**329**, 330, 73) 7-Oxo-dehydroabietic acid, methyl ester (**253**, 328, 187) (Challinor 1993)	Rosin
	2755 n/date	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**, 101) o-cyanobenzoic acid (**76**, 147, 104) Benzonitrile (**103**, 76, 50) **II.** SO_2 (64, 48), Tº max ± 566 ºC HCl (36), Tº max ± 576ºC **III.** Characteristic fragment ions for alkanes: m/z **43**, 57, 71, 85 max at 170ºC	**I.** Products from pigment: 1,2-Dicyanobenzene (**128**,191) Benzonitrile (**103**, 76, 50) **II.** Alkanes: C7 to C11	No significant products were found	N Alkanes
	PY3 0526	**I.** Products from pigment: 1 - or 4-chloroaniline (**127**, 129, 65) 2-Chlorophenylisocyanate (**153**, 125, 90, 155) Benzofuran from x ring (**124**, 154, 126) **III.**Main peak in Tº range: 250-350ºC, max 317ºC	**I.** Products from pigment: 1 - or 4-chloroaniline (**127**, 129, 65) 2-Chlorophenylisocyanate (**153**, 125, 90, 155) Benzofuran from x ring (**124**, 154, 126)	**I.** Products from pigment 1 - or 4-chloroaniline (**127**, 129, 65)	N

Hansa® Yellows	PY3 Royal Talens (2017)	**I.** Products from pigment 1 - or 4-chloroaniline (**127**, 129, 65) 2-Chlorophenylisocyanate (**153**, 125, 90, 155) Benzofuran from x ring (**124**, 154, 126) **III.** Main peak in Tº range: 250-350ºC, max 317ºC	**I.** Products from pigment 1 - or 4-chloroaniline (**127**, 129, 65) 2-Chlorophenylisocyanate (**153**, 125, 90, 155) Benzofuran from x ring (**124**, 154, 126)	No significant products were found	N
	PY74 0527	**I.** Products from pigment o-Anisidine (**80**, 108, 123) 2-methoxyphenylisocyanate (**149**, 120, 106) Main peak in Tº range: 300-350ºC, max 328ºC	NA	NA	N
	PY74 Royal Talens (2017)	**I.** Products from pigment o-Anisidine (**80**, 108, 123) 2-methoxyphenylisocyanate (**149**, 120, 106) Main peak in Tº range: 300-350ºC, max 328ºC	**I.** Products from pigment o-Anisidine (**80**, 108, 123) 2-methoxyphenylisocyanate (**149**, 120, 106)	**I.** Products from pigment o-Anisidine (**80**, 108, 123) 2-methoxyphenylisocyanate (**149**, 120, 106)	N

Note: Thermal behavior was detected. Classes of compounds and fragments of ions described through main molecular. Temperature describes range of desorption/ of formation in chromatogram.

[2] Selected, most proeminent peaks represented. Copper Phthalocyanine Blue pigment pyrolysis products attribution was performed based on investigation carried by Russel et al. (2011) and Ghelardi et al. (2015). Hansa® Yellow pigment pyrolysis products attribution was performed based on investigation carried by Russel et al. (2011) and Sonoda (1999).

[3] N: No surface treatment was found or results not significant.

[4] The phthalo blue samples Irpa, Brico and Winsor&Newton are historical and were previously investigated by Catherine Defeyt in her PhD thesis. The author established the polymorphic form and identified the presence of $BaSO_4$ in Winsor&Newton sample via XRD analysis.

APPENDIX 5. Treated or coated pigments within paints

After determining how the surface treatment or coating can be detected on the dry pigment powder, it is important to understand if after the pigment has been incorporated into the binder, it is still possible to detect the surface treatment.

For this research, a first attempt with **FEG-SEM (**performed by Ineke Joosten), was made to compare differences between uncoated and coated Ultramarine Blue pigments used in triolein paint samples prepared by Alessa Gambardella (for more details on sample materials and preparation, see appendix 2). In figure 26, the differences between the uncoated and coated pigments are evident, however, it is not possible to confirm that the material seen around the pigment particles is the coating.

The fact that image A11-b) shows a more brilliant surface might be related to aging patterns. When comparing FEG-SEM results by Ineke Joosten with those by de la Rie et al. [57][16], in figure A12 their images after aging (figure A12-a)) are similar in appearance to the uncoated Ultramarine Blue paint (figure A11-a)) while the images before aging (see figure A12-b)) are more similar to the coated Ultramarine Blue paint (figure A11-b)). Even though, this technique shows potential regarding surface coating detection and studies on more paint samples are needed.

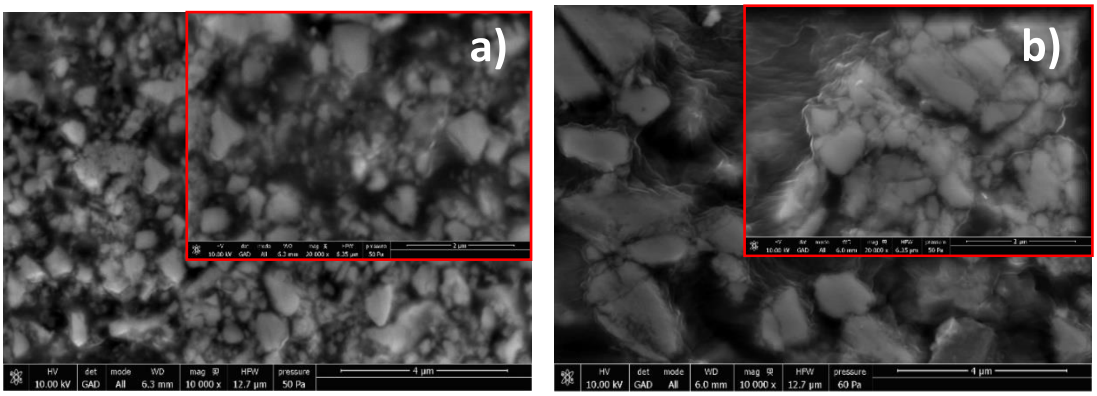


Figure A11. FEG-SEM images in CBS mode showing a) oil paint made with uncoated Ultramarine Blue and b) oil (triolein) paint made with silica coated Ultramarine Blue, performed by Ineke Joosten.

When it can be established that pigment treatments/coatings within prepared paint can be detected with analytical techniques it will be important to study the relationship between the binder and pigment treatments/coatings to determine whether this can lead to changes in paint stability.

---

[16] [57] de la Rie, R., Michelin, A., Ngako, M., Del Frederico, E & Del Grosso, C. 2017. Photo-catalytic degradation of binding media of Ultramarine Blue containing paint layers. A new perspective on the phenomenon of "ultramarine disease" in paintings. In Polymer Degradation and Stability. doi: 10.1016/j.polymdegradstab.2017.08.002

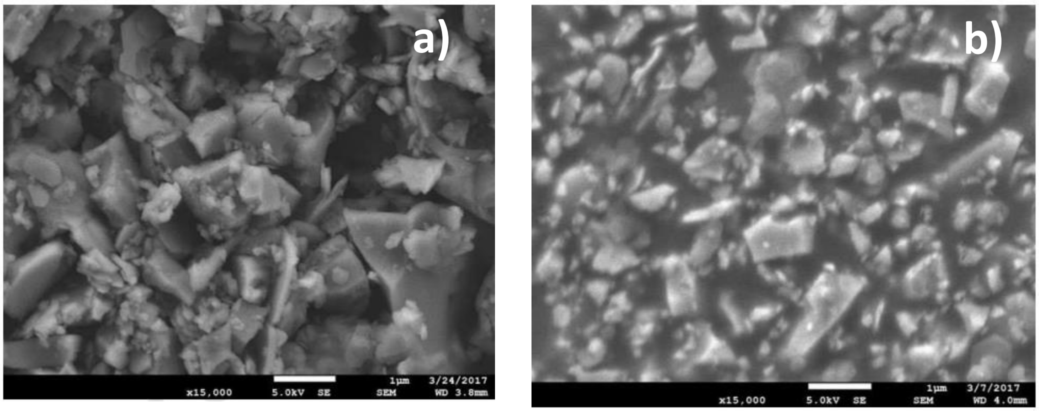


Figure A12. FEG-SEM images of Ultramarine Blue oil paint reproduced from de la Rie et al. (2017), p.9 [56]. In a) after aging and b) before aging.

APPENDIX 6. Surface Coating, dispersibility and solvent sensitivity

When it was understood that SEM-EDX would not be capable of detecting the surface treatment or coating, other experiments with dispersions were carried out.

As explained in the introduction of this study, the surface treatment/coating directly influences the ease of dispersion. Some differences were noted regarding the uncoated versus coated pigments of **Ultramarine Blue** as shown in figure A13.

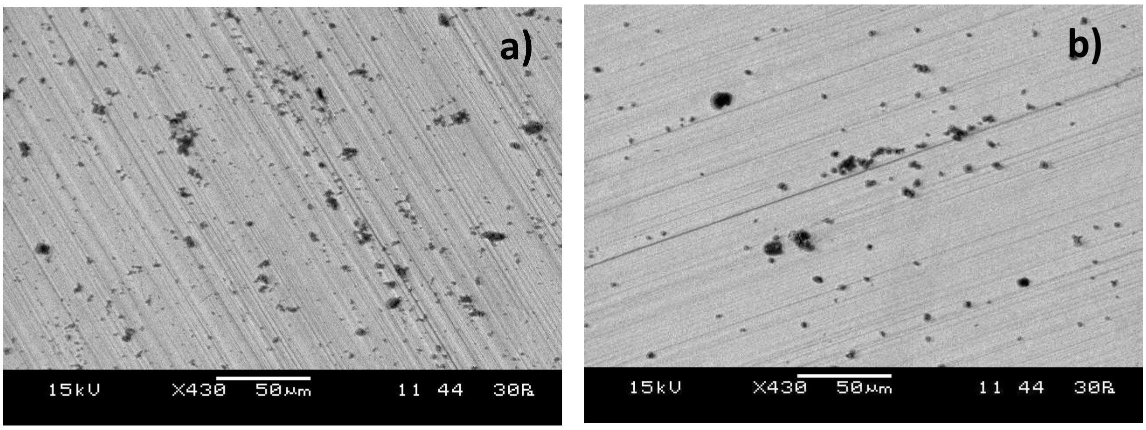


Figure A13. SEM images in LV mode of a) uncoated Ultramarine Blue and b) coated Ultramarine Blue.

Comparing the 867 and LUKAS pigments with the previous assumptions regarding the surface treatment/coating mentioned in the Results and Discussion section, the same tendency is observed. As shown in figure A14, the pigment 867 shows less agglomeration than LUKAS pigment.

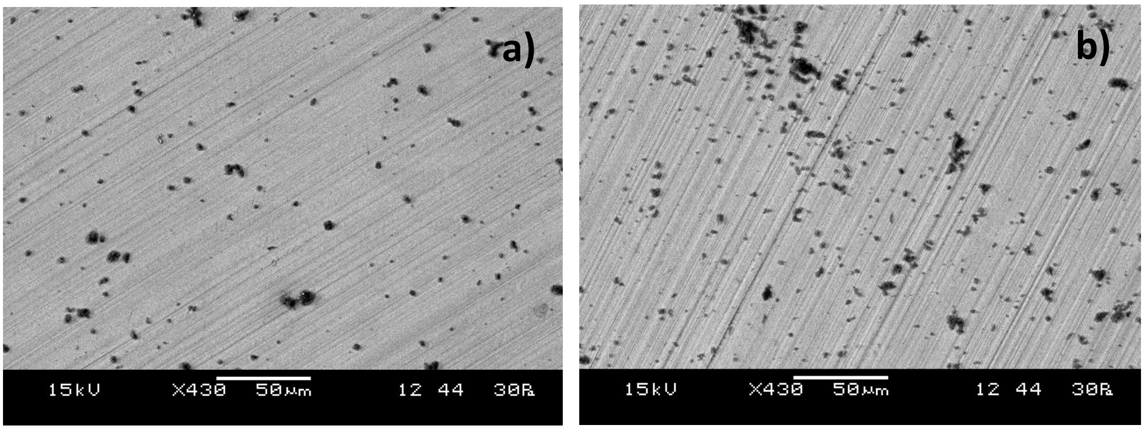


Figure A14. SEM images in LV mode of a) 867 pigment and b) LUKAS pigment.

The historically accurate pigments, Umber and Vine Black were also analysed in dispersion. When looking at the results, a variety of different particle sizes and agglomeration can be seen (figure A15). If the pigments were surface treated or coated, less agglomeration would be expected and an appearance similar to the coated Ultramarine Blue would be the result.

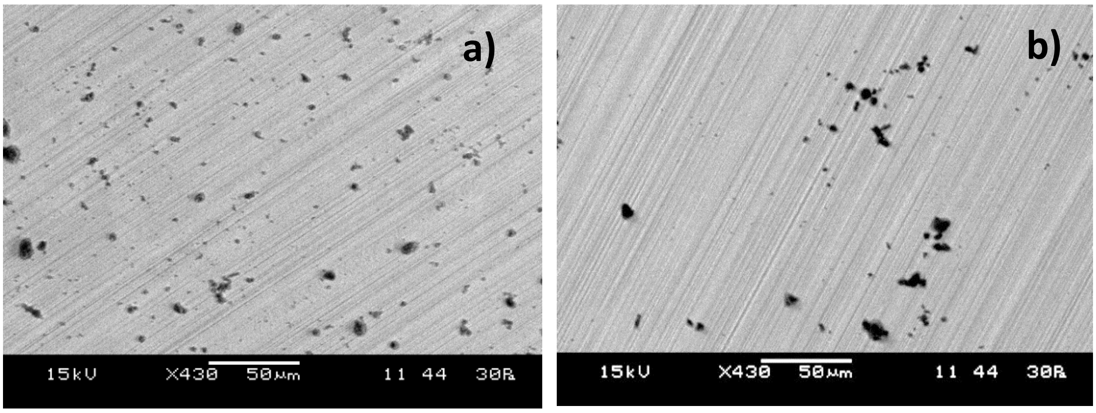


Figure A15. SEM images in LV mode of a) Umber and b) Vine Black pigments.

When looking through the **Cu-Phthalocyanine Blue** pigments, the dispersion results are less straightforward than in the Ultramarine Blue pigments. As shown in figure A16, the pigment from 1956 shows more aggregation than the two other pigments from 1978 and 1980. Historically, this makes a lot of sense, since pigment dispersions knowledge improved through the years therefore, this result is not surprising.

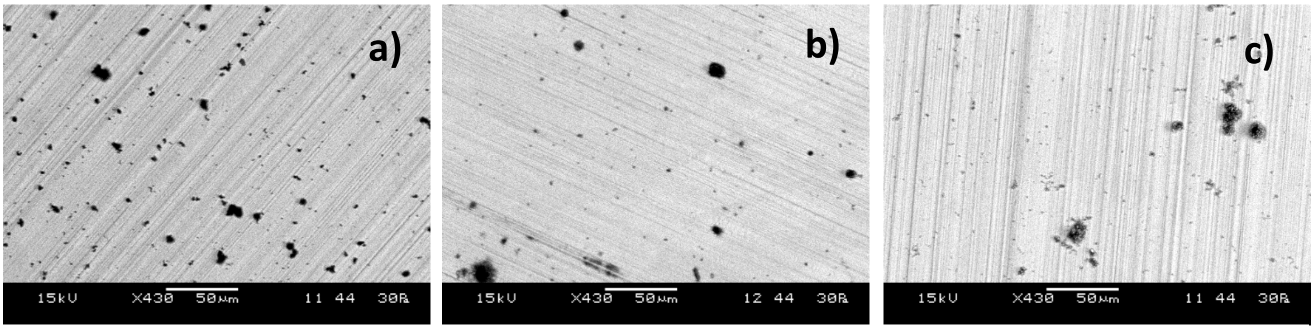


Figure A16. SEM images in LV mode of a) pigment from 1956, b) pigment from 1978 and c) pigment from 1980.

Also, according to (S)TEM-EDX results, it is possible to see treatment on the 1980 sample. This shows that, because the pigments have similar dispersibility, all the pigments might have been submitted to some surface treatments (see figure A16).

As for the pigments from the RCE reference collection, the 2755 - Monastral blue pigment shows the less dispersed behaviour than pigment 833 (see figure A17).

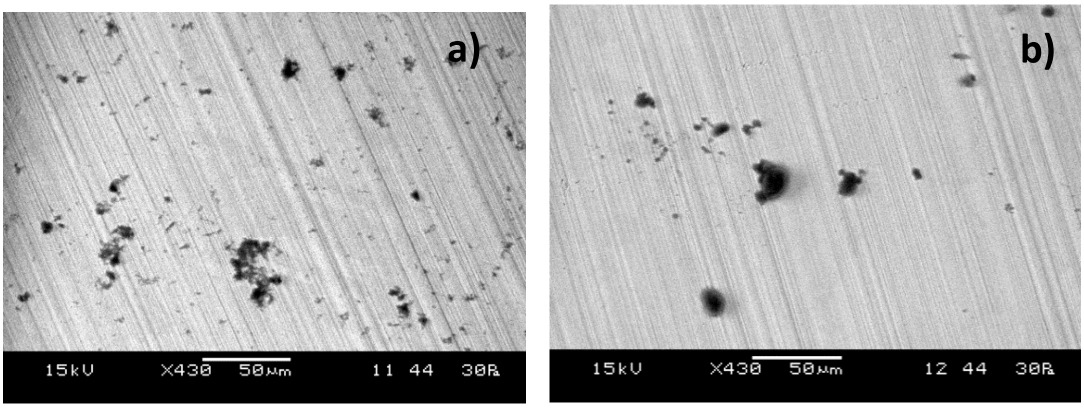


Figure A17. SEM images in LV mode of a) pigment 833 and b) 2755 – Monastral blue pigment.

From all the Cu-Phthalocyanine Blue pigments, the 2755-Monastral blue sample shows more agglomeration. This could be an indication that the pigment was not submitted to treatments. As mentioned during this study, Cu-Phthalocyanine pigments were firstly introduced in the market under the name Monastral blue. The fact that the sample shows less ease of dispersion than the other pigments, could be an indication that the pigment is in fact, from the beginning of the 20th century.

Concerning the **yellow pigments**, it was noticed that PY3 from Royal Talens shows more agglomeration than the PY3 from the RCE reference collection (figure A18). This may be contributing to the instability of the paint, noted by the manufacturer.

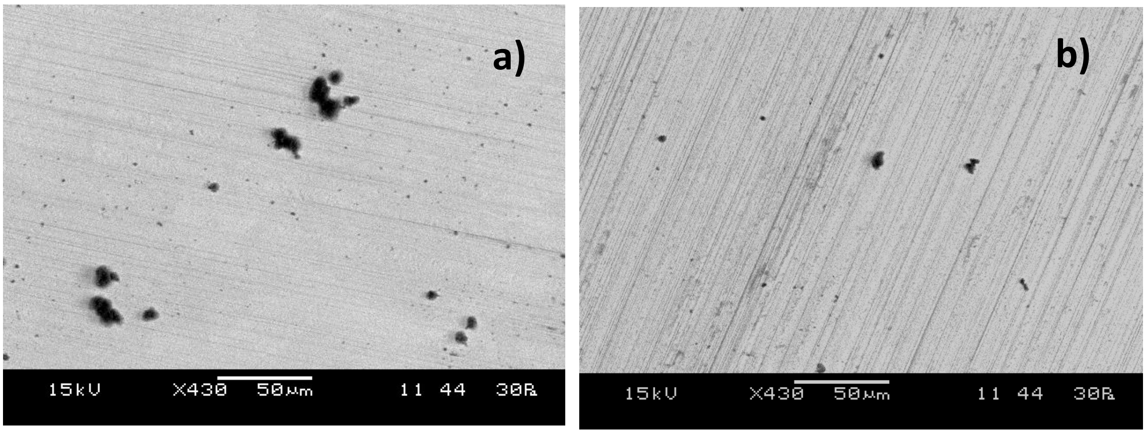


Figure A18. SEM images in LV mode of a) pigment from Royal Talens and b) pigment from the RCE reference collection.

PY74 from Royal Talens also shows more agglomeration than PY74 from the RCE reference collection, however, this last pigment reacted with the solvent, and tide lines can be observed in figure A18b) which is not observed in the pigment from Royal Talens (figure A19a).

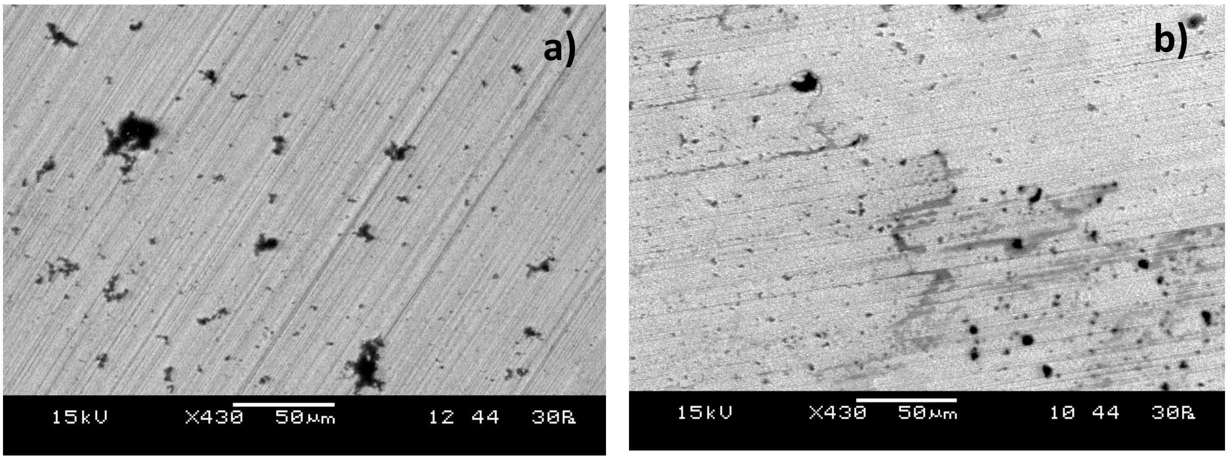


Figure A19. SEM images in LV mode of a) pigment from Royal Talens and b) pigment from the RCE reference collection.

The coated particles clearly show less agglomeration than the uncoated, meaning that SEM-EDX can also be successfully used to compare pigment dispersions. However, it is very important to note that the comparison is only valid if the exact same amount of pigment sample is used in the dispersion. Also, it is very important to see all areas where the sample has been applied since some areas might be more concentrated, which can mislead the results.

After the dispersions were analysed with the SEM-EDX, the coated Ultramarine Blue was observed under FEG-SEM. The higher resolution showed that the solvent/dispersion process interfered with the surface coating.

As shown in figure A20, after the pigment was dispersed with ethanol, the surface coating was significantly affected. The reason for this phenomenon needs further investigation, however, one hypothesis relies on the fact that an ultrasonic bath was used to disperse the pigment particles and that could have affected the pigment coating, so the role of the ethanol alone is not clear.

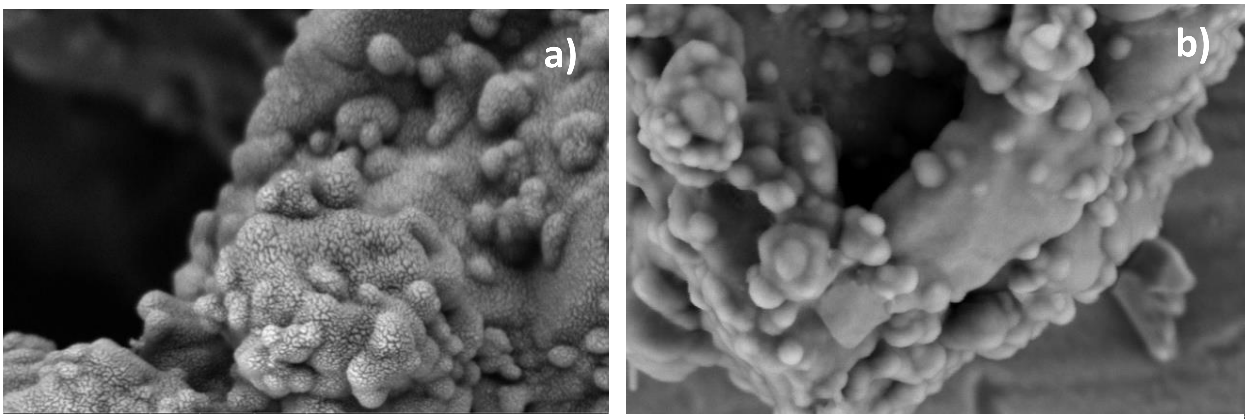


Figure A20. Coated Ultramarine Blue pigment a) before and b) after dispersion.